CHEMISTRY IN THE MARKET PLACE

BEN SELINGER

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FOREWORD

Caveat Emptor—Let the buyer beware.

In today's technological society it has become more and more difficult for the consumer to beware. The housewife is confused by advertising which claims that product A is better than all other products that are designed to do the same job.

Because the majority of the community is not aware of the intricate technicalities of the products that they buy, there has been an increasing need over the past ten years or so for the preparation and enforcement of meaningful consumer standards. There have also been demands for down to earth advertising and labelling of products. How can these demands be met if the average consumer finds difficulty in understanding the standard, the advertising on the label?

As one who has been deeply involved in preparing consumer standards, and advising on advertising and labelling claims, I welcome this second edition of Dr Selinger's book. As a member of the Food Standards Committee of the National Health and Medical Research Council, and of various Standards Association of Australia Committees, I have often been asked 'what does the consumer really want to know about a product?', or have been told 'there is no point in putting this information on a label because it will not be understood'.

While this book will not tell you how to detect Salmonella in baby food, it can provide the basis for giving the interested consumer some knowledge to ask intelligent questions and expect to get intelligent answers. It can be the basis for adult education courses aimed at the consumer who wants to know a bit more, and it can provide information for high school teachers who wish to assist their students in consumer understanding. In summary, this book can give to all concerned guidelines on what has been previously too complex to be comprehended by the average consumer.

F.E. Peters
Australian Government Analyst

PREFACE TO THE FIRST EDITION

It was over three glasses of cool, artificially coloured, artificially foam stabilised, enzyme clarified, preserved, gassed amber fluid that Mal Rasmussen, Derry Scott and myself came to the realisation that we ought to be teaching consumers some 'real' chemistry, chemistry relevant to their lives, so that they could hope to make some sense of the arguments which rage in the media on aspects of consumer products—particularly those relating to safety and efficacy. This was how the community education course under the auspices of the Australian National University Centre for Continuing Education started in 1973 with the alliterative title of 'Chemical Consciousness for Concerned Consumers'. The course took place in the Chemistry Department one evening per week and the 2½-hour period was broken up with benchtop demonstrations, films from the National Library, and coffee and biscuits (except during the laboratory session!).

A set of notes prepared for the course was rewritten in the light of this experience for the 1974 class and again for the 1975 class. This book is a partly 'de-libelled' version of the 1975 notes.

The selection of topics is somewhat arbitrary, but the emphasis is meant to be on the *product* and the chemistry necessary to understand it, rather than on the chemistry with the product as an illustration, which tends to be the traditional approach. The introductory chapter is thus somewhat perfunctory —unnecessary for those who already know some chemistry and insufficient for those who don't. I believe that this cannot be avoided without writing another book. Each of the chapters is self-contained, although some reference is made to other chapters. The chapters also differ in their degree of difficulty because of the nature of the chemistry involved. They are also fairly open-ended. I would be grateful for any criticisms of the selection of the material.

The material in the book is written with several levels intertwined: general discussion is mixed with isolated portions of solid chemistry. This follows the lead taken in the Old Testament where, at the very beginning, the Genesis is described *four* times: in four different ways so as to appeal to as wide a range of understanding as possible. You've never noticed? Well, some of us have never got much further!

I hope in this book that you do.

Ben Selinger
4 July 1975

PREFACE TO THE SECOND EDITION

This second edition has been produced because of the unexpected demand for the notes comprising the original edition. It was felt that the material should be brought up-to-date, even though the intervening period was only two years, and a number of suggestions by readers be incorporated. The purpose has remained unchanged—it is to provide a particular overview of the market place in chemical terms, although this has meant a coverage beyond what would normally be regarded as the chemical domain. The purpose is to provide a reference (rather than a course) textbook from which material can be extracted but, more importantly, from which the methods of obtaining information can be actively explored with a class.

It appears likely that some of the more important decisions to be made by our community till the end of this century will be in the area of chemical technology, be it uranium, environmental pollution or biochemical aspects of medicine, so it is imperative that we develop a scientifically literate electorate. What better place to start than in the area of our most immediate concern, as consumers.

The limitations of this book are large and obvious. It covers a limited area and from a viewpoint that is not always impartial. An effort has been made to give balance in the further reading section of the bibliography and through an expansion of some sections—in particular in the chapter on Food Additives. Provided the reader (or teacher) is armed with a reasonable degree of curiosity and persistence there is no reason why areas beyond the limits covered in the book cannot be actively explored.

Canberra
29 August 1977

B.S.

ACKNOWLEDGMENTS

While the problem with the first edition was in obtaining information, the climate generated by organised consumer activity has in the meantime resulted in a greater availability of relevant sources.

Mr Peter Strasser is thanked both as author and editor for the use of his published lecture on detergents, while New Science Publications allowed Ariadne's photograph of the royal statue attacked by detergent to appear. The *Canberra Times* provided the photograph of the foaming Molonglo River and the table of zero phosphate detergent formulations is reproduced with permission of the Gulf Publishing Company, Houston, U.S.A. A stimulating talk by Ms Marilyn Elfverson on Market Research is reproduced with permission to contrast with the report of the Industries Assistance Commission on cosmetics. Consumers' Institute (New Zealand) allowed the rewrite, summary and paraphrase of their material but not its direct reproduction for this edition. Their work in the areas of cosmetics and adhesives was appreciated. The Plastics Institute of Australia is acknowledged as the source of the table on plastic film used for packaging food and the material from the seminar on Plastics and Food Packaging in Perspective.

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Mr Mike Vernon (Canberra Consumers Inc., and Chairman, Consumer Affairs Council of the Australian Capital Territory) provided a large section of the sources of Consumer Information and assisted with the updating of consumer standards information. Dr Tom Bellas (Division of Entomology,

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From the first edition the original acknowledgment to Dr Malcolm Rasmussen and Dr Dereham Scott, without whom the course would not have come into being, remains the most important statement. That edition was typed through several years by Mrs Margaret Keys with accuracy, speed, and good humour, and indexed by Mrs Elizabeth McDonald.

A.N.U. Press turned a set of notes into this book whose remaining errors of commission and omission are mine. While every attempt has been made to find the original copyright owners, the material, having been collected over many years without thoughts to publication at the time, may still infringe some copyright. In that event I would be grateful for information so that due acknowledgment can be given.

My position on the Executive of Canberra Consumer Incorporated has been quite an education. Just what kind of an education could well be the subject of another book.

It is to my late father, Herbert Selinger, that I am particularly indebted. His long involvement with the consumer movement (he was on the Council of the Australian Consumers' Association) and his firm belief that scientists should do useful things, at least some of the time, has had a profound influence on me.

Finally I thank my wife Veronique for her patience and understanding.

A GLOSSARY FOR NON-CHEMISTS

Act	Act of parliament—law passed by parliament. Regulations are made under the Act which regulate the activities controlled by the Act. The regulations are easy to introduce or amend—the Act is not easy to change. If different States have different Acts covering the same area, then the corresponding regulations may have to be worded differently. This can introduce non-uniformity.
ADI	Acceptable Daily Intake. The amount of a substance which can be ingested per day for a lifetime without ill effects. This is based on a study of the toxicity of the substance (its poisonous nature including the possible formation of tumours). It does *not* take into account any pharmacological effects of the substance—its ability to act as a drug.
AFCO	Australian Federation of Consumer Organisations. As the roof organisation for individual consumer organisations, AFCO represents over one million consumers throughout Australia. It is primarily a federal lobby allied or competing with manufacturing, agricultural and union lobbies in Canberra. At present it is funded by the Government.

AGPS	Australian Government Publishing Service, (equivalent in the U.K. = HMSO; in the U.S.A. = Superintendent of Documents, U.S. Government Printing Office).
alkylolamide	The product from the reaction of the amine part of an alkylolamine with an organic acid. An alkylolamine is an alkylol (fatty alcohol) in which one of the hydrogens (on carbon) has been replaced by an amine group.
alcohols	Organic compounds with the functional group — OH (not when attached to an aromatic ring when they become phenols).
aliphatic	Straight or branched chain carbon compounds in contrast to aromatic.
alkaloid	Chemically defined as an organic substance containing nitrogen which occurs in plants and which behaves as a base. More generally the word implies a fairly complex substance which is biologically active.
amine	Compound formed from ammonia by replacing one or more hydrogen atoms with organic groups (of general description R,R′, etc.).
amphoteric	Having the properties of both an acid and base.
anhydroglucose	Glucose with loss of a water molecule.
antioxidant	Substance which hinders oxidation (loosely, the reaction with oxygen) of another material in which it has been included.
aromatic	Having ring type groups usually composed of carbon atoms, e.g. benzene and naphthalene which have alternating double and single bonds (these in fact *don't* alternate but are smeared around the ring uniformly as an average of one and one half bonds) in contrast to aliphatic.

aryl	The term used to refer to an aromatic group such as benzene or naphthalene (*ar*omatic + *-yl*).
atropine	Poisonous substance found in deadly nightshade —used medicinally, e.g. to widen pupils for eye examination.
bi-acid	A substance which has two acid groups instead of the more usual single acid group.
bifunctional	A molecule with two groups attached that can react rather than the more usual single reactive group.
biodegradable	The property of a complex chemical compound to be able to be broken down into simpler components under naturally occuring biological processes—such as those which form part of the normal life-cycle in a river or soil.
branched—hard	The branched chain compounds are unable to be broken down at a reasonable rate in the environment.
buffer	A mixture of substances which tend to hinder large changes in acid or basic properties of a solution—used in a more general sense outside chemistry.
carboxylic	Refers to the organic acids having functional group —COOH.
carcinogen	An agent capable of inducing cancer.
catecholamines (biogenic amines)	A series of biologically active amines, e.g. Dopamine (3-hydroxytyramine), Noradrenaline, Adrenaline.
caustic	Very alkaline—capable of dissolving skin, fat, etc. to form soap.
Chemistry and Industry	Published by the Chemical Society, U.K.

Chemistry in Britain	Journal published by the U.K. Chemical Society and the Royal Institute of Chemistry and sent to members.
ChemTech	Published by the American Chemical Society.
cholesterol	A fat-like molecule (chemically not a fat, but an alcohol) with a structure on which all the steroids (e.g. sex hormones, bile acids and cortisone, etc.) are based. Produced by the body.
chromatography	Separation of colours—now a general technique of separation of chemicals based on the difference in the strength of adsorption onto a solid.
compounding	A polymer is formed from monomer units and is sometimes called a resin. In order to make a useful plastic material, the resin must be mixed with other materials—or *compounded.*
conditional probability	The probability that an event will occur, given that some other event has already occurred.
continuous phase outer phase	The first liquid which surrounds droplets of a second liquid (being the discontinuous phase) in an emulsion.
copolymer	A polymer formed from linking two (or more) different monomer types.
CSIRO	Commonwealth Scientific and Industrial Research Organisation. This has many divisions such as Food Research; Entomology; Plant Industry; Building Research; Human Nutrition; Chemical Physics . . . engaged in research for industry.
electrode	Conductor through which electricity enters or leaves a solution of ions (gas, vacuum or other medium).
elastomer	A polymer material with elastic properties—namely the ability to return to the original dimensions after distortion.

emollient	A substance that softens and soothes the skin.
emulsions	The suspension of one liquid as fine droplets in another with which it does not dissolve.
enzyme	A biological molecule which can promote a particular reaction (to the exclusion of others).
epoxide formation	Generally formed by the addition of oxygen to a double bond. A three-membered ring (two carbon atoms and one oxygen atom).
ergot	A disease of rye caused by fungus—which causes bread made from diseased rye to be poisonous. The word also refers to the toxic substance—which is also used medicinally.
erythema	Surface inflammation of the skin.
esters	Combination of (organic) acids and alcohols. The carboxylic esters with short chains are often pleasant smelling. Fats and oils belong within the classification of esters.
excise	Duty or tax levied on goods produced or sold within the country—while customs are levied on imported goods.
fatty	Having a long chain of carbon atoms, usually 10–18 members. These chains are the backbone of the fatty acids in fats.
Feingold diet	This is a diet developed by Dr Ben Feingold, an allergist, which in *some* cases causes dramatic improvement in the behaviour of children diagnosed as hyperactive. It is a diet which excludes foods containing natural salicylates and synthetic colours, flavours and preservatives. It should not be undertaken without adequate nutritional supervision.

flammable	Easily set on fire—used now officially in place of the work 'inflammable' (which is philologically more correct) because of the confusion whereby inflammable was thought to mean non-fammable.
fluorescence	The rapid emission of light at longer wavelengths than that which is absorbed, e.g. adsorption of ultra-violet light can yield blue fluorescence.
Food Technology in Australia	Published by the Council of Australian Food Technologists Association, Inc. (CAFTA).
glycerides	Esters of the tri-alcohol glycerol; sometimes called triglycerides (fats). Mono-glycerides are made synthetically and used as emulsifiers.
half-life	The length of time taken for a substance to drop in concentration to half its original level. Strictly true only for exponential decay (which never reaches zero) but used more generally.
hazardous	Risk depending on chance. Hazard depends on the *chance* of contact or injection (of a toxic material). Flammable materials become hazardous if there is a chance that they will be exposed to fire.
heavy metal	The metals with higher atomic weight tend to form compounds which are more poisonous.
hygroscopic	Materials which absorb water from the air. This property depends on how much moisture is in the air.
humectants	Additives for keeping a product moist—or a product for keeping something else (e.g. skin) moist.
hyper-	Prefix meaning high—poor use of language because of the similarity in sound of the word 'hypo' which has the opposite meaning— HYPERkinetic = overactive HYPERtension = high blood pressure.

hypo-	Prefix meaning low—see also the opposite prefix meaning high. These prefixes are generally restricted to medical terms, but: photographic 'hypo' (sodium thiosulphate) has one sulphur atom with a low valency of two.
Industries Assistance Commission (IAC)	Was known as the Tariff Board. A Commonwealth statutory body which holds enquiries and makes reports on the level of protection it believes necessary for industries.
infra-red	The region of the sun's radiation which lies beyond the red colour as seen in a rainbow. It is not visible but it is sensed as heat. Just as materials absorb different colours from white light they also absorb different sections of infra-red radiation.
initiator	A substance used to start a polymerisation reaction.
ions/ionic	Chemical entity carrying electric charge (positive or negative). Ions occur in equal number of oppositely charged members either close together as in solid salt (Na^+Cl^-) or free to wander as in a salt solution in water.
JAOAC	Journal of the Association of Official Agricultural Chemists (U.S.A.).
kilojoules	One thousand joules. A joule is about one quarter of a calorie (kilojoule is about one quarter of a kilocalorie—written *C*alorie).
latex	An emulsion of rubber globules (in water) (extended to include globules of synthetic materials).
linear—soft	The straight chain compounds are able to be broken down rapidly in the environment.
lipids	What chemists call fats, biochemists call lipids (to a first approximation).

mole/moles/mols/mol.	Bakers have their dozen (=13) and so do chemists. The chemist's one is called a mole and contains 6.023×10^{23} single molecules. This number is chosen because this number of atoms and molecules always weighs in grams an amount equal to the atomic (molecular) weight. Thus a mole of carbon weighs 12 grams and a mole of oxygen weighs 16 grams. A mole of carbon monoxide (CO) weighs 28 grams.
monomer/polymer	The single units which on linking together form polymers (plastics).
mutagen	An agent capable of causing mutations in the genetic material which can affect either the organism or its offspring depending on which cells are affected.
NBSL	National Biological Standards Laboratory, Canberra, A.C.T.
New Scientist	U.K. Science weekly. Available at larger newsagents or on subscription.
NHMRC	National Health and Medical Research Council.
organic	Originally referred to chemicals produced by living organisms—today it simply refers to the chemistry of carbon compounds.
organochlorine	Compounds which are generally composed only of carbon and hydrogen to which chlorine has been added. These compounds are often biologically very active but not easy to break down—hence they are persistent.
oxalic acid	The simplest organic acid with two carboxylic acid groups—poisonous.
parenteral	(Drugs) absorbed into the body by a route other than by the intestinal tract.

phenols	Aromatic groups such as benzene and naphthalene with the functional group —OH attached.
phocomelia	From the Greek: having limbs looking like the flappers of seals.
photodynamic	Caused by light.
plasticiser	This is an additive which makes a plastic material more flexible or less rigid.
plastisols	A plastic formulation that has a high degree of fluid behaviour generally due to a large amount of added plasticiser.
poison	Substance that when introduced into or absorbed by a living organism, destroys life or impairs health. (Used anthropomorphically by chemists when referring to catalyst—which when 'poisoned' can no longer function.)
polymerisation	The process by which single units (monomers) are joined together, like linked paper clips, to form a giant molecule.
polymorphism	A substance which can occur in a number of solid forms.
precipitate/ation	To fall out of solution as a sediment.
ppm	Parts per million (by weight)—equivalent to a grain of sugar in a cup of tea (very approximate) —also called milligrams per kilogram, or given as 0.0001 percent.
PRACI	Proceedings of the Royal Australian Chemical Institute—renamed after July 1977 as *Chemistry in Australia.*

prostaglandins	Biological chemicals isolated most readily from sperm and prostate glands of sheep, but very widespread in animals. These compounds are hormones with widely differing functions.
racemic	A one-to-one mixture of left- and right-handed form of the same molecule. Most chemical reactions produce products as such mixtures.
refractive index	A measure of the ability of a material to bend a ray of light.
resin	See compounding.
R,R′	The R designates an undefined organic group—in our case, generally a hydrocarbon chain. The R′ just says it is not necessarily the same as R.
salicylic acid	= o-hydroxy benzoic acid. *acetyl salicylic acid* = aspirin (analgesic) *methyl salicylate* = oil of wintergreen (used as a liniment for sore muscles). *phenyl salicylates* (salol) = used in sunscreens and as a stabiliser in plastics. *salicylanilides* = compound of salicylic acid and aniline derivatives—used as antiseptics in soap.
sequester	To take out of circulation, to tie up metal ions so that they don't interfere (by precipitating soaps, etc.)
sequestering agent	A chemical which ties up metallic ions in solution.
spectroscopy	The noblest science of them all! The separation and analysis of light into its component parts and study of the interaction of materials with the different regions of light. Now applied over the whole range of electromagnetic radiation from radio waves to gamma and X-rays—the most powerful and most common source of information on the structure of molecules.

stereospecific	Applied to polymers it is the ability to cause a polymer to be formed in a single geometry rather than as a mixture of structures. This often means the polymer can pack together more efficiently to give a material of greater order and higher density.
substrate	A basis on which something else is placed; a starting material.
sulphonation	The addition of the functional group $-SO_3H$ to a molecule.
sulphonic acid/sulphonate	Organic compound with the functional group $-SO_3H/-SO_3^-$.
surface tension	The force of attraction for itself which gives a liquid such as water an apparent skin which contracts so as to form drops rather than sheets (on waxy surfaces). On some surfaces, e.g. clean glass, the attraction of the water is greater for the glass than for itself and so the water wets the glass.
surfactant	A molecule attracted to the surface of water and capable of changing the properties of the surface generally by lowering the surface tension.
synergist	A substance which itself has no activity but increases the activity of another substance when it is added to it.
Tappi	Technical Association of the Pulp and Paper Industry (name of their journal).
teratogen	An agent capable of inducing monstrosities (in the newborn).
thermoplastic	Applied to a polymer that melts on heating (its structure consists of independent long molecules).

thermosetting	Applied to a polymer that is sometimes made by heating but once formed does not melt on heating, charring instead (its structure has cross-linking from one chain to the next).
threshold	(of poisons) the maximum level of intake which produces no clinically detectable effect—no response dose. This is not necessarily the level below which no damage is done.
toxicity	The *property* of poisons.
toxin	Generally used for poisons secreted by microbes.
trade mark	A device or word legally registered as distinguishing a manufacturer's or trader's goods. It is spelt with a capital letter to distinguish it from a common name, e.g. Coke produced by the Coca Cola Company (both coca and cola are common names).
urticaria	Nettle-rash, but used to describe other skin allergies often made worse by exposure to sunlight.
viscosity	Resistance to change in shape or form of a material—'internal friction'.
volatile	Readily forming a gas.
'wetting'	The covering of a solid by a liquid with a thin film. The contact angle the liquid makes on the solid is small.
WHO	World Health Organisation (United Nations).

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Chapter 1

SOME BASIC CHEMICAL IDEAS

LANGUAGE AND LABELS

To talk about chemistry, or any other subject for that matter, you need to know some of the jargon. The existence of a specialised language peculiar to a particular field can be the most formidable obstacle in approaching an unfamiliar subject. Let us try to overcome this hurdle first.

Atoms

All matter is composed of atoms, of which there are about ninety distinctly different kinds occurring naturally on the earth. In very simple terms each atom consists of a *positively-charged nucleus* surrounded by a cloud of *negatively-charged electrons,* so that, overall, the atom has no electrical charge.

Elements

Substances that contain only one of the ninety different types of atoms are called elements. Consequently, there are only about ninety natural elements; familiar examples are copper, tin, iron, aluminium, oxygen, nitrogen, hydrogen, and carbon. Each element is given a symbol—O for oxygen, H for hydrogen, C for carbon, and so on. These symbols may be regarded as the letters of the chemical alphabet.

Compound substances

The remainder of the millions of other substances around us are either *compounds,* formed by specific combinations of different elements, or *mixtures* of a number of compounds. The basic combination of atoms characteristic of each compound is called a *molecule* for which a formula can be written using the symbols of the elements making up the compound, together with an indication of the number of each different type of atom present. For

example, carbon, C, forms two compounds with oxygen, O: carbon (mon)oxide, CO, and carbon (di)oxide, CO_2; water is a compound of hydrogen and oxygen, H_2O. Most molecules are *polyatomic*, i.e. having many atoms, up to many thousands; table sugar, for example, has the molecular formula $C_{12}H_{22}O_{11}$. Since these formulae are combinations of the letters of the chemical alphabet, we can consider them chemical words.

Of some relevance here is the relation between the English and Chinese languages.[1] English reading these days is taught by familiarising the pupils with word outlines (rather than spelling with letters). Chinese reading is taught the same way. The constituents of the English word outline (called letters) offer the reader some guidance to pronunciation. A Chinese word outline or character consists of some 214 available radicals of which 150 are often used and about 50 are major radicals. These provide meaning. Then an additional symbol chosen from several hundred gives a phonetic guide. Thus an ordinary Chinese speaker has several thousand characters at his disposal while a scholar might have tens of thousands. The Chinese character is a stable unit which can be combined with others to give new words.[2]

Valency

Just as there are spelling rules for putting letters together to form words, so there are the rules of *valency* (or *combining power*) for constructing the formulae of molecules from the atomic symbols. In water, H_2O, for example, hydrogen has a combining power of one, while oxygen has a combining power of two. Thus one oxygen atom may combine with two hydrogen atoms; consequently, the arrangement of atoms in the water molecule must be something of the form H . . . O . . . H, with the oxygen atom in the middle.

Elements often show different valencies in different compounds; e.g. lead, Pb, forms two compounds with chlorine: $PbCl_2$ and $PbCl_4$, showing valencies of two and four, while chlorine in both compounds has a valency of one. Some of the elements you will meet are shown in Table 1.1.

Bonding

Since all molecules of any one compound are composed of the same atoms arranged in essentially the same way to satisfy the rules of valency, there must be some definite forces holding the atoms together in that particular way. These forces are the *chemical bonds* and, broadly, they arise from the sharing of electrons between the atoms. Thus in the molecule of hydrogen, H_2, the two atoms are bonded together by the sharing of two electrons, one from each atom. We write it H : H, where the two dots represent the electrons, or, more commonly, H–H, where the dash represents the electron pair or the chemical bond between the atoms. A bond of this sharing type is called a *covalent bond,* by far the most common kind.

TABLE 1.1 *Some common elements*

Element	Hydrogen	Oxygen	Carbon	Nitrogen	Phosphorus	Lead	Mercury
Symbol	H	O	C	N	P	Pb	Hg
Valencies	1	2	4	3, 5	3, 5	2, 4	1, 2

Again, for hydrogen chloride, we can write H : Cl or H–Cl, but here, because the two atoms of the molecule are different, the bonding pair is not shared equally; rather, the chlorine has more than its fair share. We could show this as H :Cl, or, because the chlorine not only has its own electron but a share of the electron from the hydrogen as well and hence has gained a slight additional negative charge, as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

Because this molecule has positive and negative ends, or *poles*, it is said to be a polar molecule and the bond is called a *polar bond*. As you will see, this uneven distribution of electrons can have most important consequences for the behaviour (or *properties*) of the molecule, in comparison with the behaviour of *non-polar* molecules.

The bond in hydrogen chloride is still a covalent (or sharing) bond, albeit a polar one, but in some extreme cases one of the atoms can assume virtually complete control over both electrons. We show this as, for example, Na^+Cl^-, sodium chloride, common salt. Here the chlorine atom has taken the bonding electron completely from the sodium atom, assuming in the process a unit negative charge (the charge of one electron) and becoming what is called a *negative ion* or *anion*. Similarly, the sodium atom has become a *positive ion* or *cation*. Compounds composed of ions are called *ionic compounds* and are said to be held together by *ionic bonds*. As a general rule ionic compounds are water-soluble and fat-insoluble while the reverse is true of covalent compounds. Where a molecule has both types of bonds intermediate behaviour is to be expected.

Chemical equations

Equations are chemical sentences, composed of words (molecules) and conveying information about the transformation of chemical substances, i.e. they describe *chemical reactions*. Thus

$$2H_2 + O_2 \longrightarrow 2H_2O$$

tells us that two molecules of hydrogen combine with one molecule of oxygen to give two molecules of water. These chemical equations are a statement of the overall change and make no attempt to indicate *how* the change occurs.

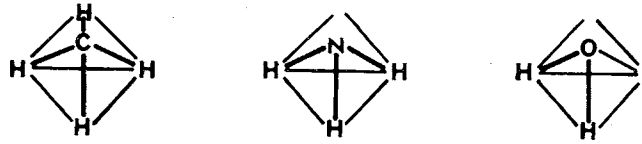
Shapes of molecules

Earlier we concluded that the arrangement of the atoms in the water molecule was something of the form H—O—H, where one oxygen atom with a valency of two forms two covalent bonds with two hydrogen atoms. These bonds are polar and we could show this as

$$\overset{\delta+}{H} - \overset{\delta-}{O} - \overset{\delta+}{H}$$

But do the three atoms of the water molecule lie in a straight line? If not, what is the shape of the water molecule? Consideration of molecular shapes and their consequences is known as *stereochemistry*, a most important aspect of the properties of the molecule.

Consider the three compounds: methane or marsh gas, CH_4, ammonia, NH_3, and water, H_2O. Carbon has a valency of four, and in methane the four hydrogen atoms lie at the corners of a tetrahedron with the carbon atom at the centre. Ammonia, containing the central atom of nitrogen with a valency



1.1 Structures of methane, ammonia and water

of three, has a similar shape, except that one of the corners of the tetrahedron does not have a hydrogen atom; the ammonia molecule is pyramidal in shape. The water molecule, with only two hydrogen atoms, is bent, as shown in Figure 1.1.

Names of chemicals—chemical nomenclature

In order to communicate information about chemistry and chemicals there has to be a way of identifying and naming them. A trade or brand name can be given to a chemical or a formulation of chemicals and registered by a firm for its exclusive use. Such a trade name gives no information, and the composition of the product to which it refers can vary. In many cases a trade name can be so popular that it becomes, by common usage, a common name, e.g. aspirin, biro, cellophane, bakelite. Manufacturers must keep on insisting that their trade name be spelt with a capital letter because once a trade name has become a common name it may be legally defined as the *generic* or non-proprietary term for a particular material. Today aspirin is not the Bayer trade mark but the generic name for a particular chemical substance. Whereas there can be an enormous number of trade names for a chemical, there are only one or two generic names. The generic name can then be qualified to provide further generic names for related compounds, e.g. penicillin and penicillin G.

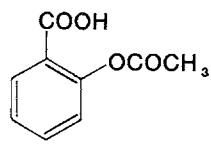
In order to have an unambiguous precise name for a chemical substance a system has been devised to provide a *systematic name* for any substance. These names are built up according to strict rules; each compound has only one correct systematic name and that name conveys the complete information about the detailed structure of the compound—i.e. it is a stylised written description of the chemical structure. For example, Aspro (trade), aspirin or acetylsalicylic acid (generic), 2-acetyloxybenzoic acid (systematic).

Chemical formulae and diagrams

Chemical formulae and diagrams are symbolic representations of the composition and structure of molecules and compounds. There is a variety of conventions for them, depending on the sort of information to be conveyed.

At the lowest level of information is the *empirical formula*—e.g. for aspirin it is $C_9H_8O_4$—which only lists the numbers and types of atoms present in the molecule and tells us nothing about the structure. Many different chemicals can have the same empirical formula. The *group formula* places atoms together in groups which correspond to the grouping in the actual molecule and gives some indication (using prefix symbols) of how the groups fit together, e.g. the group formula for aspirin is $2\text{–}CH_3COO—C_6H_4COOH$. With experience these group formulae can give a fairly complete, marginally ambiguous, description of the structure.

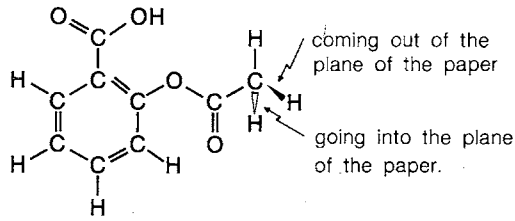
The *condensed structural diagram,* the most common form of line diagram, gives a two-dimensional representation of a three-dimensional structure leaving out a lot of the atoms whose presence is implied by the shorthand conventions, e.g. for aspirin the condensed structural diagram is as shown in Figure 1.2.



1.2 Condensed structural diagram for aspirin

The hexagon is a ring of six carbon atoms (called the benzene ring) joined by alternating double and single bonds. Carbon has a valency of four so that any missing bonds are taken up by a bond to a hydrogen atom. There are other apparent ambiguities (although convention clarifies them). In fact these diagrams are condensations of the *full structural diagram*, which is rarely used, in which the three-dimensional structure of the compound and the bond angles are indicated; the full structural diagram for aspirin is shown in Figure 1.3.

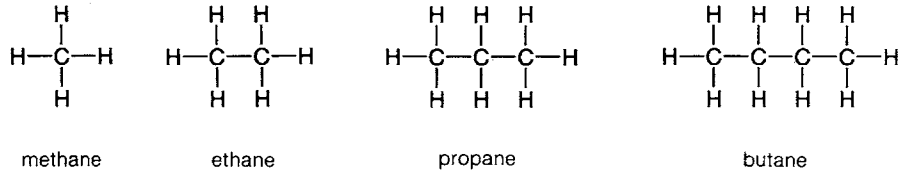
Note that each carbon atom C and hydrogen atom H is specifically depicted, whereas in the more usual condensed version the carbon atoms are implied to be at the intersections of the bond lines and the hydrogen atoms are implied to fill positions so that the valence of four for carbon is satisfied. Throughout the text condensed structural diagrams will be used, with extra information included when required for the emphasis of a particular feature.



1.3 Full structural diagram for aspirin

Organic Chemistry

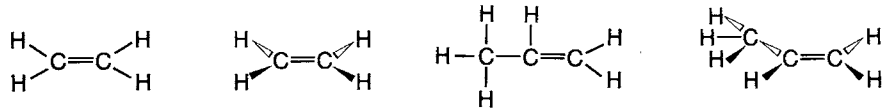
As its name implies, this branch of chemistry originally dealt with chemical substances produced by living organisms. The key element in all organic molecules is carbon, which forms many more compounds than any other element (with the possible exception of hydrogen). In its stable compounds, carbon always has a valency of four, and when it is bonded to four other atoms, they are arranged tetrahedrally about the carbon atom (see Figure 1.1). Carbon also shows, to a remarkable extent, the property of *catenation* (chain forming); i.e. many carbon atoms can bond together to form chains or rings.



1.4 Formula of some paraffins

The simplest group of these chain molecules are the *paraffins*, or *alkanes*, which are found in natural gas and petroleum. The first members of the series are methane, CH_4, ethane, C_2H_6, propane, C_3H_8, and butane, C_4H_{10} (Figure 1.4). Propane and butane are the main constituents of bottled fuel gas, while petrol contains principally the members with seven (heptane) or eight (octane) carbon atoms; the lubricating oils have much longer chains.

In all of the paraffin compounds, the carbon atom shows its constant valency of four and the atoms bonded to it are arranged tetrahedrally. However, in many cases, two or three of the four valencies may be used up in forming a *double* or even a *triple* covalent bond with another atom. Carbon dioxide, O—C—O, is a familiar example. There is a series of compounds, called the *olefins* or *alkenes*, which are closely related to the alkane series discussed above, but each member has two less hydrogen atoms than the corresponding alkane, which means that each has one double bond. The olefins are the simplest unsaturated compounds. Figure 1.5 gives the structural formulae for ethylene, C_2H_4 (compare ethane), the basic molecule from which polythene (polyethylene) is made; and for propylene, C_3H_6, which is used in the new plastic polypropylene. Note that the ending *-ene* is indicative of the alk*enes*, as *-ane* is of the alk*anes*.

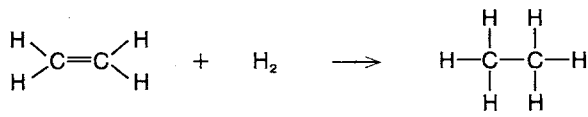


1.5 Structural formulae for ethylene and propylene

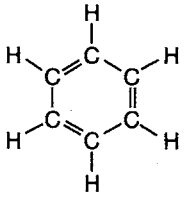
Another type of unsaturated hydrocarbon is, for example, butadiene, C_4H_8, which contains two double bonds (see Figure 1.6); it is the basic constituent of the earliest synthetic rubbers.

1.6 Butadiene

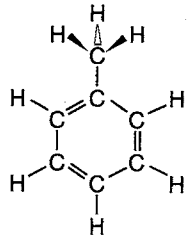
The simplest member of the triply-bonded series, the *alkynes*, is acetylene, H—C≡C—H, the familiar gas used in welding. Such carbon compounds containing *multiple* bonds are said to be *unsaturated*—as in polyunsaturated margarine, which we shall discuss in Chapter 3—because it is possible to add more atoms to their molecules, thereby *saturating* them. For example, ethylene can be simply converted to ethane by the addition of two hydrogen atoms.



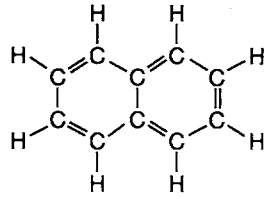
Another important group of carbon compounds are those containing ring molecules, such as benzene, toluene, and naphthalene (Figure 1.7).



benzene
(benzol)



toluene
(methyl benzene)



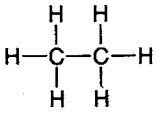
napthalene
(moth balls)

1.7 Some aromatic hydrocarbons

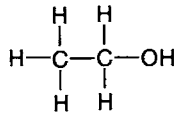
So far we have considered only organic molecules containing carbon and hydrogen—the hydrocarbons—but it is possible, by replacing some of the hydrogen atoms with other atoms, to make whole new series of compounds, with different properties depending upon the nature of the *substituting* atoms. It is important to note at this stage that apparently minor changes to a molecule can produce major changes in physical, chemical, and physiological properties. Thus from methane, CH_4, we can prepare CH_3Cl (methyl chloride), CH_2Cl_2 (methylene chloride used in paint strippers), $CHCl_3$ (chloroform, the first anaesthetic other than alcohol and blunt instruments), and CCl_4 (carbon tetrachloride, once widely used in dry cleaning until its toxic properties were admitted).

CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
non-toxic flammable gas	methyl chloride; toxic	paint stripper; relatively non-toxic	first anaesthetic; damages liver	erstwhile drycleaning fluid; more toxic than $CHCl_3$ fire (electrical) extinguisher (no longer)

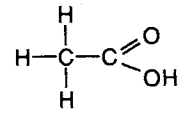
Some other examples of property changes due to small changes in a molecule are the differences between ethane, C_2H_6, ethyl alcohol, C_2H_5OH, and acetic acid, CH_3COOH; and between benzene, C_6H_6, benzoic acid C_6H_5COOH, and acetylsalicylic acid, $CH_3COOC_6H_4COOH$ (Figure 1.8).



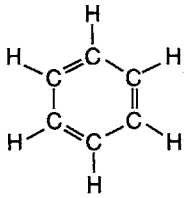
ethane
(colourless,
non-toxic gas)



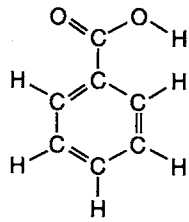
ethyl alcohol
(the common alcohol
in drinks)



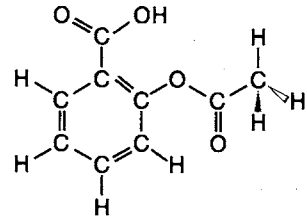
acetic or ethanoic
acid (gives vinegar
its bite)



benzene (liquid)
(toxic)



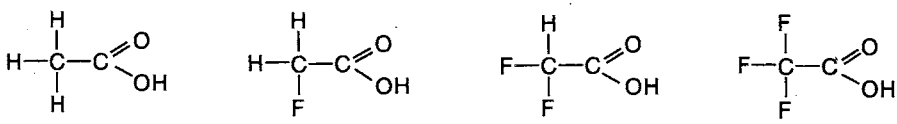
benzoic acid (solid)
(food preservative)



acetylsalicylic acid (solid)
(aspirin, analgesic)

1.8 Property changes due to molecular changes

Yet another example is given by the successive replacement of the hydrogen atoms of acetic acid with fluorine (Figure 1.9). Acetic acid, in vinegar, is relatively non-toxic, fluoroacetic acid is used as the sodium salt in 1080 rabbit poison and is highly toxic to humans, it also is the poisonous constituent in some poisonous plants; difluoroacetic acid is not primarily toxic, while trifluoroacetic acid forms the basis of some weed killers, such as Dalapon.



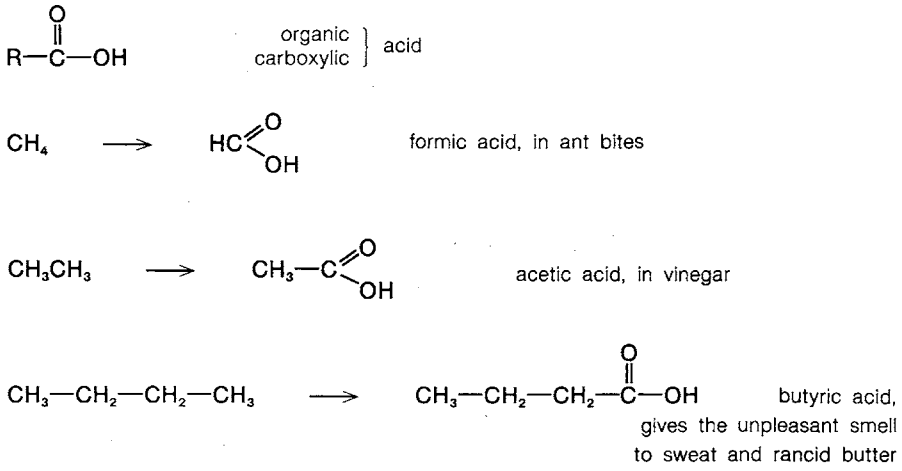
acetic acid | fluoroacetic acid | difluoroacetic acid | trifluoroacetic acid

1.9 Replacement of hydrogen atoms of acetic acid with fluorine

Many of the changes in physical and chemical properties accompanying substitutions of this sort can be predicted, but changes in physiological properties are often quite unexpected. However, by the same token, certain groupings of atoms within a molecule are known to produce certain physiological effects and much drug research is devoted to modifying these basic structures in the hope of enhancing the pharmacological activity and, at the same time, reducing undesirable side effects. It is safest to assume that all chemicals are toxic.

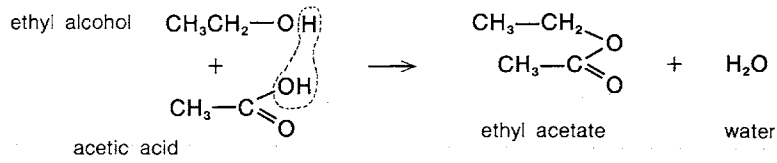
Organic compounds may be classified according to the nature of the *functional groups* that have replaced hydrogen in the basic molecule. Three important functional groups are:

1. *alcohols,* having the general formula R—OH, where R stands for the rest of the hydrocarbon skeleton. The simplest alcohol, derived from methane, CH_4, is methyl alcohol, CH_3—OH; this substance, often called wood alcohol because it is obtained by heating wood, is more toxic than the familiar ethyl alcohol, CH_3CH_2—OH.
2. *organic acids* containing the characteristic carboxyl group, COOH. Any molecule containing this group is called a *carboxylic acid*; some examples are illustrated in Figure 1.10.



1.10 Organic acids

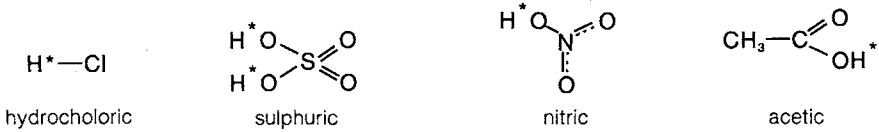
3. *esters*, which are produced by the combination of alcohols and acids in an *esterification* reaction:



Ethyl acetate is an important solvent in the paint and adhesive industries. Many of the natural flavours and smells are due to the presence of volatile esters in flowers and fruits, while meat fat consists of solid esters, and oils are liquid esters.

Acids and bases

You will have heard of sulphuric and hydrochloric acids; and of caustic soda, which is a member of a group of compounds called bases. You may know that if caustic soda is mixed with hydrochloric acid, the acidic and corrosive properties of the acid are overcome, i.e. *neutralised*. The chemical basis for the concepts of acidity and basicity is rather complex and we must begin with a simplified approach. For our purposes, all substances which we will consider as acids, such as hydrochloric acid, HCl, sulphuric acid, H_2SO_4, nitric acid, HNO_3, and acetic acid CH_3COOH, are characterised by the presence, in the molecule, of one or more reactive hydrogen atoms that can be displaced by a base in the process called neutralisation. The reactive or *acidic* hydrogen atoms in the molecules shown in Figure 1.11 are marked by asterisks; notice that the methyl hydrogens of acetic acid, the ones attached directly to the carbon atom, are non-acidic. Among the common bases are sodium hydroxide—caustic soda, NaOH; calcium hydroxide—slaked lime, $Ca(OH)_2$; and ammonia—ammonium hydroxide, NH_4OH.



1.11 Reactive or acidic hydrogen atoms in acids

The neutralisation reaction between an acid and a base follows the general pattern

$$\text{an acid} + \text{a base} \longrightarrow \text{a salt} + \text{water}$$

e.g. $\overset{*}{H}—Cl + Na^+OH^- \longrightarrow Na^+Cl^- + H—OH$

which is clearly very closely related to the esterification reaction between organic acids and alcohols already discussed.

Simple acids have one other important property: when dissolved in water they can, to a greater or lesser extent, transfer the reactive hydrogen atom to the water molecule, forming ions. Thus

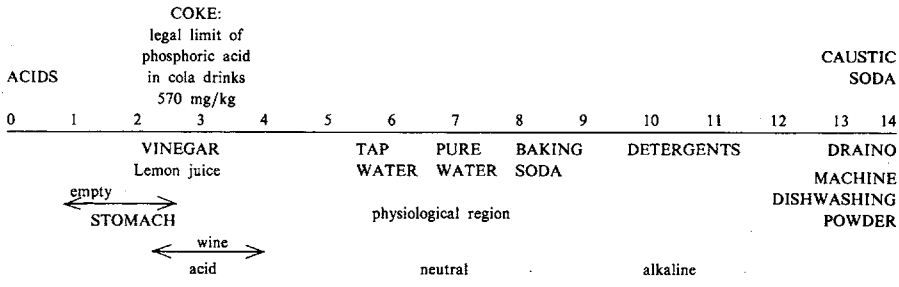
$$\overset{*}{H}—Cl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$CH_3COO\overset{*}{H} + H_2O \longrightarrow H_3O^+ + CH_3COO^-$$

On solution in water then, acids produce the H_3O^+ ion. *Strong acids* such as HCl transfer the active hydrogen completely; weak acids, such as CH_3COOH, are capable only of a partial transfer (statistically).

The amount or rather the concentration of the species H_3O^+ produced when a given acid is dissolved in water may be expressed on a scale known as the

pH scale (see Figure 1.12). Pure water has a pH of 7. A solution of a strong acid in water at unit concentration (in the proper units) has a pH of 0, while a solution of a strong base at unit concentration has a pH of 14.



1.12 pH scale

Solubility

Ordinarily when we say a substance is soluble, we mean that it dissolves to an appreciable extent in water. However, we do make every-day use of other solvents—dry cleaning spirit for grease stains, turpentine for paints, and so on. The question of solubility in oils and fats is of great importance to the physiological action of pesticides and drugs, the cleaning action of detergents, etc. There is a simple rule which works well in predicting solubilities of substances in various solvents—*like dissolves like*. This means that ionic and highly-polar substances are usually soluble in polar solvents such as water, while covalent non-polar substances are soluble in non-polar solvents such as benzene, petrol, and carbon tetrachloride.

Although many substances do not dissolve in water or other solvents, it is often possible to produce a stable or semi-stable mixture or *dispersion* of solute and solvent. This process is called, broadly, *solubilisation.* The resulting dispersion may be stabilised by the addition of another substance, such as a detergent. *Emulsions* are an important group of these dispersions, milk and cream for example are emulsions of fat in water stabilised by the emulsifying agent casein (a protein). When producing butter from cream the emulsion changes to one of water in oil (20 per cent water). In egg mayonnaise, the oil–water emulsion is stabilised by the egg white (also a protein). (See also Chapter 4). These principles will be illustrated in our discussions on detergents and cosmetics.

ON STANDARDS[3]

The word *standard* has a variety of meanings—from a flag, to a weight or measure, to a connotation of average quality: being of a low/high standard. Standards are very much part of our everyday lives. After all, language itself

is standardised although its standard is constantly changed by common usage or agreement.

It is by mutual consent that standards are currently set in Australia. The main body concerned with this area is the Standards Association of Australia (SAA) which derives its legal status from a Royal Charter and its finance from government grants, subscriptions, and the sale of documents detailing SAA Standards. It would be fair to say that this body has been mainly concerned with industrial standards of interest to suppliers and consumers in industrial trade. Although these standards may be of importance to 'the consumer in the street' this has never been terribly obvious. There is now a Consumer Standards Advisory Committee whose task is to define areas in need of consumer standards as consumers expect the term to mean.

Not surprisingly these consumer standards are directed in the first instance at safety—for instance, the safety of children's toys, furniture, playground equipment; of protective helmets for pedal cyclists, or swimming pool covers, the safety of swimming aids, and of plastics for food contact. Secondly, they are directed towards provision of information—for example the care labelling of textiles; contracts for consumer transactions; the burning behaviour of textiles and textile products. These are the two categories that can be regulated under Section 63 of the Trade Practices Act. See also Appendix 1.1.

While there can be considerable argument on SAA committees between suppliers and consumers in reaching a consensus on these points, there is at least a reasonably well defined aim. A safety standard sets a level of *maximum acceptable dangerousness* and this can be fairly arbitrary—an example is the regulatory speed limit aspect of road safety—an arbitrary maximum speed is chosen which is deemed to give a reasonable compromise between convenience and safety. The extent to which an electrical appliance is shielded against giving its user a fatal shock is another example.

The same arbitrariness is true for a third classification, namely that of performance. Defining standard performance is the aim of committees involved in dealing with electrical appliances, quality of school and college wear, contraceptive devices, and household detergents. However, a little contemplation reveals that, for many consumer products at least, the performance, like beauty, is in the eye of the beholder. Having mentioned beauty, a pertinent example is that of cosmetics, which is at one end of the spectrum where the consumer is buying a fervent hope, while at the other end the suppliers are selling an image (see Chapter 4). Setting of performance standards here would require the skill of a catcher of mirages.

On the other hand, for contraceptives performance is well defined but cost, convenience, and possibly unwanted side-effects are other important parameters. Consumers are not going to agree on the combination which represents an optimum—even the same consumer will have different views in different circumstances.

What a performance standard should provide is a benchmark upon which further decisions can be made. To take a specific example, I have chosen a standard with which I have been extensively involved—that for household detergents. A liquid hand dishwashing detergent consists of water, surfactant (the active agent), colour, perfume, thickening agents, etc. Some products have lots of water and are cheap, some have less water and are more expensive. Sometimes the correlation does not hold all that well. Well, what does it matter —if we could define performance? The composition would be irrelevant and the suppliers could keep their sordid watery secrets.

Unfortunately testing performance with panels of average users shows that the perfume and thickeners are among the most important ingredients, but somehow this does not seem to be scientifically respectable in a standard. If performance is tested using a standard soiled plate and a mechanical washer-upper, then manufacturers can make products which score well on this test but may be quite poor on more general objective testing. And if a battery of tests is provided to cover a variety of circumstances the possibility of cheating can be reduced but then the exercise becomes very expensive for a relatively cheap product. Such tests can also provide headaches for legal draftsmen. Even if one doesn't have too much sympathy for these legal gentlemen, any difficulties they encounter are quickly translated into periods of delay before implementation.

On the assumption that making a detergent is not completely a random process, it seems reasonable that there should be some correlation between the ingredients and the performance—so that the next best thing might be to define a composition standard. In the case of our detergents, designating several levels of surfactant such as for example 12 percent regular, 36 percent premium, and 84 percent concentrate might seem attractive. (The level for concentrate has dropped to 45 percent in the latest standard AS1999, and for regular it is 6 percent!) The disadvantages of a composition standard of this type are that it requires the definition of all possible (and likely) ingredients, and preferably the prediction of future developments; and it also requires that allowance be made for different ingredients having different effectiveness, and for mixtures being better (or worse) than the sum of the parts.

This second point means that performance could still vary considerably at say a constant active level of 12 percent. Well, that's great—it means our standard doesn't stifle performance competition (until formulating skill can convert the performance of a 12 percent active into that of an average 36 percent our composition benchmarks remain reasonable). If manufacturers argue that performance is very much more independent of surfactant level then they must have some very good performance criteria which would be extremely useful to the standard-making committee. Although it must obviously be conceded that standards do have a certain inhibitory effect on

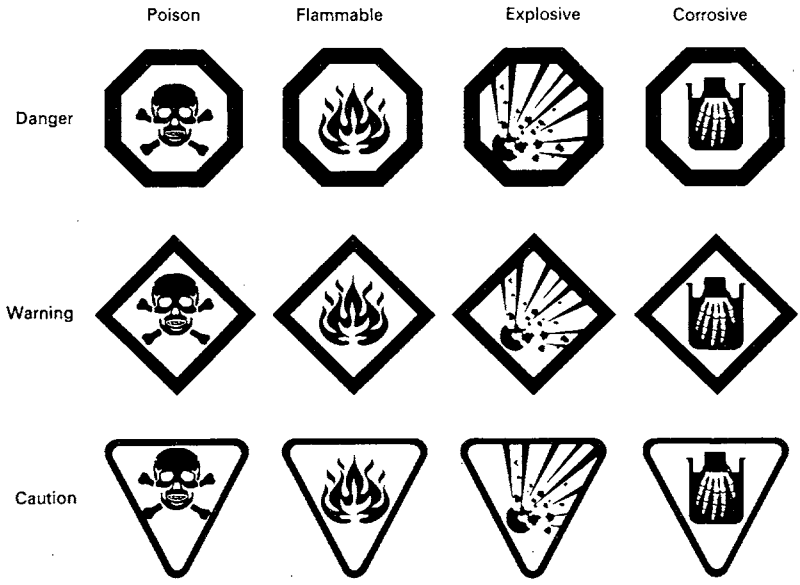
development, one cannot help feeling that the manufacturers' concern is that they have an even greater inhibitory effect on selling by brand and image rather than product. It is again the classic decision-making process of cost and benefit except that now consumers want to be part of the equation.

This same story is repeating itself in the various other consumer standards, including food standards handled by the National Health and Medical Research Council (NHMRC). Consumers should be made aware that the items selected for standardisation can be suggested by the public and that representation can be made for participation in some of the standard-making committees. Food items intended for standardisation will now be reported in the Government *Gazette*, as will the draft standards when they are formulated (see Chapter 12). The NHMRC standards are only recommendations to the States, which must then make them law for them to be enforced.

The Standards Association of Australia issues a quarterly publication on its consumer work. It is called *Consumer Report* and is available on request from the SAA, 80 Arthur Street, North Sydney, 2060.

APPENDIX 1.1

Canadian hazard symbols



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[1] Schoenfeld, R. 'The Chemist's English—XXIII, Alphabetical Disorder', *Chemistry in Australia*, **44** (8), 1977, 202. (See also the earlier sections for interest.)

[2] Needham, J. *Science and Civilization in China*, vol. 5: *Chemistry and Chemical Technology*. Cambridge University Press, 1976. Perhaps one of the greatest works on history in the twentieth century, written by a Cambridge biochemist—fascinating reading.

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Further Reading

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Chapter 2

CHEMISTRY IN THE LAUNDRY

SOAPS, DETERGENTS, AND OTHER CLEANING AGENTS

In primitive societies even today clothes are cleaned by beating them on rocks near a stream. Certain plants such as soapworts have leaves which produce *saponins*, chemical compounds which produce a soapy lather. These were probably the first detergents used by man.[1]

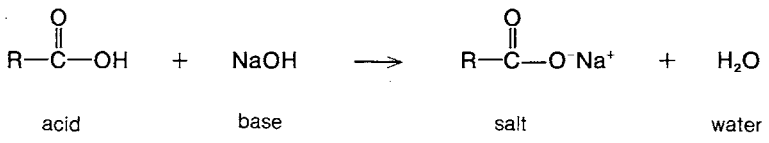
If you look up the word *detergent* in a dictionary it is simply defined as *cleaning agent*. During the past two to three decades, however, the word detergent has tended to imply synthetic detergent, or *syndet* for short, rather than the older *soap*. In fact commercial formulations consist of a number of components and we shall use the term *surface-active agent*, or its abbreviation *surfactant*, to describe the special active ingredients which give detergents their unusual properties.

Soap, by this definition, is a surfactant. In fact it is the oldest one and has been in use for more than four and a half thousand years. Some soap manufacture took place in Venice and Savone in the fifteenth century, in Marseilles in the seventeenth century, by the eighteenth century manufacture was widespread throughout Europe and North America, and by the nineteenth century the making of soap had become a major industry. As a matter of fact, soap became a detergent in 1907 when the German firm Henkel & Co. put on the market the product Persil, which contained sodium perborate, sodium silicate, and sodium carbonate in addition to the carboxylic acid soap —hence *per*borate + *sil*icate = *Persil*.

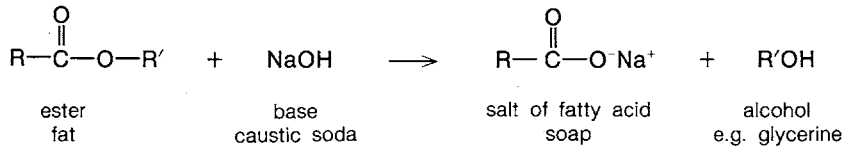
Soaps

Ordinary soaps are the sodium salts of long-chain fatty acids. They have the general formula $RCOO^-Na^+$, where R is a long hydrocarbon chain:

$CH_3(CH_2)_{10-16}$. These salts can be made by the simple neutralisation reaction



However the cheapest sources of the fatty acids are animal fats and certain vegetable oils, which are largely *esters*. Soaps are therefore made in practice by the *saponification* reaction



which is essentially the reverse of the esterification reaction. Beef tallow gives principally sodium stearate, $CH_3(CH_2)_{16}\,COO^-Na^+$, the most common soap, while palm oil gives sodium palmitate, $CH_3(CH_2)_{14}\,COO^-Na^+$.

The standard for personal soap in Australia provides for not less than 70 percent of fatty matter—actual soap plus so-called *superfatting* agents which can be fats, fatty acids, wool wax, etc., but these agents are limited to a 10 percent maximum. The total amount of water allowed is 17 percent. In addition there will be some sodium chloride and glycerol left from the production process. Also added are preservatives, antioxidants, perfume, and colouring matter (titanium dioxide in the case of white soaps). In laundry soap the amount of fatty material allowed is lower (60 percent) and of water is higher (34 percent).

If the sodium ion of ordinary soap is replaced by other metal ions, soaps with different properties are produced. When potassium hydroxide is used instead of sodium hydroxide in the manufacturing process, *soft soaps* are formed. These are semi-solid soaps once used in shampoos and special-purpose soaps. They are however more expensive than the ordinary soaps. Most other metals give soaps that are insoluble in water. Clearly these are not much use for washing, but they do find applications as additives for greases and heavy lubricating oils where their principal function is still as detergents. Copper stearate has been used as a waterproofing colour agent: not only is it water-repellent, but the copper ion is poisonous to mildew. The heavy metal stearates are also used as stabilisers or release agents in plastics such as PVC and polythene (see Chapter 6).

Synthetic surfactant or soap?

You may well ask why soap, which served well for so many years, was eventually displaced. Ordinary soaps have some real advantages over the newer detergents. They are cheap and they are manufactured from a renewable source whereas many of the synthetic detergents are made from petrochemicals. Soaps are biodegradable, i.e. they are readily broken down by bacteria, and they do not pollute rivers. Soaps however do have a greater tendency to clog sewerage reticulation systems than synthetic detergents because of their gelling properties. The grease trap of a non-sewered house was often laden with soap. But the most important reason for the displacement of soap is the fact that when a carboxylic acid soap is used in hard water precipitation occurs. The calcium and magnesium ions, which give hardness to the water, form insoluble salts with the fatty acid in the soap and a curd-like precipitate occurs which settles, of course, on whatever is being washed. By using a large excess of soap, it is possible to redisperse the precipitate, but it is extremely sticky and difficult to move. This problem with soap can be demonstrated by a simple experiment in which a concentrated solution of hard-water salts is added to a 0.1 percent solution of soap and also to a 0.1 percent solution of synthetic surfactant. The soap precipitates, but the synthetic surfactant remains clear as its salts are water soluble.

You may live in an area such as Melbourne where the water is extremely soft. But calcium and magnesium ions are present in the dirt which you wash out of your clothes, so that some precipitation still occurs if soap is used, and gradually deposits are built up in the fabric.

There are other disadvantages with soap: it deteriorates on storage, and it lacks cleaning power when compared with the modern synthetic surfactants, which can be designed to perform individual and specialised cleaning tasks. Finally, and very importantly from a domestic laundry point of view, soap does not rinse out but tends to leave residues behind in the fabric that is being washed. These residues gradually build up and cause bad odour, deterioration of the fabric and other problems.

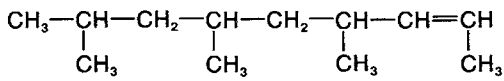
What is the difference between a surfactant and soap? In general terms the difference can be likened to that between cotton and nylon. On the one hand, soap and cotton are each produced from a natural product by a relatively small modification. On the other hand the synthetic surfactant and nylon are each produced entirely in a chemical factory. Synthetic surfactants are not very new, either. Back in 1834 the first forerunner of today's synthetic surfactants was produced in the form of a sulphated castor oil which was used in the textile industry. The development of the first detergents in an effort to overcome the reaction of soaps with hard water provides a good illustration of one of the standard chemical approaches. If a useful substance has some

particular undesirable property, an attempt is made to prepare an analogue, a near chemical relation, which will prove more satisfactory.

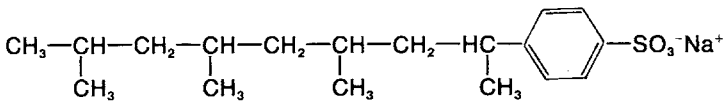
The petroleum industry had, as a waste product, the compound propylene,

$$CH_3—CH=CH_2$$

which used to be burnt off. By joining four of these propylene molecules together the substance in Figure 2.1 is obtained. If benzene is attached at the double bond, the result reacted with sulphuric acid, H_2SO_4, and then sodium hydroxide is added to neutralise the sulphonic acid, the sodium salt shown in Figure 2.2 is obtained, which is a branched-chain alkylbenzene sulphonate (ABS).

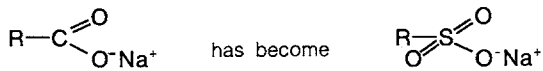


2.1 Propylene tetramer



2.2 Alkylbenzene sulphonate

The new substance is clearly closely related to an ordinary soap, and is an excellent detergent.



2.3 Soap and detergent

The detergents produced in this way are much more soluble than soap, and their calcium and magnesium salts are soluble so that a scum is not formed with hard water. However, they are more stable than soaps and persist in the waste water long after use. The consequence of this was the fouling of sewerage works and rivers with tremendous masses of froth. The increased stability of the detergents was due both to the greater stability of the sulphonate grouping and the fact that the raw material hydrocarbon chain molecules contained large proportions of carbon chains that were *branched*, in contrast to the straight-chain hydrocarbons from animal fats. Bacteria break down the branched chains more slowly and so the detergents were once considered not biodegradable at all (see later this chapter).

How do surfactants work?

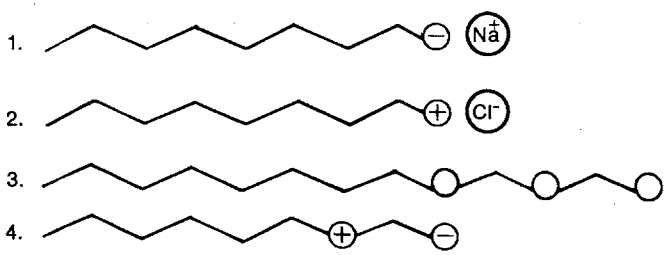
The surfactant molecule is often described as tadpole-like, having a fairly long fatty tail which is water-insoluble or *hydrophobic*, and a small often electrically-charged head which is water-soluble or *hydrophilic*. There are four possible combinations which are illustrated in Figure 2.4. They are:

(1) The *anionic* surface-active agents in which the surfactant is an anion, that is it carries a negative charge, and the charge is concentrated in the hydrophilic or water-soluble head.

(2) The opposite: the *cationic* products in which the head carries a positive charge.

(3) The so-called *non-ionic* detergents which do not have a specific charge, but where the hydrophilic or water-soluble portion of the molecule is usually achieved by incorporating a polyethylene oxide group into the molecule (see later this chapter). You can see that, because it is less polar than an ion, the hydrophilic portion of these molecules is usually rather bigger than in the case of the ionic surfactants.

(4) Finally, there are some specialised products which carry both a positive and a negative charge in the same molecule. These are called *amphoteric* and are particularly useful for very specialised applications (such as hair shampoos). Because they carry both an anionic and a cationic centre, they behave as either an anion or a cation depending on the pH of the solution in which they are used.



2.4 Diagrammatic representation of the shapes and electric charges of surfactant molecules

In domestic detergents, anionic surfactants are the predominant species. Non-ionics are increasingly used but cationic surfactants are not. Cationic surfactants have two interesting and useful properties. First, they are mildly antiseptic and may be used (in combination with non-ionic surfactants) for happy washes, hair shampoos, and throat lozenges. Secondly, the positive

charge on the chain makes them useful for washing plastic articles but not glass. Glass normally acquires a surface negative charge which to a certain extent attracts dirt; anionic detergents can remove this dirt, but cationic surfactants are attracted to the glass so strongly that a thin layer adheres to the glass with the long fatty hydrophobic chain outwards, thus making the glass non-wettable and apparently greasy. The reverse is true for plastic articles, which normally have a positive surface charge—have you ever noticed how dirt clings to plastic and is hard to remove by ordinary washing? The positive charge also makes cationic surfactants useful as fabric conditioners (Comfort, etc.) because the cationic charge has a strong affinity for wet negatively charged fabric, and forms a uniform layer on the surface of the fibres, thus lubricating them and reducing friction and static.

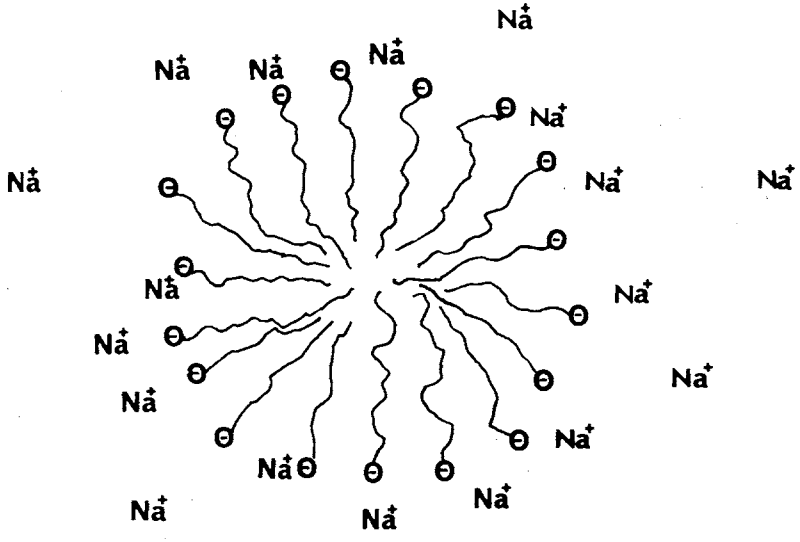
Because their chains have opposite charges, anionic and cationic surfactants are incompatible; on mixing they give a scum, so, except in very special cases, it is not possible to formulate a detergent that contains both types of surfactant and hence combines their advantages.

The cleaning action of surfactants

The molecules of these substances tend to concentrate in the surface layers of the water (because the water-insoluble portion wants to get out of the water), lowering the *surface tension* of the water and thus effectively making the water 'wetter'. Some of the cleaning power of surfactants is thus due to the enhanced ability of the water to wet the dirty surface and lift off the dirt. If you place a strip of cotton fabric, weighted at one end to pull it into the liquid, in a 0.1 percent solution of surfactant, and another in pure water, you will see a difference in behaviour. Because the pure water alone does not wet the cotton, the fabric strip remains 'upright' whereas the fabric in the surfactant solution wets out and sinks immediately.

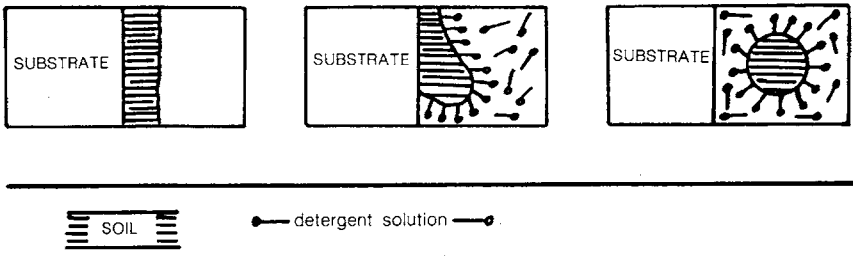
The long hydrocarbon tails of the detergent molecules are soluble in non-polar substances such as oil, while the polar carboxyl or sulphonate groups are soluble in water. Thus the molecules promote solubilisation of oil in water by lying across the oil–water interface. When the concentration of the detergent molecules in the water reaches a certain value called the *critical micellar concentration*, the molecules aggregate into communes called *micelles*, containing roughly 40–100 molecules. In these aggregates, which at high enough concentrations give soap solutions their cloudy appearance because they scatter light just like dust does in the air, the hydrocarbon tails lie towards the centre, while the surface of the micelle contains the water-soluble polar ends (see Figure 2.5).

How does a surfactant remove the oily soil and, with that, frequently a lot of the particulate soil? This is a complex process. The inside of the micelles



2.5 A surfactant micelle

are virtually small oil droplets and so can dissolve oily materials, but the main action of the surfactant is to stimulate emulsification. If some olive oil is carefully poured into water and also into a solution of surfactant and each vessel vigorously shaken and then put down again, it will be found that the oil immediately rises to the surface in the water vessel but remains emulsified and dispersed in the detergent solution and can therefore be rinsed out. The process of emulsification is illustrated in Figure 2.6.



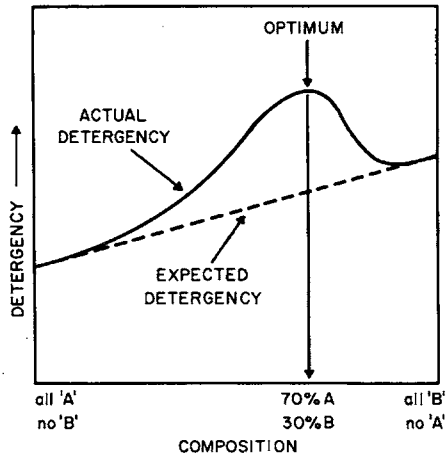
2.6 Emulsification

DOMESTIC LAUNDRY DETERGENTS—FIVE GROUPS OF INGREDIENTS

The ingredients in any commercially-produced detergent fall into five groups: the surfactant system, the builders, an electrolytic filler, bleaches, and fluorescers.

Surfactant

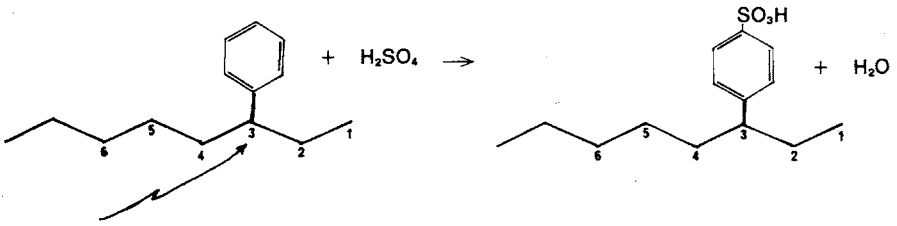
You may wonder at the term *surfactant system*. In most modern detergents more than one surfactant is used. There are a number of reasons for this, the most important of which is the property of *potentiation*. By this is meant a mutual reinforcement of the cleaning actions of two surfactants used together. Figure 2.7 illustrates. The horizontal axis represents the compositions of mixtures of two surfactants A and B, grading from 100 percent 'A' and 0 percent 'B' on the left to 0 percent A and 100 percent B on the right. If we measure the detergency or cleaning power of these blends by any convenient method then the intermediate detergencies frequently do not lie on the expected straight line. On the contrary, there is a peak which clearly shows that there is an optimum composition of two surfactants.



2.7 Potentiation

The starting material for the synthetic surfactant which forms the major active ingredient is a material known as alkylbenzene. In appearance it is a

kerosene-like liquid with a slight oily odour. It is in fact a product of the petroleum industry and is made by the condensation of an α-olefin with benzene. As such it is completely insoluble in water. By treating this material in a process called sulphonation it is converted to the corresponding sulphonic acid, which is a viscous dark brown material. Chemically, sulphonation is achieved by treating alkylbenzene with an excess of sulphuric acid, giving the sulphonic acid plus water.

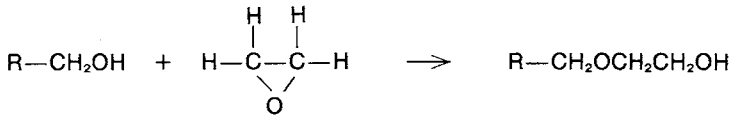


2, 3, 4, 5, or 6 position can be attached depending on the catalyst

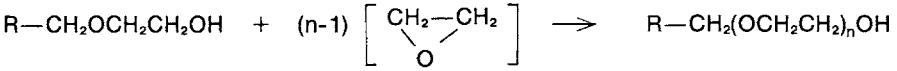
An excess of sulphuric acid must be used to drive this reaction to completion, because any unreacted alkylbenzene reduces the detergency of the resulting surfactant. Sulphuric acid may be regarded as a compound of sulphur trioxide, SO_3, and water; if you look at the equation you can see that it would be very convenient if the water could be left out. In fact, that is what is done today; in a modern sulphonation plant, alkylbenzene is treated with SO_3 vapour and the sulphonic acid is formed in a single-step continuous process. At this stage the material is already water-soluble and exhibits surface-active properties, because the surfactant part of the molecule, with the sulphonate group forming the anionic head, already exists. It is, however, unpleasant to handle in this form and it is normally neutralised with caustic soda, forming the sodium salt, giving a slurry containing about 45 percent of *sodium alkylbenzene sulphonate* and water. In the case of a domestic laundry detergent, the second surfactant is frequently a non-ionic one and it may be either a *coconut diethanolamide* (an alkylolamide) or a *tallow alcohol ethoxylate*. Both of these are rather waxy products, substantially all active material. The alkylolamide is prepared by making the fatty acids obtained from coconut oil react with an ethylene oxide derivative called monoethanolamine. A condensation reaction takes place with the elimination of water and a waxy product is formed. On the other

fatty acid monoethanol amine alkylolamide

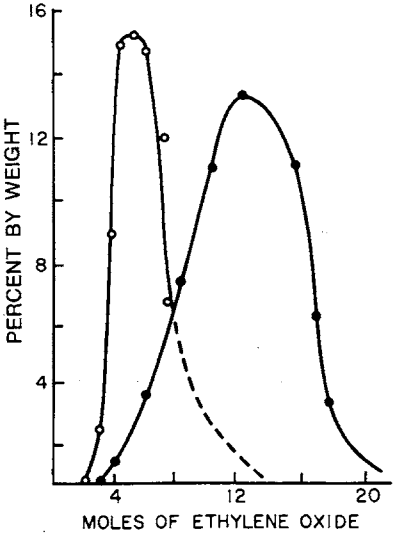
hand, the formation of a tallow alcohol ethoxylate illustrates the method of manufacture of an ever-increasing class of surfactants, the ethylene oxide condensates. They are now made in very large quantities all over the world including Australia. Ethylene oxide is a toxic gas, it is flammable, and it forms explosive mixtures with air in any proportion from 3 percent upwards. Whereas in the sulphonation reaction the chemical nature of the product is relatively definite (as is also the case for the coconut monoethanolamide), this is not so for the ethylene oxide condensation products, because we are now dealing with a type of *polymerisation* (see Chapter 6). It is usual for these condensation reactions to take place by starting with a fatty alcohol, which is also a waxy material and chemically is the long fatty chain forming the hydrophobic part of our surfactant. It has a terminal hydroxyl group to which a molecule of ethylene oxide can be added thus:



Further molecules of ethylene oxide can then add on to the terminal hydroxyl group which is formed at each step of the addition:



If ethylene oxide and tallow fatty alcohol are reacted together in the proportion of ten molecules of ethylene oxide to one molecule of tallow fatty alcohol, then not all of the ethylene oxide molecules will combine with the tallow alcohol molecules in the proportion of ten to one. You will in fact get some molecules with fewer ethylene oxide groups and some molecules with considerably more. The graph in Figure 2.8 illustrates the kind of distribution curves which are obtained when different ethylene oxide condensates are manufactured.

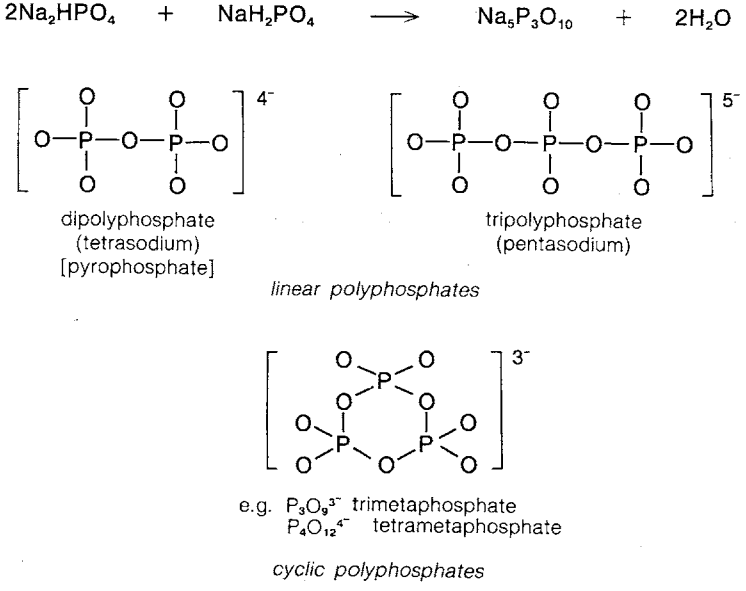


2.8 The distribution of the number of ethylene oxide molecules in the surfactant molecule for two different mean values of ethylene oxide reacted

An interesting non-ionic surfactant called TAL (Tate and Lyle) is made by reacting a triglyceride (fat)—tallow or palm oil (see Chapter 3)—with sucrose (sugar) to produce a complex mixture of sucrose monoglyceride (27 percent), potassium soaps (30 percent), unreacted sucrose (13 percent), and unreacted fats, in which the *sucrose monoglyceride* is the main surfactant. Thus TAL is a non-ionic surfactant which is not dependent on petrochemically-based products.

Inorganic builders

Turning now from the surfactant system, let us look at the builders. Builders are included in modern domestic laundry detergents in order to assist the surfactant system in its action. Builders are both organic and inorganic. Among the inorganic builders *sodium tripolyphosphate* is the major builder used. It is a polyphosphate equivalent to having been formed from two molecules of disodium monohydrogen phosphate with one molecule of monosodium dihydrogen phosphate to give what is correctly called pentasodium triphosphate, by the elimination of water, as shown in Figure 2.9



2.9 Polyphosphates

Why should tripolyphosphate be put into a detergent? It has a number of advantages from the point of view of safety. It is non-toxic (toxicological

information indicates that it is comparable to common table salt) and non-irritant. It does three things in the detergent. It buffers the wash liquor to a milder pH than would otherwise be obtained. You may recall that soap became a detergent with the introduction of Persil, in which sodium carbonate and sodium silicate had been added to soap. One of the drawbacks of the early versions of Persil was its high alkalinity and the damage which this could do to fabrics. On the other hand, a certain amount of alkalinity is needed to wash fabrics, particularly cotton, successfully. Secondly, sodium tripolyphosphate sequesters hard water ions. Although synthetic surfactants do not precipitate with the ions in hard water, the presence of these ions does tend to decrease detergency to some degree. The full cleaning power of the surfactant is preserved if the ions are sequestered by tripolyphosphate. Finally, tripolyphosphate is important in its deflocculating action, that is to say it helps to keep a clay-type dirt in suspension.

The second inorganic builder is a *sodium silicate*, a material that children play with under the name of water-glass. It is silicate obtained by having a ratio of sodium oxide to silicon dioxide different from that of metasilicate (see section on dishwashing detergents). It is in fact 1:2. This product in the detergent further controls the alkalinity. It acts as a corrosion inhibitor, protecting especially aluminium washing machine parts; and finally it plays an important role in strengthening the physical form of the detergent powder. To explain how it does that, we need to look at how the powder is made.

You will recall the slurry containing the first of our surfactant ingredients, sodium alkylbenzene sulphonate. In practical manufacture, to this slurry are then added the other ingredients. This gives a much more viscous, very hard-to-stir slurry, which must be kept hot to ensure that it does not set into an intractable lump. It is pumped to the top of a large vertical, usually cylindrical, chamber and sprayed into a counter current flow of hot air, so that each droplet dries into a virtually spherical particle in which every component of the detergent mixture is contained in the correct proportions. Such uniformity cannot be achieved by dry blending the individual ingredients—because each constituent has a different density, layering would occur in a simple dry blend, especially during transport over long distances, which involves a lot of vibration. The function of the silicate is to give strength to the individual spray-dried beads, which are hollow in cross-section thus improving the solubility of the product.

The organic builder

The organic builder used in detergents is a product called *sodium carboxymethyl cellulose*. This mouthful is arrived at by treating pure cellulose with caustic soda. It is used at a concentration of less than 1 percent and its major

function is to act as an anti-redeposition agent: it *increases the negative charge* in fabrics, which then repel the dirt particles since they are themselves negatively charged. If you imagine having a white handkerchief with a black sooty spot in one corner, and you washed this in a detergent not containing an anti-redeposition agent, then the soot would be dislodged but would tend to redeposit all over the handkerchief so that it would emerge a uniform grey.

An inert filler

Some *sodium sulphate* (~6 percent) is produced during the neutralisation of the excess sulphuric acid or sulphur trioxide but up to 50 percent may be found in some products. A certain amount is needed to form a crisp powder. Although it is marginally useful in lowering the critical micelle concentration of ionic surfactants and thus possibly reducing the amount of detergent needed, its main purpose would appear to be to produce a free flowing powder and to add bulk to the product.

Sodium perborate, $NaBO_2.H_2O_2.3H_2O$ (10–20 percent)

In water this compound releases hydrogen peroxide, which is a powerful *oxidising* agent. The oxidation removes a lot of the stains while generally not affecting fast colours. It is particularly effective when the material is left to soak, and requires a fairly high temperature to be effective during a wash.

'Whiter than white'

In the good old days we added 'blue' so that cotton ageing naturally to yellow would look white. Today very small amounts of *fluorescers* are added to detergent powders. They are in fact already in the new gleaming business shirt when you buy it but wear and washing remove them. These compounds absorb ultraviolet light (which is invisible) and re-emit blue light (which yellow fabrics do not reflect fully from sunlight), and so restore the mixture of colours reflected to that which a white fabric would reflect. The exact nature of the brighteners differs with geographic location. We are conditioned to blue-white as the accepted hue for cleanliness while in South America a red-white colouration is the culturally accepted colour for clean. Optical brighteners do not clean but they do whiten the fabric, which some consumers consider to be aesthetically desirable. On the Australian market the main reason for using a combination of fluorescers is to cope with the variation in washing conditions —notably wash temperatures, wash time (rate of adsorption of the fluorescer), and the comparatively high incidence of re-use of wash solution for two or more loads. Also, different fabrics carry different charges: nylon carries a positive charge, cotton a negative one, and so oppositely charged fluorescers are needed.

Foam

The relationship between foaming power and detergency has always been of interest, and foaming power has become associated in many consumers' minds with high detersive power. The first liquid detergent on the Australian market was Trix. It was non-foaming and was soon replaced because of consumer resistance. However, it is generally conceded by detergent technologists that foam has no direct relationship to detergency in ordinary fabric washing systems.

But in systems where the amount of washing fluid is low, foam may play an important role. The individual foam films tend to take up and hold particles of soil that have been removed from the item, preventing them from being redeposited and allowing them to be washed or scraped away. This effect is very important in the on-location shampooing of carpets, and to a certain extent in the cosmetic shampooing of hair. However, some washing machines tend to choke up with lather and so lose their efficiency if the detergent produces too many suds. The suds can also cause electrical short circuits in time switches, etc. This can be avoided by adding less than 2 percent of soap to the powder, which counters the foaming action of sulphonate detergents, particularly during the rinse cycle.

TABLE 2.1 *Composition of laundry powders (%)*

	Unilever			*Colgate-Palmolive*		
	OMO	RINSO	SURF*	AJAX	FAB*	SPREE
Alkylbenzene sulphonate	16.4	15.4	14.0	14.9	14.8	13.3
Anhydrous soap	2.0	3.4	2.8	none	none	none
TOTAL SURFACTANT	18.4	18.8	16.8	14.9	14.8	13.3
Sodium tripolyphosphate	28.2	31.2	27.2	26.1	30.0	23.2
Sodium silicate	16.0†	14.0†	13.0†	5.0†	6.0†	6.0†
Sodium carbonate	8.6	11.1	8.6	none	none	none
Sodium sulphate	19.0	18.0	26.0	40.0	41.0	48.0
Fluorescing agents	#	#	#	#	#	#
Perfume	#	#	#	#	#	#
Sodium perborate	none	none	none	2.0	none	none
Pigments	#	#	#	#	#	#
Sodium carboxymethyl cellulose	#	#	#	#	#	#
Moisture	9.9	7.8	9.5	10.0	7.7	6.8

*Analysis indicates that some lemon oil could be present.
†Calculated as if $Na_2O:SiO_2$ = 1:1. Since some of the silicates will have a higher ratio of $SiO_2:Na_2O$ these results are probably high.
#Present

Source: Report of the Joint Parliamentary Committee on Prices.[3]

Washing in machines

The type of washing machine used in Australia tends to control the standard of wash, since more than 86 percent of single home dwellings in Australia have washing machines. Automation has brought with it daily washing (Monday wash-day is a myth!), small loads, little soaking, little sorting of fabric types, and less care about the end result. Where English and European women wash most loads for at least one hour in water up to 80°C and use plenty of detergent, Australian women wash a load for an average of ten minutes in water around 40°C using one third of the detergent their European counterparts do (Unilever market research).[2] The cold water detergents developed to meet Australian habits still work better in hotter water. In this respect it is interesting to note the comments in a report of the Joint Parliamentary Committee on Prices.[3] Six commercial laundry powders were analysed by the Australian Government Analytical Laboratories. The results are set out in Table 2.1. All six products analysed contain a similar amount of detergent (alkylbenzene sulphonate). In addition, the Unilever products contain a small percentage of powdered soap.

TABLE 2.2 *Test detergent for comparison of washing machines: percentage composition for standard washing agents (SAA draft 1976)**

Ingredient	Type A (for agitator and impeller type machines)	Type B (for drum type machines)
Sodium dodecylbenzene sulphonate	13.0	7.0
Sodium stearate (soap)	—	7.0
Linear alcohol ethoxylate (e.g. Teric G15A18)	—	4.0
TOTAL SURFACTANT	13.0	18.0
Sodium tripolyphosphate	30.0	30.0
Alkaline sodium silicate ($Na_2O—2SiO_2$)	10.0	8.0
Sodium carboxymethyl cellulose	0.8	1.0
Tetrasodium EDTA	—	0.2
Sodium sulphate	36.2	19.3
Water	10.0	8.5
Sodium perborate (supplied separately)	—	15.0

*Available from the General Development Manager, Lever & Kitchen Pty Ltd, Sydney.

The figures in Table 2.1 can be compared with those for a standard detergent in Table 2.2. Since this standard detergent was developed for testing washing

Courtesy of New Scientist Publications

PLATE 2.1 *Ariadne's statue. This first appeared in* New Scientist, London, *the weekly review of Science and Technology*

machines, it could be expected to be marginal in quality in order to differentiate the performances of machines. It is a specialist formulation designed to make comparisons easier.

BIODEGRADABILITY

A sight such as that in Plate 2.II was once relatively common under normal weather conditions. That was in the days before detergents were what is called *biodegradable*. Biodegradability is a term which always requires careful definition. In essence it means the process of decomposition of an organic material, and note that it applies only to organic materials, by naturally occurring micro-organisms. Such a process is one which obviously depends on time, concentration, and temperature. The surfactants which were used previously were biodegradable but only very slowly. They did not degrade quickly enough for the surfactants to be destroyed in the conventional sewage treatment plant, or to be decomposed reasonably rapidly in flowing rivers.[4]

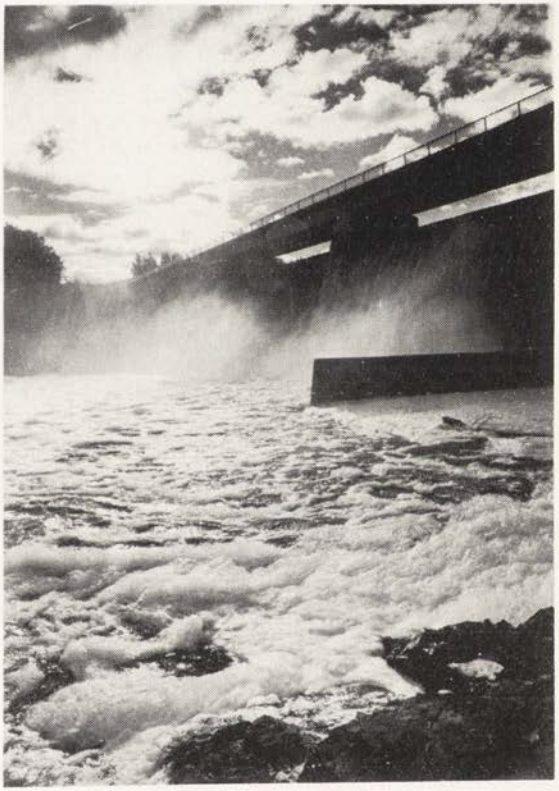
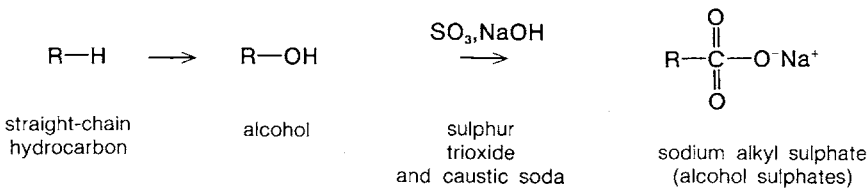


PLATE 2.II *Detergent foam below the Scrivener Dam, which holds back Lake Burley Griffin in Canberra, during one of the overflows of the (upstream) Queanbeyan sewerage system* (Canberra Times, 25 June 1975)

Should we re-use our water?[1]

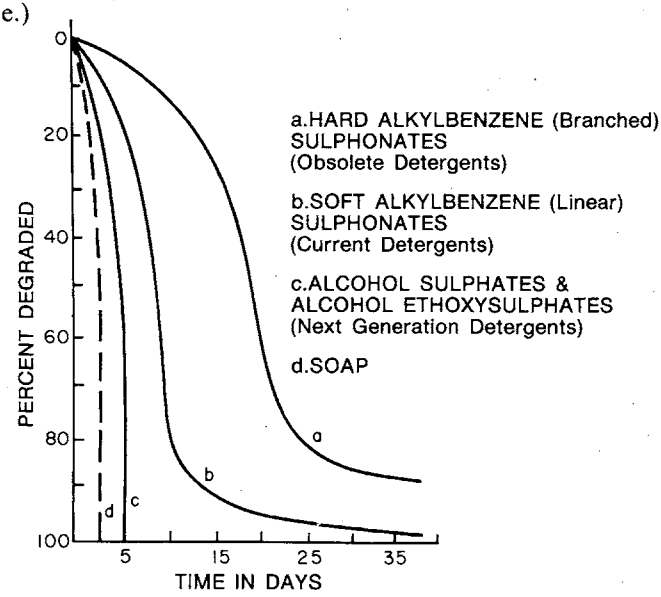
We are very fortunate in Australia that we are not yet faced with a problem of water re-use. After all, most of the population lives in a relatively narrow coastal strip and its effluent, particularly that from the main cities, goes into the sea more or less treated. On the other hand, the regular droughts which have caused water supply problems in Canberra, Sydney, and Melbourne over the years clearly show that a case could be made for the re-use of at least some of our water. In Australia we do not have long rivers along which cities are located, taking their water from and returning it to the river. It has been said, only half jokingly, that if you live in a city near the mouth of the Mississippi River then the water you drink has probably passed through eleven stomachs before yours.

The fact that sewage treatment was incomplete, as shown by the appearance of foam in what was regarded as 'treated' water, caused chemists to look at what might be done to improve the biodegradability of surfactants. In the case of alkylbenzene, this was achieved by changing the structure of the alkyl part of the alkylbenzene. In Australia before 1971, the alkyl part came from a propylene tetramer and was what the organic chemists call 'branched in its chain'. It was shown that this branching inhibited attack by the micro-organisms and, as a result, slowed down biodegradation. The remedies for this problem are again an interesting illustration of how chemistry works. With the advent of plastics, propylene was suddenly useful again for making polypropylene. The long-chain branched hydrocarbons were a desirable component in automobile petrol because they contributed a high octane (anti-knock) component, so the straight-chain hydrocarbons were now available for making detergents; they are converted into the soft (biodegradable) linear alkyl sulphonates (LAS). However, instead of simply sulphonating the straight-chain hydrocarbons directly, they can first be converted to the alcohol, and then sulphated:



Notice the slight difference between the sulphonate, where the alkyl group is attached directly to the sulphur atom (see Figure 2.3), and the sulphate, with an oxygen atom between the sulphur atom and the alkyl group. The sulphate is readily *hydrolysed*, i.e. attacked by water to give the original alcohol

—which has no detergent action. (Toothpastes use alkyl sulphate detergents because the abrasive contains minerals which would react with the soap and make it unusable.)



2.10 Biodegradation using SAA standard for biodegradability AS1792 (Surfactants Association of Victoria[1])

Figure 2.10 illustrates the differences in the biodegradability between the different types of detergent. Soap, as you can see, degrades completely, and there are surfactants available which will essentially do the same. They are at present too expensive but it is only a matter of time before they are incorporated in domestic detergent powders.

OTHER HOUSEHOLD CLEANING AGENTS

Hand dishwashing detergents

Other detergents used in the household are liquid ones, mainly used for dishwashing. Much the same grouping of ingredients is used in these liquid detergents, except that inorganic builders are usually omitted. In order to provide greater solubility, the alkylbenzene sulphonic acid is neutralised not only with caustic soda, but also with, for example, triethanolamine, $(HOCH_2CH_2)_3N$. The salts formed are soluble in both water and hydrocarbons and so are good emulsifying agents. (The triethanolamine is produced from ethylene oxide and ammonia.) Salt and urea are often added as thickening

agents, so that the cleaner does not run out of the bottle too fast, and to give that feeling of value![5]

On that last point—surveys carried out in mid-1974 and 1977 found the percentages shown in Table 2.3 for the water content of the listed liquid dishwashing detergents. The figures were calculated by weighing accurately approximately 10g of detergent and distilling it with about 90 ml of toluene or hexane in a Dean and Starke apparatus, and then weighing the amount of water distilled over.

TABLE 2.3: *Water content in dishwashing detergents*

Detergent	Mean (as % w/w) 1974	Mean (as % w/w) 1977
(a) *Concentrates.*		
Add (150 ml: 2 l)	6*	47
Amway	13	—
Bushland (250 ml: 2 l)	48	47#
Dux	61	—
Kit (150 ml: 2 l)	12	10#
Myo	12	—
Scotts	62	—
U-mix	14	—
Woolworths (150 ml: 2 l)	—	10#
(b) *Regular*		
Bushland	93	91
Dux	—	92
Embassy	84	88
Jently	90	—
Kwit	—	87
Lux	71	76.5
Palmolive	77	78.5
Sunlight	72	69
Trix	82	81
Velvet	76	—

*A 1974 pack of Add measured in 1977 still registered 6% solvent. Liquid hand dishwashing detergents are covered by a Standard AS 1999, 1977.
#These 1977 concentrates give about 6% 'active' on dilution, which meets AS 1999.

Source: Canberra Consumers Inc.[5]

Machine dishwashing detergents

These products in fact generally contain only about 2 percent of low-foaming non-ionic surfactant (usually the block copolymers of propylene oxide and ethylene oxide). Their efficiency depends more on their physical characteristics

and how well they are matched to the dispenser. A typical formulation might be approximately

anhydrous sodium tripolyphosphate	50 percent
anhydrous sodium metasilicate	40 percent
anhydrous sodium sulphate	7 percent
dichlorisocyanurate as sodium salt (25 percent available chlorine)	3 percent

The sodium metasilicate in particular is quite caustic and very dangerous if swallowed. Some commercial powders contain 65 percent hydrated metasilicate, and we have the ironic situation that this substance is not covered by Poisons Regulations and so products containing it need not be labelled with a warning, whereas the less dangerous hand dishwashing detergents must carry a caution. Preparations with greater than 5 percent sodium carbonate can cause sheet erosion of glassware which gradually thins the glass. The chlorine-containing powders can cause deterioration of plastic kitchenware, but without chlorine the tannin stains from tea are not removed. Aluminium-ware is also attacked quite strongly and your pots are probably losing weight at an appreciable rate!

The standard rinse agent consists of 60 percent low foaming wetting agent (Teric 164 or Triton DX12) plus 20 percent isopropyl alcohol and 20 percent water.

Scouring powders

These products consist mainly of abrasive powder (~80 percent) which can be screened silica, felspar, calcite, or limestone with the bulk 44 microns or smaller. The rest of the powder is sodium carbonate or similar alkaline salts with about 2 percent surfactant and in some cases chlorine bleach. The blue dye which appears on wetting could be finely divided copper phthalocyanine and this sometimes bleaches while in use.

Drain cleaners

Drain cleaners are a mixture of caustic soda (NaOH), and aluminium filings, which react with water to provide heat to melt fat and to saponify the fat to soap.

Bleach

Hypochlorite salts (e.g. sodium, potassium, calcium, magnesium) serve as disinfectants, bleaches, and deodorisers. Specifically they are used to disinfect contaminated utensils, nappies, and water for drinking or swimming. Liquid

household bleach is usually 5 percent sodium hypochlorite, NaOCl. Commercial solutions are made by adding gaseous chlorine to 12–15 percent sodium hydroxide solution until alkalinity is just neutralised, and the resulting solution diluted to 5 percent. Because even a little too much free chlorine means an acidic solution which is unstable, manufacturers with inadequate production controls use too little chlorine and market a product with a free alkalinity that may run as high as 1 percent NaOH, whereas a well controlled product has a pH of 9–10 with a very low titratable alkalinity.

Dangers

Mixing household bleach with preparations containing ammonia leads to the formation of chloramines, NH_2Cl, $NHCl_2$, which form acrid fumes and cause respiratory distress but have no serious consequences. Household bleach causes immediate vomiting in children but with no serious consequences except those associated with vomiting in general. The treatment for the ingestion of bleach is to swallow immediately one or more of milk, egg white, starch paste, milk of magnesia. Avoid sodium bicarbonate because it releases carbon dioxide. *Do not* use acidic antidotes.

General-purpose liquid cleaners

Products such as Swipe contain about 10 percent butyl cellosolve—ethylene glycol mono-n-butyl ether. (Ethylene glycol itself is used in permanent antifreeze.) This solvent is classed as *moderately toxic* with a probable lethal dose to humans of 0.5–5 g/kg or 3.5 g–35 g for a 70 kg person (ten times that amount for a 10 percent solution).

Cloudy ammonia

When ammonia was first made from coal tar, the solutions were very murky. Later the Haber process for 'fixing' the nitrogen of the air gave a very pure product but by this time housewives were used to 'cloudy ammonia'. For this reason soap is added to keep pure clear ammonia cloudy. Fresh household ammonia ranges in concentration up to 10 percent NH_3. Ammonia vapour is extremely irritating and the solution is very alkaline and acts as a caustic. A little ammonia in a dish of hot water placed in the oven overnight will saponify the fat to a certain extent and make oven cleaning easier.

General rules for the treatment of ingestion of ammonia:

1. No emetics—*do not* induce vomiting.
2. Drink large quantities of water or weak acids such as diluted vinegar or lemon juice.
3. Egg white, milk, olive oil, etc. act as soothing agents.
4. Contaminated eyes or skin should be washed with copious amounts of tap water.

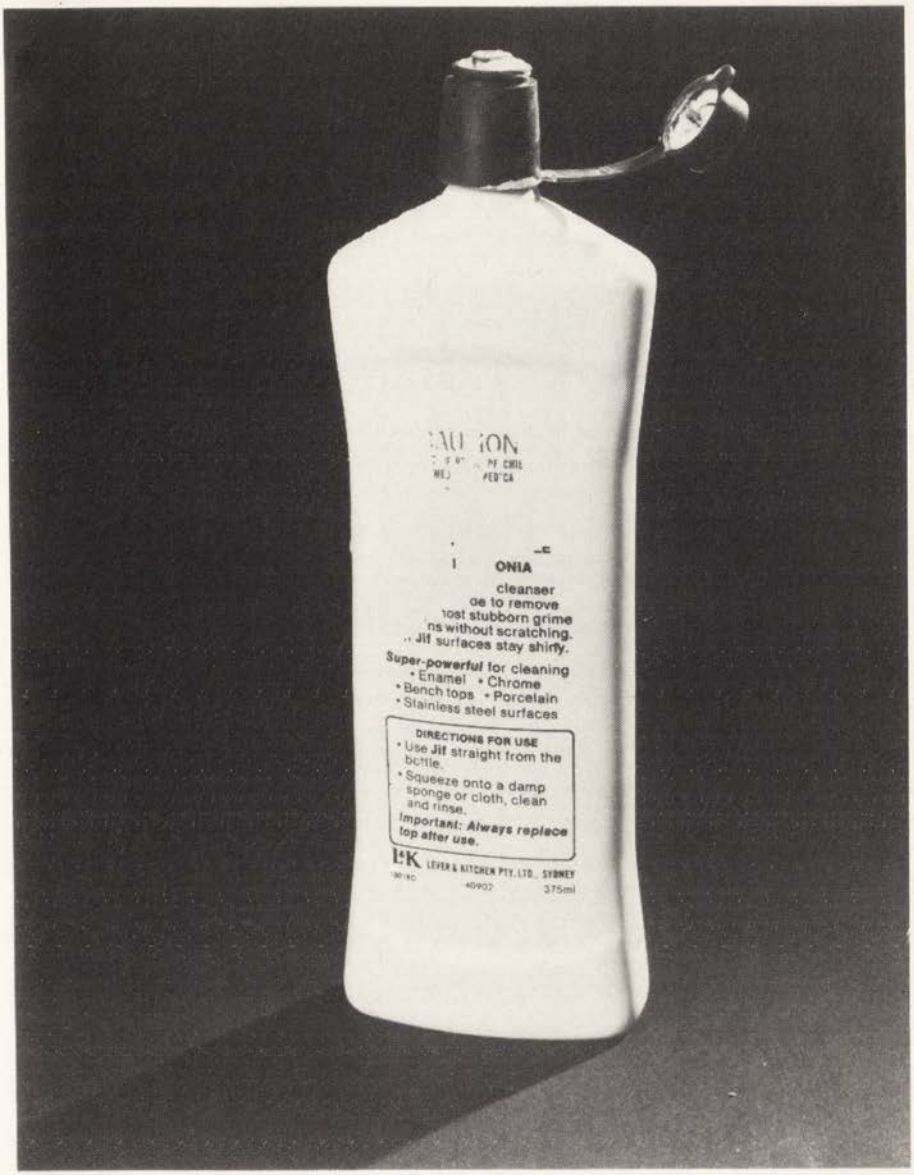


PLATE 2.III *Self-cleaning agent. The author's complaint about this product resulted in a fast design change by the manufacturer. Note the statutory warning label has washed off and the top (which we are told must be replaced) is such that it clogs preventing closure. Examine the design of the product on sale now.*

STAIN REMOVAL

To a large extent, stain removal procedures are based on solubility patterns (like dissolves like) or on chemical reactions. Stains caused by fatty substances such as chocolate, butter, grease can be removed by treatment with typical dry cleaning solvents such as tetrachloroethylene,

$$CCl_2{=}CCl_2$$

Iron stains (rust, some inks) are removed by using a chemical reaction: treatment with oxalic acid (poisonous!) forms a soluble complex with the iron. Much stain removal is carried out by oxidation, with oxidising bleaches such as hydrogen peroxide, sodium perborate (which forms hydrogen peroxide), or laundry bleach (sodium hypochlorite). These bleaches work on mildews, blood, etc., but bleach should not be used on wool because it attacks the linkages that hold the wool together.

The working of some methods is not completely understood. For example the use of copious amounts of salt on a red wine stain on a table cloth probably operates by *osmosis*—the salt drawing out the water from the fibres of the cloth and taking the red stain along with it; this method only works on a fresh stain before the red dye becomes firmly attached to the cloth.

DRY CLEANING

The term *dry cleaning* has been introduced generally for the cleaning of textile goods in organic solvents. When cleaning in aqueous media, the water-soluble components of the soil are not taken into account, because they spontaneously dissolve in the water and so their removal is no problem. In dry cleaning the situation is quite similar with regard to oily and greasy dirt; the necessity for also removing water-soluble substances such as salt and sugar is one of the reasons why *water* is usually added to the dry cleaning bath.

The organic solvents most frequently used in dry cleaning can dissolve only extremely low quantities of water. Generally, chlorinated hydrocarbons such as chlorinated ethylene are used. However, surfactants added in most cases to the solvent form 'inverse' micelles, with the polar groups *inside* and the hydrocarbon tails *outside* in the solvent phase (compare Figure 2.5). The interior of these micelles can dissolve additional water (about 1½ molecules of water per surfactant molecule). The removal of solid particles is promoted by surfactants in dry cleaning as well as in aqueous laundering. Sufficient water is solubilised to maintain a reasonably high relative humidity of water vapour above the solvent; this is a convenient measure of the 'activity' of water *in* the solvent. (An explanation of the Biblical phenomenon of Gideon's fleece [Judges VI] is given by C.M. Giles in *J. Chem. Education* **39** (1962) p. 584, and is vaguely relevant to this discussion.) In practical dry cleaning, however, an upper limit to the relative humidity is determined by the fact that textile material shrinks, wrinkles, or felts at too high a relative humidity.

DISCUSSION TOPICS

1. What would be the problems associated with a return to using only soap? [Competition with fat used for food—e.g. margarine.]

2. The production of soap requires a lot of caustic soda which is made by electrolysing salt. The other product of the electrolysis is chlorine. What is it used for? [PVC] Balancing the need and production of caustic soda and chlorine is the basic problem of the chemical industry in any emerging chemical technology.

3. Are phosphates a real environmental problem in Australia?[4]

4. How much more does it cost to wash with hot compared to cold water? [Water capacity of washing machine; number of cycles requiring fresh water; cost per unit of electricity. For example, if you normally use 55 litres of hot water in your average-sized machine, and cold water for rinsing, then using the fact that one unit of electricity will raise the temperature of 15.4 litres of water by 55°C (i.e. from 15°C to 70°C) and that a unit costs say 3 cents (including heat losses), the cost per wash will be 11 cents.]

5. What advantages would a good liquid laundry detergent have?

[1. Smaller companies could compete because the manufacture does not require expensive spray drying equipment. 2. The variety of products could be greater because there are fewer formulating difficulties. 3. The use of detergent could be automated, by having a reservoir in the washing machine to automatically dispense liquid laundry detergent—and save on wastage due to lazy measuring of solids. 4. The type of surfactant used in liquid detergents is generally less affected by hard water.]

6. At present liquid laundry detergents are not as good as the formulated solid ones. Why? [Generally lack phosphate.]

7. How much laundry powder detergent should you use?[6] [Well, the amount of surfactant in the final wash should (according to the manufacturers) be at the critical micelle concentration. For anionic surfactants this is relatively high, although it is lowered by all the other ingredients present ($\sim 5 \times 10^{-2}$ mole l^{-1}) A powder designed for an expected dose of 2 g of product per litre of water might contain 20 percent surfactant. The molecular weight of sodium dodecylbenzene sulphonate is 340 so this dose represents $\sim 10^{-3}$ mole l^{-1}. The amount of tripolyphosphate etc. will also be adjusted accordingly. 2 g/l is equivalent to 4 oz/12 gal (100 g/50 l); and 1 gal (British) = 1.2 gal (US) = 4.54 litres.

Note that detergent powders differ quite considerably in density so that measuring by volume, which the manufacturers specify in their instructions on the packet, can be misleading as a basis for comparison. With a cost for detergent powder of say $1 per kilogram—a wash costs about 10 cents—about the same cost as the hot water. If cold water detergents really worked as well in cold water as normal detergents do in hot water they would certainly be more economical. Unfortunately, . . .]

8. Have you ever had medical problems with a detergent or soap, such as asthma, dermatitis, photodermatitis (caused by sunlight on a skin sensitised by a chemical)? Why do you buy the brand that you do—advertisement on television; well-known company; washes better; cheaper; on special?

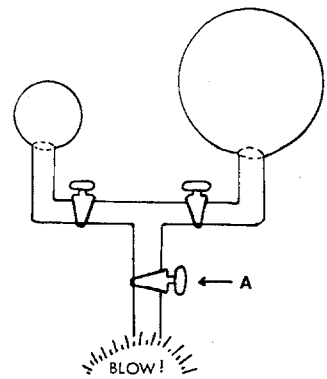
9. Have you ever wondered why packets of laundry detergent from the two major companies cost approximately the same in all the eastern capital cities?[3] Both companies manufacture in Sydney and the freight costs are quite large. [Ask the companies.]

10. Divide the cost of the packet of detergent up into:

(a) ingredients
(b) production costs
(c) packaging
(d) advertising and sales
(e) research

Would it be easy to bias these figures depending on the case you were trying to present?

11. Soap bubbles are blown on a tee-piece with three taps so that one bubble is bigger than the other. The input tap A is closed and the other two taps are opened so that air can pass from one bubble to the other. The question is—does the big bubble blow the little bubble up till they are equal (socialist) or does the big bubble get bigger and the little get littler (capitalist)? [You're wrong —they are capitalist! Why?]



APPENDIX 2.1

Formulations used in the United States for the major zero phosphate heavy duty laundry detergents (%)

Procter & Gamble's powder Tide	
Sodium sulphate	29
Sodium carbonate	20
Sodium silicate	20
Alkybenzene sulphonate	15
Alcohol ethoxylated sulphate	6
Sodium toluene glycol	1.5
Polyoxyethylene glycol	1.5
CMC, water, other	7

Colgate-Palmolive's powder Ajax	
Sodium sulphate	35
Sodium silicate	26
Linear alkylbenzene sulphonate	20
Sodium soap	6
CMC, water, other	13
Lever Bros.' powder All	
Sodium carbonate	55
Sodium sulphate	16
Alcohol ethoxylate	9
Sodium silicate	8
Sodium alcohol sulphate	1
Perborate	2
Borax	1
CMC, water, other	8
Procter & Gamble's liquid ERA	
Anionic surfactant (linear alkylbenzene sulphonate)	10
Non-ionic surfactant (alcohol ethoxylate)	33
Triethanolamine	8
Ethanol	8
Water	35
Miscellaneous	6
Colgate-Palmolive's liquid Dynamo	
Anionic surfactant (linear alkylbenzene sulphonate)	10
Non-ionic surfactant (alcohol ethoxylate)	39
Ethanol	12
Triethanolamine	2
Water	35
Miscellaneous	2

Source: H.A. Segelas, 'Synthetic Detergents—1975.' *Hydrocarbon Processing.* March 1975. p. 71.

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[1] Strasser, P.H.A. 'Surface-activity in the Service of Women' (the Hartung Youth Lecture 1973), published in *Proceedings of the Royal Australian Chemical Institute* **41**, April 1974, is to a large extent the basis for this chapter.

[2] Jay, C. 'Soap powder success—it all comes out in the wash', *Financial Review*, 21 June 1973.

[3] 'Soaps and Detergents'. Joint Parliamentary Committee on Prices (Hurford Committee), AGPS, Canberra, 1974.
The report they didn't dare show on television. (The Minister for Science and Consumer Affairs, Mr W. Morrison, was allegedly refused time to appear on Channel 9, Sydney, because of an alleged threat by soap advertisers to withdraw custom.) Gives an insight into the products and the operation of the industry.

[4] Philp, D.M. 'Advanced Waste Water Treatment', *Water*, **1** (2), 8 and **1** (3), 11. A discussion of the water treatment plants in Canberra.

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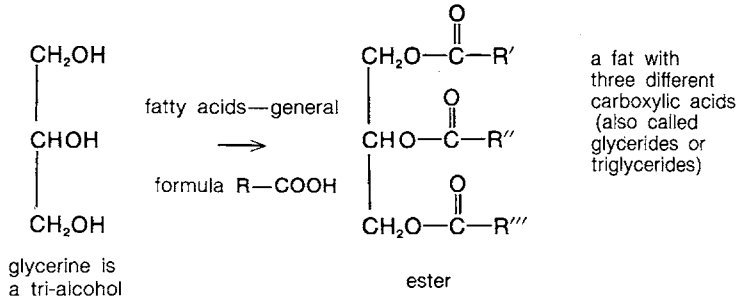
Chapter 3

CHEMISTRY IN THE KITCHEN

BUTTER AND MARGARINE—AND OTHER FATS, OILS, AND WAXES

Fats, oils, and some waxes are the naturally occurring *esters* of long straight-chain carboxylic acids.[1] These esters are the materials from which soaps are made (see Chapter 2). We have seen that an ester is produced when an organic acid combines with an alcohol (Chapter 1). Whenever the alcohol is *glycerol* —glycerine, a by-product in the manufacture of soap from fat—the esters are fats or oils. The difference between fats and oils is merely one of melting point: fats are solid or semi-solid at room temperature whereas oils are liquids.



Since glycerol is common to all fats, whether animal or vegetable, it is the fatty acid part of the fat that is of interest: the differences between fats depend on the nature of the acid groups—the length of the chain (which controls the molecular weight), and the number and position of double bonds (unsaturation). Before proceeding further I will briefly describe the acids. There are three groups important to this discussion:

1. The normal saturated fatty acids
2. The normal straight-chain unsaturated fatty acids
3. The polyunsaturated fatty acids.

Normal saturated fatty acids

These have the general formula $CH_3(CH_2)_nCOOH$, Where n is usually even, and varies from 2 to 24. The building block for producing fatty acids is the acetate ion, CH_3COO^-, hence the predominance of even carbon chains. The most common examples of normal saturated fatty acids are palmitic acid (n=14), and stearic acid (n=16) which is illustrated in Figure 3.2; others are lauric acid (n=10), which is dominant in coconut and palm kernel, and myristic acid (n=12), dominant in nutmeg.

Even shorter-chain fatty acids (n less than 10) form a large proportion of the fats in milk fats, especially those of ruminants. Odd-numbered acids do occur, but only in traces, and then over a wide range up to n=23—generally in ruminants. The unusual composition occurs because it is bacteria in the rumen that carry out the reactions for the animal. For this reason there can be geographic variations in products such as milk, which can cause temporary diarrhoea until the readjustments are made by the victim's body.

Normal straight-chain unsaturated fatty acids

The most important unsaturated acids have eighteen carbon atoms, usually with one double bond at the middle of the chain. If other double bonds are present they lie closer to the carboxyl group. The double bond cannot be rotated and so there are two distinct geometries possible, which are called *cis* and *trans* (Figure 3.1). Oleic acid, the most abundant of all fatty acids, is

$$CH_3(CH_2)_7CH\overset{cis}{=}CH(CH_2)_7COOH$$

(see also Figure 3.2). The vast majority of olefinic (unsaturated) linkages in fats and oils are *cis*.

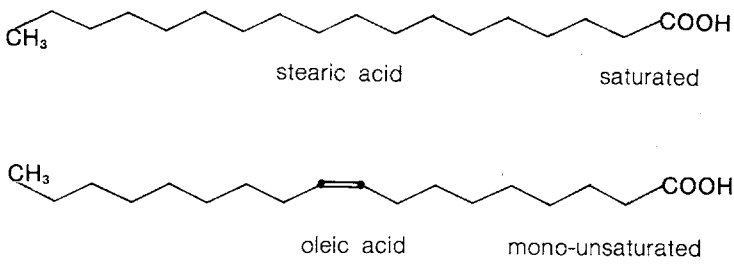
3.1 *cis* and *trans* isomers

Polyunsaturated fatty acids

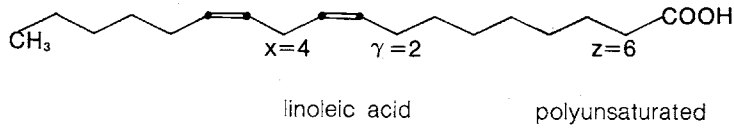
The polyunsaturated acids are those having more than one (*cis* methylene interrupted—see later) double bond, and they have the general formula

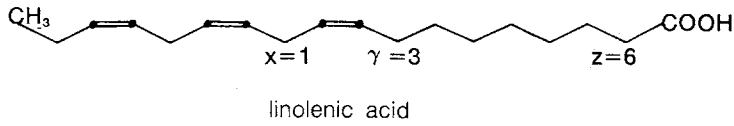
$$CH_3(CH_2)_x(CH{=}CHCH_2)_y{-}(CH_2)_zCOOH$$

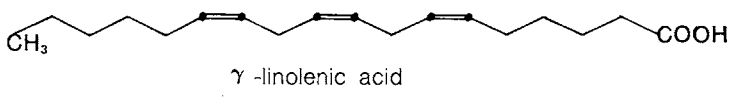
Several polyunsaturated acids are illustrated in Figure 3.2.

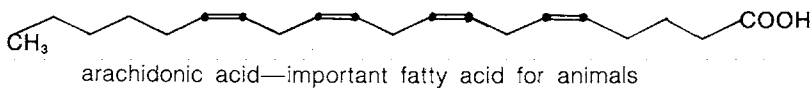


Below this line usable by the body for further introduction of double bonds









3.2 The structure of some fatty acids

FATS AND OILS

Although polyunsaturated fats occur only in plants they are essential to the animal organism; they could be the building blocks for the important prostaglandins, and they are also alleged to be effective in lowering the cholesterol content of the blood.[2]

The double bond(s), especially when *cis* (see Figure 3.1), means that the molecules do not pack together easily, which is seen in the low melting point of double bond containing material, i.e. oils. Substances made up of shorter chains also melt at lower temperatures.

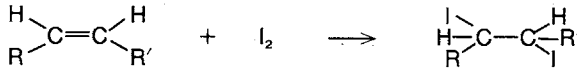
Why do animals produce fats—mainly saturated, while plants produce oils —mainly unsaturated? Plants suffer extremes of temperature and require their fats/oils to be semi-fluid even at the low overnight or winter temperatures, whereas animals can maintain a high temperature through internal heating and insulation, and in the case of mammals can even regulate it. In this case a higher melting compound is preferable because the fats also have a structural part to play and must not be too fluid. Kidney fat is solid so as to provide mechanical support for the organ, although fat circulating in the cells is fluid even at lower temperatures—otherwise you might get a solid casing in a cold shower.

The distribution of fats and oils varies in different plants and animals. Fats and oils appear to be a biological solution to the problem of storing, transporting, and utilising those fatty acids which an organism requires for its metabolic processes. The ester bond is quite stable but is easily split when required, by a specific *enzyme*. Fats are often called *lipids* by biochemists. They are the major energy storage in animals (38 kilojoules per gram, compared with 17 for carbohydrates and 23 for protein). When fats are 'burnt' in the body to produce energy they also produce water, more than from sugar. The hump of the camel in fact is a fat storage unit which provides the camel with both energy and water: hence the snide camel-selling trick of pumping the hump with air!

Plants, including moulds, yeasts, and bacteria, synthesise both fats and their component fatty acids. Animals can synthesise much, although not all, of their fatty acid requirements, but they prefer to ingest plant foods and modify them to their own needs. Only plants are known to synthesise oleic, linoleic, and linolenic acids but animals can increase the chain length and further increase unsaturation, giving for example acids characteristic of fish oils which are particularly rich in unsaturated acids with up to six double bonds.

Fats are traditionally classified by two chemical tests which measure two important characteristics of fats and oils, and which lead to two index numbers.[1]

1. *Saponification value.* The test for this index number involves the hydrolysis of the fats into their component fatty acids (as their anions or soaps) and glycerol. The saponification value is defined as the number of mg of potassium hydroxide required to saponify one gram of fat (or oil). It gives a measure of the average chain length—i.e. the molecular weight—of the fatty acids. Coconut 'oil' (actually coconut oil is solid outside the tropics i.e. a fat—it occurs in a tropical plant and can afford to have a higher melting point) has a saponification value of 250–260, while for butter it is 245–255; these high values are due to a large percentage of short chains. Some other saponification values of kitchen interest are: lard 193–200 and peanut oil 185–195; and outside the kitchen: linseed oil 189–196.
2. *Iodine value.* This second index number is a measure of the number of double bonds present. The iodine reacts with the double bond:

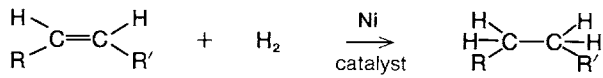


The number of grams of iodine which reacts with 100 grams of fat/oil is known as the iodine value. Some iodine values are

coconut oil	8–10	low—predominantly saturated
butter	26–45	
lard	46–66	
peanut oil	83–98	high because of polyunsaturated component
linseed oil	170–204	

Hydrogenation

In general, vegetable oils are a good source of polyunsaturates and animal fats are a poor source, although there are exceptions to this rule, e.g. coconut oil. However unsaturated fats can be saturated by adding hydrogen to the double bonds in the presence of a nickel catalyst. This hydrogenation converts a substance with the properties of a vegetable oil into one with the properties of an animal fat, i.e. changes a liquid into a solid. Thus linoleic and oleic acids would turn into stearic acid (see Figure 3.2). When margarines are said to be made *from* pure vegetable oils the emphasis could be very much on the 'from'.



Rancidity

The effect of the oxygen in the air on unsaturated fats is to cause oxidation, which is basically the addition of oxygen. This addition occurs adjacent to the double bond and further reactions are then possible which produce a complex mixture of volatile rancid-smelling products (the chain is split at the double bond giving smaller and hence more easily evaporated compounds). The fatty acids in butter are already fairly short (4, 6, or 8 carbon atoms) and merely producing the fatty acids from butter fat gives these products, whereas with margarine the longer chains must first be 'broken' before the short-chain rancid-smelling substances can be produced—hence margarine rarely becomes rancid. Commercial fats and oils have *antioxidant* added to them (see Chapter 12).

The same short acids as those present in rancid butter are produced by bitches on heat to make them attractive to the opposite sex! They are also present in human perspiration, although the sex attractant properties in this case are still under dispute.[3]

An intriguing study carried out by the United States armed forces over the years has to do with 'close' situations in submarines and spacecraft. It involved collecting and identifying the chemicals given off by humans as vapours. The list is enormous and obviously will give air pollution authorities a fascinating task to deal with (banning public meetings because safe levels of mercaptans have been exceeded!). Quantitative data were reported for five compounds, as set out in Table 3.1; the presence of isoprene as one of the most common effluents was unexpected.

TABLE 3.1 *Rates of emission of five human effluents*

Compound	Rate of emission (μg/hour)		
	Subject 1	Subject 2	Subject 3
ethanol	25	58	100
isoprene	425	251	270
acetone	360	240	470
butanol	16	26	41
toluene	0.6	14	13

Source: Journal of Chromatography. Vol. 100, 1974. p. 137

Heating of oils and fats

There are three important points in the heating spectrum of an oil or a fat.[4] The first is the *smoke point*, the temperature at which thin wisps of bluish smoke begin to rise from the surface. The *flash point* (see Chapter 11) is reached when brief but sustained bursts of flame start to shoot up. Higher still is the *fire point*, a temperature at which the entire surface of the frying medium becomes covered with a solid and continuous sheet of flame.

The temperature of smoke point does not stay constant: it tends to decrease with continued use of the oil or fat (due to a certain amount of decomposition and the fat residues from previously cooked foods). It drops about 20°C per use for thirty minutes at 270°C. Thus the higher the initial smoke point the longer the fat is usable before smoking. The United States Consumer Union and the Australian Consumers' Association have both carried out tests on fats and oils. They agree that the smoke point of an oil or fat is an important piece of information for consumers and should be listed on the label. Table 3.2 details some results published in *Choice*.[4]

TABLE 3.2

Oil type	Av. smoke point range in °C	P/S ratio*
Safflower	246–258	6.0–7.4
Sunflower	229–252	4.7–5.2
Maize	229–268	3.1–4.2
Peanut	246–251	1.9–3.5
Soyabean	256	3.7–3.9
Olive	204	0.5–0.7

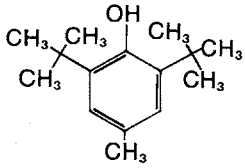
*The P/S ratio is the ratio of polyunsaturated fatty acids in the fat or oil to the saturated fatty acids present. Monounsaturated acids are ignored. The range of P/S values can depend on factors such as where the seeds are grown.

Heating does not significantly change the P/S ratio of polyunsaturated oils, but it can cause the formation of oxidised compounds which tend to destroy the vitamin E content, and can also cause the oils to have a tendency to polymerise that makes them unpalatable (see section on oil-drying paint in Chapter 8). Olive oil contains mainly oleic acid which is monounsaturated.

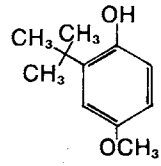
ANTIOXIDANTS

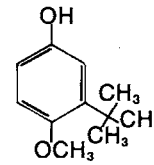
The two most common antioxidants added to consumer products during processing are butylated hydroxyanisole and butylated hydroxytoluene; their

structural formulae are given in Figure 3.3. A third compound is at present (1977) under consideration by the Australian Food Standards Committee as an allowed antioxidant: mono-*tert*-butylhydroquinone (TBHQ). Its structural formula is illustrated in Figure 3.4.



BHT

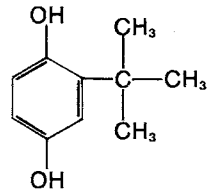




BHA

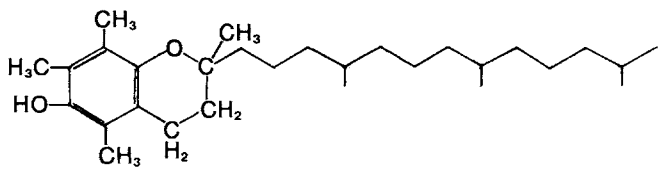
3.3 The antioxidants BHT and BHA

Butylated hydroxyanisole (BHA) is legally allowed in edible oil and fat products at levels of 0.01–0.02 percent (NHMRC). It is also allowed in cream cheese, dried mashed potatoes, edible oils and fats, margarine, essential oils. *Butylated hydroxytoluene* (BHT) is used in petrol, lubricating oils, rubber, but not generally in foods although there are exceptions. As it is used in polythene film, a legal standard allowing an amount of up to 2 ppm to be absorbed out on to the food has been set (see Chapter 12).



3.4 The antioxidant TBHQ

BHA and BHT are preferentially oxidised—i.e. they, and not the fat, are attacked by oxygen. They are oil-soluble, easy and cheap to produce, and are related to the 'natural' oil-soluble antioxidant—α-tocopherol, vitamin E (Figure 3.5). Vitamin E occurs in vegetable oils—the most important source is wheatgerm oil—and protects them against oxidation. It has been found to be essential for the growth and reproduction of rats, but these results cannot be extrapolated to humans. Currently it is the subject of controversy as an anti-ageing pill.



3.5 Vitamin E

Humans have a need for vitamin E in an amount proportional to the amount of polyunsaturated fat in the diet—it is apparently required when the fats are laid down in the body, and presumably also as an antioxidant—but note that excessive amounts of any oil-soluble vitamin can be dangerous.

MARGARINE

The origin of margarine dates back to 1869 when Napoleon III proposed a competition with the aim of discovering 'for the use of the working class and, incidentally the Navy, a clean fat, cheap and with good keeping qualities, suitable to replace butter'.

The legal definition of margarine recommended by the NHMRC Food Standards is: Margarine is a mixture of edible fats, oils and water prepared in the form of a solid or semi-solid emulsion (water in oil). It includes all substances made in imitation or semblance of butter and all preparations resembling butter, the fat contents of which are not derived exclusively from milk, and it should not contain more than 16 percent of water nor more than 4 percent salt (i.e. in terms of energy margarine is equivalent to butter). This definition therefore includes a product such as Dairy Spread, which is made from butter and vegetable oil and was introduced into the market to compete with margarine while not being subject to margarine restrictions. Table margarine must contain at least 8.5 milligrams of vitamin A and at least 55 micrograms of vitamin D per kilogram.

3.6 The distinction between polyunsaturated and polyene

The use of the term *polyunsaturated* is permitted where 'the proportion of *cis*-methylene interrupted polyunsaturated fatty acids [see Figure 3.6] present in the margarine is at least 40 percent [this requirement is to prevent the inclusion of synthetic materials], and the proportion of saturated fatty acids does not exceed 20 percent of the total fatty acids, and the ratio of polyunsaturated to saturated fatty acids is at least 2:1. The total cholesterol content expressed in mg/100 g must appear with equal prominence'. The other 40 percent of the fatty acids can be *mono*unsaturated—e.g. oleic acid—which neither increases nor decreases the problem of cholesterol deposition. Part of these recommendations has been adopted by some of the States.[5]

Manufacturers also produce a margarine with a polyunsaturation (P/S ratio) of 3:1; it is softer than the other margarines, and requires constant refrigeration.

Antioxidants, flavouring (3-hydroxy-2-butanone, and diacetyl, which give butter its characteristic flavour), and vegetable colouring (usually carotene,

a source of vitamin A, which gives the colour to butter) may be added to table margarine (but not to cooking margarine in Victoria, Tasmania and Western Australia). In the United States prior to 1950 margarine manufacturers could not colour their product unless they paid an additional 10 cents per pound Federal tax, the result of the dairy lobby. By changing from coconut oil to soyabean oil as a raw material, the makers of oleomargarine were able to enlist the aid of soyabean growers to combat the dairy lobby, and the law was repealed in 1950.

The composition of an exhaustive list of foods can be obtained from a publication of the Commonwealth Department of Health, *Tables of Composition of Australian Foods*, and some of the values are given in Table 3.3.

TABLE 3.3 *Composition of some Australian foods*

	Total saturated fat (g/100g food)	Unsaturated fat (g/100g food)		Cholesterol (mg/100g food)
		oleic	linoleic	
Butter*	45	27	3	260
Cotton seed oil	25	21	50	0
Corn oil	10	28	53	—
Dripping:				
beef	48	44	2	95
lamb	56	36	3	95
Lard	38	46	10	95
Margarine*				
cooking	33	36	5	
industrial	25	44	5	Not
polyunsaturated	11	26	38	avail-
soft spread	35	33	8	able
table	35	22	14	
Olive oil	11	76	7	—
Peanut oil	18	47	29	—
Safflower oil	8	15	72	—
Sunflower oil	12	20	63	—
Soyabean oil	15	20	52	—

*Butter and margarine are about 80 percent fat/oil 20 percent water. The margarine figures are representative for 1970.

CHOLESTEROL

Cholesterol is not technically a fat but a steroid related chemically to the bile acids, cortisone, the sex hormones, and vitamin D: a motley collection. Cholesterol is a necessary substance which is found in all the cells of the body. It is produced in the liver and it may also be taken in directly from foods

of animal origin, so that the level in the blood comes from two sources, both of which can vary. Nevertheless the level of cholesterol is influenced by diet and can often be reduced by *replacing* saturated fats in the diet by polyunsaturated fats (monounsaturated fatty acids exert little influence either way).[2] Medical authorities emphasise that people should not radically alter their diets without being advised by their doctor.

Vegetable oils contain the phytosterols instead of cholesterol. Isolation of ergosterol used to be employed as evidence for the addition of vegetable oil to animal products.

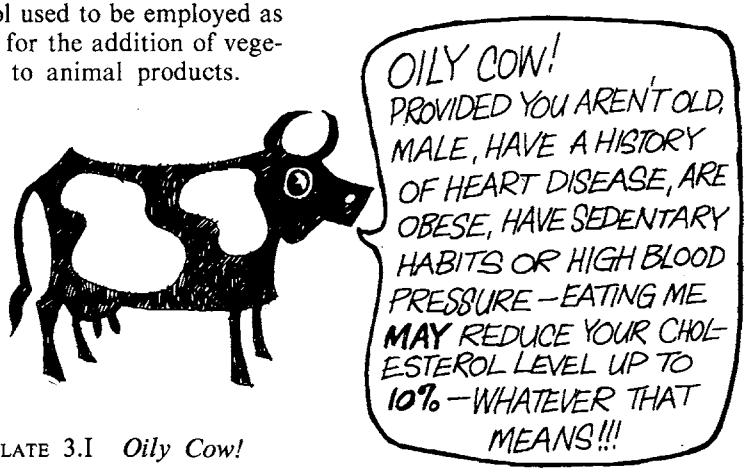


PLATE 3.I *Oily Cow!*

MARKET CONSIDERATIONS

Limits to the amount of table margarine which may be produced in Australia are set by the Australian Agricultural Council, a body that is basically controlled by the dairy industry. The quotas limit production to less than 2 kg of table margarine per head per annum. 'Table' margarine includes polyunsaturated table margarine. Margarine in excess of the quota is 'cooking' margarine, which is required by State law and NHMRC recommended standards to contain at least 90 percent beef or mutton fat. (The Australian Capital Territory and South Australia have abolished quotas.)

There are two types of cooking margarine. One is soft even under refrigeration, and the other has 'spreading' properties similar to butter, which becomes hard at low temperatures. The soft cooking margarines result from removal of some of the stearic acid from beef fat, leaving oleic acid. The fat is emulsified with skim milk.

Quotas on the production of table margarine were imposed during World War II (1940) to protect the butter industry at a time when table margarines were highly saturated because they were made from imported coconut oil, but as Table 3.4 shows, almost all the table margarine quota is now devoted to polyunsaturated margarines. The oil for these margarines is produced to some extent from locally grown oil seed.

Fat consumption

A survey of purchases of margarine and butter gave the details shown in Table 3.4 for March 1974, projected nationally from 1200 dairies, and showed that butter purchases were 6530 tonnes ($8m), while margarine purchases were 5400 tonnes ($5m).

SOME TOPICS FOR DISCUSSION

Polymeat, milk, and cheese

Scientists of the CSIRO have developed a feed supplement for the production of ruminant meat with a level of about 20 percent of the fat being polyunsaturated. The supplement consists of vegetable oils embedded in a matrix of formaldehyde-treated protein obtained from oil seed with added

TABLE 3.4 *Details of margarine sales (%) weight*

Margarine Types	N.S.W.	VIC.	QLD	S.A.	W.A.	TAS.
Table						
polyunsaturated	27	46	36	32	49	50
saturated	5	12	22	7	10	24
Cooking						
soft	27	28	25	27	24	11
hard	41	15	18	35	17	15

National brand shares of the market

polyunsaturated		*saturated*	
Miracle	19.5	Daffodil	7.9
Flora	8.0	Meadow Lea	11.5
Meadow Lea	33.6	Golden Pastures	0.9
Golden Pastures	2.6	Spreadwell	—
Dixibell	11.2	Other	0.8
Sunbeam	0.4		21.1%
Other	2.5		
	77.8%		
Soft cooking		*hard cooking*	
Eta Super Spread	18.9	Marville	13.9
Mothers Choice	1.1	Fairy	34.1
Astra	4.4	Tulip	3.7
Stork	19.4	Dixie	1.9
Jonquil	—	Other	—
Dell	0.1		53.4%
Kirrabel	1.1		
Other	1.5		
	46.6%		

Source: Retail World 24 December 1974

casein (see Chapter 6). The linoleic acid of the feed supplements is effectively protected from hydrogenation (hardening) by bacteria in the animal rumen and is readily incorporated into milk and meat fat. The level of cholesterol in meat and milk products is *unchanged*. It is doubtful whether this 20 percent level of polyunsaturation (compared to 40–60 percent for the fat in polyunsaturated margarine) would be beneficial except where the whole diet is carefully monitored. It is however an interesting technology and leads the way to the incorporation of other materials directly into food obtained from animals; and it raises some very important philosophical questions.[6]

Polyeggs

Because of the low fat content of eggs (11 percent—all in the yolk which is thus 30 percent fat) even high polyunsaturation would be a negligible contribution to diet. Cholesterol levels are unchanged.

Erucic Acid

Erucic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$, is a monounsaturated fatty acid with the double bond not in the middle of the chain. It is found in the seed of *Brassica rapa*. It has been implicated in the causation of heart lesions.[7] Current *recommendations* are that it should not be present in margarine and vegetable shortenings and that its level in edible oils should not exceed 1.5 percent. (Erucic acid levels in rape seed were about 40 percent but have been reduced —1972, New South Wales and Victoria—to 20 percent with consequent loss in shattering resistance in the seed. New Canadian varieties are being introduced.) The cheaper blended salad oils may contain rape seed oil, and a listing on the label of erucic acid content should perhaps be considered if low levels cannot be achieved. Rape seed oil is also used as a bread release agent (i.e. for greasing of bread pans) and levels of erucic acid in rape oil are currently being monitored.

Waxes

Spermaceti crystallises and separates when the oil from the head of the sperm whale (Cetacea) is chilled; it is mainly the ester cetyl palmitate, $C_{15}H_{31}COO{-}C_{16}H_{33}$, which has a melting point of 42–47°C.

Beeswax. The cells of the honeycomb contain esters of C_{26} and C_{28} acids with the C_{30} and C_{32} alcohols plus 10–14 percent hydrocarbons—C_{31} mainly.

Carnauba wax, the most valuable of the natural waxes, is obtained from the coating on the leaves of a Brazilian palm. Hard and impervious, it is used in car and floor polishes. It has a melting point of 80–87°C, and consists of the esters of the C_{24} and C_{28} acids with the C_{32} and C_{34} alcohols. There is also a considerable amount of ω-hydroxy fatty acids, $HO\text{-}(CH_2)_xCOOH$, x = 17–29 (ω omega, the last letter of the Greek alphabet, means that the —OH is at the end of the chain); these ω-hydroxy fatty acids can form long polymer esters (see Chapter 6) which give this wax its unique properties.

Wool wax (wool grease, degras) is recovered from the scouring of wool and is unusual because it forms a stable, semi-solid emulsion containing up to 80 percent water—a purified product known as lanolin is used as a base for salves and ointments in which it is desired to incorporate both water- and fat-soluble substances. This 'wax' is not an ester.

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Chapter 4

CHEMISTRY IN THE BOUDOIR

COSMETICS

In 1770 a bill was introduced into the British Parliament which read

> '. . . that all women, of whatever age, rank, profession or degree, whether virgins, maids or widows, that shall impose upon, seduce and betray into matrimony, any of His Majesty's subjects by the scents, sprays, cosmetic washes, artificial teeth, false hair, Spanish wool, iron stays, hoops, high heeled shoes and bolstered hips, shall incur the penalty of the law in force against witchcraft and like misdemeanours.'
>
> —J.T. Brennan, *PRACI* **41**, 1974, 125

Although cosmetics have been used—by men as well as women—since prehistory, the popular general use of cosmetics is a modern phenomenon. Many new and improved cosmetics have been made available by scientific research, and large-scale advertising has been an important factor in bringing them to the awareness of consumers and in increasing the number of people who use cosmetics. Consumer products span a spectrum from those in which it is the composition and performance of the product that are of fundamental importance to the consumer, to those where the image and personality of the product virtually is the product. With cosmetics, the consumer is buying a hope. The chemistry of a hope might be best described by the market researcher and for this reason the first part of this chapter is an edited version of a talk given by Ms Marilyn Elfverson to the Australian Cosmetics Association in Canberra in April 1975 followed by a brief description of the Australian cosmetics industry. The second part of the chapter is more chemical but is still fairly descriptive.

PART I THE COSMETICS INDUSTRY

Market research

What is market research? Essentially, market research operates as a channel of communication between the marketer and his market. It is a *dialogue* with the consumer, a means of keeping the marketer in touch with the consumer. Market research provides the marketer with vital feed-back about consumers' needs, attitudes, and behaviour. This *understanding* of the consumer is an essential basis for successful marketing. It is essential because, in many product areas, consumers can satisfy their basic needs in a variety of ways: they have a *choice* and it is this choice which has led to the marketing philosophy of consumer orientation. Take the example of a woman who has just purchased a bottle of skin cleanser. This purchase involved a *choice* not only between different *brands* of cleanser, e.g. Revlon, Helena Rubenstein, and between different *types* of cleanser, e.g. cream or lotion, but also a choice about whether to use a special cleanser product or to use soap and water—or just water. Marketers are in a better position to channel consumers' generalised needs and wants into specific product and brand purchases if they have a full understanding of the consumer and of her attitudes towards competing alternatives.

Market research would not be needed if management was in direct contact with its market. As an example, imagine the case of a very small company which makes hand lotion. The company consists of one person who spends his mornings making hand lotion and his afternoons selling it directly to consumers. This manufacturer has a first-hand knowledge of each and every customer. He receives instant feed-back on his product and on his new market offerings and, because he knows each customer in a personal sense, he can develop products and a selling approach to meet their individual needs. For example, he may know that Mrs Jones has six children and does a lot of washing and a lot of washing up. She has a problem with her skin drying out and cracking. She wants a product with healing properties and our manufacturer can develop a product to meet that need. Mrs Smith does a lot of gardening and spends a lot of time out-doors; she wants something to protect her hands and he can sell her a hand care product with this benefit. Miss Brown is eighteen. She doesn't spend much time with her hands in detergent, but she wants her hands to feel soft to touch. He can sell a product to her that promises to make her hands nice to hold. His thorough understanding of his market leads to success and soon he outgrows his manufacturing capacity. He puts on an assistant to help manufacture his hand lotion, and then another. Soon he needs a second car and then a third to sell his product and he is beginning to lose that personal contact with his customers. *As his firm grows, so does the need for research.* Research is a substitute for personal contact with the customer. As the firm grows, the personal communication to and from customers has to be replaced by other media: advertising and promotion on the one hand, which communicates to the consumer, and *research* on the other hand, to obtain feed-back from the consumer about his market offering.

Market research covers a lot of areas—it is used for a variety of purposes. For example, it is used to provide feed-back about *what* is happening in the market place: where does a specific brand stand in relation to competition? Where is the industry as a whole going—is it expanding, is it contracting? This type of research is often described as 'market intelligence'. It helps the marketer to define his current position, predict his future position, identify strengths and weaknesses. Research is also used to help the marketer develop and present a product that will sell. Some people do that very effectively without ever doing any research. But research can help to reduce

the risks of introducing a new product, or of modifying the mix of an existing product; it can help to identify opportunities for new products, or new product positionings; and it can help to maximise the effectiveness of the product's marketing mix.

When we talk of a *product* we are talking about more than a set of physical properties. We are talking about the *overall impression* that a product makes on the consumer through the *collective* impact of its physical characteristics, its performance characteristics, and its presentational elements, including its brand name, packaging, price, distribution, and advertising. *In most product categories, we are not just selling a product, we are selling a proposition.* Toilet soaps share a number of physical properties and they all clean—but what determines whether I choose to pamper with Palmolive, luxuriate with Lux, or freshen up with Lime Fresh? These different brands do much the same thing. And if one of them was to go off the market, consumers could quite happily make do with another one. The consumer's relationship with a product goes beyond what the product is or what that product does. A product has a *personality* and this personality may be the strongest element in attracting purchase. Research is often used to help in the development of a brand personality, and to ensure that this personality is being effectively communicated to the target market.

The way a *product* dresses tells you something about that product. If the pack design tells you something you don't like about that product, maybe you won't give it a chance. Impressions count with products as well as with people. If I take two identical hand lotions and put one in an Estee Lauder pack and one in a Woolworths pack, and ask women which one they want, I would predict that the majority would go for the Estee Lauder—as long as they didn't have to pay for it! But more than that, the impression they get from these packs will probably affect their perceptions of the product itself. If they are asked to try the lotions, it is likely that they will say that the Estee Lauder product smells nicer, makes their hands feel softer, has a finer texture, and is more effective. And they will actually believe that. Of course, not all women will be attracted to the Estee Lauder personality—for some it may be threatening, for some it just may not be the kind of personality they can relate to, or aspire to.

What people say and *how* they say it influences how you feel about them. Products talk too. They talk through advertising, they talk through their pack copy. It is important for a product to say the right thing to the right people. Where a person lives, how much money they earn, whether they are successful, influences how you feel about them. The price of a product, where you buy it, the advertising medium chosen for it—*Vogue* or the *Women's Weekly* or the particular radio station—the types of presenters used in its commercials, all communicate in a similar way. A higher price *tends* to suggest better quality, a headache remedy retailed only through pharmacies tends to have more ethical overtones than one sold through a supermarket.

A very useful way of establishing how consumers really feel about a product is to ask them to talk about it as if it were a person. Often when you ask a person why they buy one brand rather than another, they can't really tell you 'why', or they give you superficial answers such as 'it gets clothes whiter'; yet when you ask them to talk about the two brands as if they were people, they may have very different images and feelings about these two brands that come out in these descriptions. Try it for yourself: try to think about some products in personality terms. Let's take *Brut*—after-shave or perfume. Think about the Brut brand—think about Brut as if it were a person. Let's say that suddenly Brut came to life as a person. What kind of person would Brut be? For starters, is Brut male or female? Is Brut a young person or an old person? How does she/he get on with the opposite sex?

OK, now let's take Lux—Lux toilet soap. If Lux were to come to life as a person,

what kind of person would Lux be? Male/female? What would Lux's favourite colour be? What kind of clothes would Lux wear?

People are more likely to buy a product if they like its personality. People buy products that they feel comfortable with, products that they trust. People buy a product or brand that feels 'more me' than others. The product personality can act as an affirmation of their own self-image. For example, when a woman is buying soup for her family, she may be looking for a product to match her image of herself as someone concerned to provide wholesome, nutritious food. When she is buying cosmetics, she may be looking for a product to express her more glamorous sensual potential.

The importance of the personality varies to some extent depending on the product, but it is probably true to say that most products having a strong distinctive personality that consumers can relate to improves their chances of success. The product personality may not be a major consideration for a product such as a scouring pad, but it is a definite consideration in the choice of many every-day food and toiletry products, and it is at work in full force in the purchase of cigarettes, cars, *cosmetics*, and alcohol. It is particularly important in these categories because they are *social* products. In these categories, brand choice says something to other people about 'me'. We buy the brand that will create the impression of ourselves that we want to create.

Now, let's look at how research is used in the development of a brand personality. Research needs to take into account all the elements that contribute to the personality, that is, it needs to cover the whole spectrum of consumers' contact with the brand: the product's attributes—its appearance, smell, texture, and performance characteristics; its packaging; its pricing; its advertising; its retail outlet; and so on. The interaction between these elements is important. If the personality is to be strong, these elements need to be consistent, they need to be mutually reinforcing.

The research question differs a little depending on whether we are dealing with an existing brand or introducing a new brand or a new product. With an existing brand, the first step is to find out how consumers see its current personality and how they see the personalities of its competitors. With an existing brand, it is often difficult to completely change the personality: it is difficult to change people's attitudes to a brand overnight, and while they may respond to being shown a different side of the brand's personality, they may not be able to relate to a complete change of face. However, when the positive and the negative aspects of the brand's personality are known, it is possible to develop strategies which will reinforce its positive aspects and play down its negative aspects.

When a completely new personality is to be developed for a new product or a new brand, the first step is to find out how consumers feel about the product category and about available brands. Brand personality must be consistent with product personality. For example, some products are seen as 'goodies' and some are seen as 'baddies'. Lemonade and milk chocolate are products which tend to be seen as virtue products; cola and coffee tend to be regarded a bit as vice products. If you try to infuse a tough product with a tender personality, this incompatability is likely to result in a weakened impact. In the same way, product characteristics must be consistent with expectations for the product category. For example, if you take a mouthwash product, consumers have certain expectations about it: they expect it to work, they relate to it as a medicinal product. Medicinal products are expected to have certain attributes, e.g. a bad taste; that is, these products almost need to punish you before you feel that they are doing you any good. Listerine has capitalised on this expectation; rather than changing the taste of the product, or trying to tell people that it doesn't taste too bad, they have played up its bad taste in their advertising strategy. There would be no point in giving a product which is seen as having an almost medicinal function, a personality which

is bright, happy, easygoing. The product is essentially serious, and although the creative approach can be humorous, the product itself must be seen seriously.

Research can help to provide this understanding of what the product means to consumers and this understanding can help in setting parameters for the product or brand personality. If a personality is being developed for a new brand, then it is important to understand the personalities of existing brands. A personality will have more impact if it is unique; there is no point in being a 'me too' personality. The final personality probably will not come out of research but from creative inspiration; however, research can help in defining the parameters for the personality.

A typical research program might start with some basic attitude and motivation research. The technique that is mainly used for this type of research is the group discussion technique. This technique involves getting together small groups of consumers, usually about six to eight, and just having them talk about the product category. Group discussions are usually conducted by a psychologist and the approach taken is relatively non-structured. At the beginning of the discussion consumers are just invited to talk together about the product category in any way they want to; this is called the non-directive approach. And it is a good way of getting to understand the consumer's point of view. It provides an opportunity for ideas to come up that the marketer and researcher might not have thought about. A typical group discussion might last for about two hours—this allows time for a relaxed atmosphere to develop in which the consumer feels free to express her thoughts and feelings about the topic and to express them in her own way and at her own pace. The group discussion technique also allows a range of probing techniques to be used to elicit in-depth understanding of consumers' attitudes, needs, and motivations.

From such research we find out what motivates consumers to use the type of product under discussion. We find out what they are seeking from the product both in terms of performance benefits and in terms of more subjective benefits. We find out whether they have any dissatisfactions with available products which could be capitalised on by a new brand. We find out how consumers perceive existing brands, what image they hold of each brand, and how they relate to these different images. We also find out how they actually use the products—the way they use a product may suggest opportunities for new positionings in terms of usage, or may suggest a creative approach to capitalise upon usage factors.

There are some problems in obtaining an understanding of what really influences consumers' behaviour. For example, if we are trying to find out attitudes to toilet paper, consumers are likely to say things like, 'I want it to be soft'. If the softness dimension in toilet paper is to be fully understood, we need to know a little more than that. We need to know what softness *means* in consumer terms, whether this positive dimension has any implicit negatives, e.g. in relation to strength, and how important softness is in relation to other product attributes and benefits. Let's just look at the question of what softness means to the consumer. When a consumer says she wants a soft toilet paper, it is possible that she doesn't have a very strong feeling about it, it's just a word that springs to mind when she's asked to say what she likes in a toilet paper. Consumers have learned a vocabulary from advertising and they will often use words that seem meaningful, but which really may just be a play-back of an advertising claim. Examples of such words are: soft, pure, mild, natural, reliable.

The research problem is to break through the superficial response and find out whether these words do signify something important to consumers and what it is that they signify. One way of doing this is to ask people the *opposite* of the word. For example, if consumers are talking about a skin care product, and they describe it as 'pure', we might ask them, 'What's the opposite of *pure*?', and this procedure often

helps to reveal the dimensions of the word *pure*. The opposites they give might be *irritating, contaminated, perfumed, artificial, harsh, cheap*. Consumers often find it easier to talk about negatives, what they don't want, rather than what they do want, and the emotional implications of a product attribute or benefit are often clearer when examined from the opposite point of view.

Another problem in research is that often people's behaviour is influenced by emotional factors that they are not fully conscious of. For example, if you ask a woman why she likes a particular brand of detergent, she's not going to tell you that it is because she can identify with the attractive, competent, efficient, modern, interesting image of the brand—she is more likely to say that it is because it gets clothes really clean, that it is economical. She is more likely to say that she doesn't use another brand because it doesn't get clothes as clean or bright rather than because it connotes to her a rather frumpy, fairly sloppy, harrassed mother who leads a fairly housebound existence. So, how do we find out the underlying *emotional* relationship with the brand which is probably the most important factor determining behaviour? One way is the one already discussed—ask consumers to personify the product, to describe it as if it were a person. Another technique is what we call the *projective technique*. With this technique, we might show to respondents two pictures of women. These pictures will be fairly unstructured, they will be more an outline than a concrete picture of two women. We then say, 'this woman uses brand A and this woman uses brand B', and we ask the respondents to just tell us about these women: What are they like? How old are they? What kind of life do they lead? How do they approach the washing? This technique often brings out well-defined and very different images of the users of these different brands.

Another technique for getting at consumers' emotional relationship with a product or brand is to use what we call a *fantasy*. For instance, if we are trying to find out what deodorant means to a woman, we may ask her to sit back, close her eyes and have a fantasy about a time when she's run out of deodorant. We then ask her to talk about what was happening, where she was, how she felt. This fantasy approach helps to bring consumers into contact with their feelings about the product. For example, they might play-back a fantasy of being alone, sitting all scrunched up, avoiding people, feeling dirty, and so on.

Group discussions are the most useful technique when we are trying to get an in-depth understanding of consumers' relationships with a product or brand. However, the technique is based on small sample sizes and for this reason the findings often cannot be extrapolated to the whole population. Consumers often differ in their attitudes to a product and in their motivations for using it. Similarly, a brand personality which has strong impact is unlikely to appeal to all consumers because consumers themselves differ in terms of personality, life-style, income, and so on. To provide an indication of the size of different market segments, a large-scale survey needs to be conducted. The group discussion technique is often used in an exploratory fashion to identify the factors that are important in the market and to identify the range of consumer attitudes and images; this information can then be used to structure a questionnaire for use in a large-scale survey of the market.

Depending on the marketing problem—e.g. are we looking for opportunities for introducing a new brand, are we looking for ways of revitalising or repositioning an existing brand whose sales' performance is dropping off, are we simply checking whether our market offering is as effective as it could be—the research findings will be analysed in various ways. For a *new* product or brand, we will probably look very carefully at any consumer needs that are not being satisfied, any dissatisfactions with available

products, and at the strengths of available brands. If we already have a brand in this market, it is possible that it is appealing to a particular segment of people and not touching others, and this may indicate an opportunity for a line extension or a new brand. With an existing brand, we will probably be looking carefully at its strengths and weaknesses relative to competing brands and at whether its consumer appeal could be strengthened in any way.

Let's take as an example the problem of introducing a new brand into an existing market. Our exploratory research has indicated that there is an opportunity for a new brand and has provided broad guidelines in terms of desirable product attributes, the benefits that should be promoted and the kind of personality that this brand should project. The next stage of research will probably be concept testing. The product or advertising concept usually embodies the key claims that will be made for the product and some elements of the product personality. It might take the form of some advertising copy, a product name, a pack design, and it might be presented in the form of a fairly rough press layout. Often at this stage, we will develop a number of alternative concepts to see which is the strongest. These are then researched to check that the intended product benefits are being clearly communicated, that they are meaningful to consumers and that they generate interest in the product. We can also check whether the name and pack design elements are consistent with the expectations generated by the advertising copy. This stage of the research may identify problems in communication or in the mix which can then be modified before going into expensive creative production. We can also probe the kind of product expectations generated by this concept, in terms of attributes such as texture, colour, perfume and so on. If a product has already been developed, it can be shown to consumers to see if the actual product matches their expectations.

Another important research stage is *product testing.* Once a product has been developed it is usually tested on a sample of consumers in a real-life situation, that is, in the home. The product is left with consumers for a typical usage period and then they are interviewed to determine their reactions to it. Their reactions to the product are often assessed in comparison with their reactions to the brand they usually use. This stage of the research is very important; the ultimate test of the consumer/product relationship is whether the product matches their expectations. A brilliant brand personality might achieve a first sale, but if the product itself disappoints the consumer, it will not obtain a repeat sale. If the product test indicates a high level of acceptance of the product, the program will probably move into the final stage. If the product does not achieve a high level of acceptance, the research will usually indicate where the weaknesses are. The product can then be modified and re-tested. Before reaching this stage, *elements* of the product may have been tested, for example, taste characteristics, perfume characteristics, may all be examined in separate research projects to ensure consumer acceptability.

When we know we have the right concept, the right pack, and the right product, it is time to develop the final program. Again, this should be researched to check that it is an effective expression of the intended strategy. The advertising is tested in the target market to find the answers to the questions: Does it have impact? Does it communicate effectively? Does it generate purchase interest? The final packaging is tested both in terms of design and function. In terms of design we ask: Does it stand out—will it be noticed on the shelf? Is it consistent with the product personality? If there are no problems, we are ready to go.

PLATE 4.1 *I had no idea what the analytical chemist could do for me!*
Courtesy of Science Museum, Kensington London. U.K.

Some facts about the Australian cosmetics industry

In May 1975 the Industries Assistance Commission presented its report *Cosmetics and Toilet Preparations*. It contains some interesting information about the Australian cosmetics industry.

The local manufacturing industry has a turnover of over $100 million and employs directly about 5000 persons, the majority of whom are women. The industry is mainly located in Sydney [and] . . . is largely foreign owned and controlled . . . In addition to companies which manufacture and sell their own products, there are contract manufacturers which produce cosmetics . . . for marketing companies, other manufacturers and retailers . . . .

Local production was encouraged in 1929 when the Australian Government raised the customs duties . . . to 45 percent Preferential [most favoured nation agreements] and 60 percent General.

The report goes on to say that when an additional special duty of 50 percent of the Customs Tariff duty was imposed in 1930, this represented such a virtual embargo on imports that many Australian importers and, later, large multinationals commenced production in Australia. It continues:

Avon, an American owned company . . . , commenced local manufacturing operations in 1968 and is now believed to be the largest local manufacturer and the largest marketer of cosmetics and toilet preparations in Australia.

The production of aerosol deodorants and antiperspirants has risen significantly from approximately 6 million units in 1969, to around 17 million units in 1973. Other products which have shown considerable growth since 1966/67 are facial creams and lotions, hair tonics, suntan oils and shampoo. Products which showed a decrease . . . were face powder, hand cream, barrier creams and certain hair preparations . . . .

The number of individual ingredients used in a product varies according to the formulation used. . . . the cost of ingredients ranged from about 3 percent to 40 percent of the cost to manufacture, although the percentage for most of the products was below 25 percent . . . .

Packaging accounted for between 20 percent to 60 percent of cost to manufacture, exceeding 40 percent in most instances . . . This expenditure on packaging materials represented 58 percent of the total cost . . . compared with a figure of only 5 percent for all manufacturing industry. . . .

Avon estimated that the total Australian cosmetics and toilet preparations market at the retail level was valued at about $230 million in 1973. . . . [and] that the medium priced segment accounted for about 70 percent of total sales . . . while the high priced and low priced segments accounted for 20 percent and 10 percent respectively.

Information presented to the Commission indicated that the high priced segment is usually restricted to major department stores and selectively franchised pharmacies; that the medium priced products generally have high quality packaging and are sold through pharmacies, major department stores and by direct selling methods; and that the low priced segment products are less expensively packaged, are sold through chain stores, department stores and pharmacies, and include the house brands supplied by the local contract manufacturers in competition with low priced imported cosmetics mainly from Britain and the United States.

It is understood that most of the major cosmetics suppliers trade on a franchise system where one or two pharmacies in a district are given the exclusive agency for a particular brand. Avon, however, distributes solely by direct selling methods using mainly part-time representatives. . . .

The report quotes figures from the Australian Bureau of Statistics for 1968/9 which show that pharmacies made 51 percent of all retail sales (excluding direct selling) while department stores made 18 percent, and continues, *inter alia,*

The limited information available revealed retail mark-ups of up to 150 percent on estimated total cost . . . Mark-ups on imports appear to be significantly higher and in some instances retail prices were found to be more than 2000 percent of declared [import] value . . . the Commission noted that as the mark-up increased, the significance of the duty in the final price of the product decreased. . . .

Avon stated that its experience of the Australian cosmetic market had shown that it was not particularly sensitive to price changes. . . .

Consumer behaviour in Australia appears to conform with observed overseas patterns in that consumers associate high quality and prestige with higher prices. *Avon stated that there was little difference in the functional quality of the high and low priced products* [my italics]. The Commission believes that the industry uses packaging,

advertising and promotion, and pricing to create, in the mind of the consumer, distinctions between basically similar goods. . . .

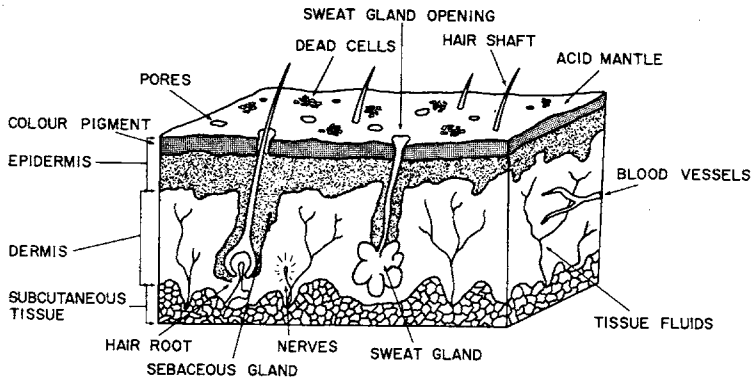
The final recommendation of the Industries Assistance Commission in its report was that most cosmetics be dutiable at a rate of 15 percent. However, industry lobbyists tend to adopt a strategy of working towards a delay in the introduction of a lower tariff, as it can then be argued that the data on which the recommendations are based are out of date. The Government finally set a level of 20 percent.

PART II THE CHEMISTRY OF COSMETICS

Having discussed the advertising and sale of cosmetics we will now have a closer look at the cosmetics themselves. The range of goods covered by the term *cosmetics* is very large, and in general it includes: skin care products, eye and face make-up, fragrances, hair care products, hand creams and lotions, nail care preparations, bath products, deodorants, depilatories, toothpastes and mouthwashes, shaving lotions and soaps, and sunscreens (see Appendix 4.1 and 4.2). But by way of introduction, before going on to discuss several of these commodities, here is some background information on the skin—since cosmetics are applied to the skin it is helpful to understand its functions.

The Skin

The skin is an important organ with many tasks to perform: it encloses the body, preventing some internal materials from escaping while allowing others to pass through, at the same time keeping most external materials out. Among its duties are the regulation of body temperature by controlling the escape of water—as sweat; the regulation of the penetration of sunlight—allowing sufficient for the production of vitamin D, but not so much that the underlying tissues are damaged; and the sensing and transmission of information on temperature and pressure.[1]



As the diagram shows, the skin consists of a large number of components, which are divided, for convenience, into three layers—the subcutaneous tissue (underlying fatty material), on top of which is the dermis or true skin, which in turn is covered by an outer layer called the epidermis.

The *epidermis* contains the pigment-producing cells that determine the degree of darkness of the skin, and has a deep layer of growing cells with an outer layer of dead cells, the horny protective layer that is continuously being sloughed off—it is obvious on the scalp where the cells stay caught in the hair to give the effect called dandruff.

The *dermis* contains the working elements of the skin in the form of sensory nerves, hair follicles, blood vessels, and sweat glands. Associated with each hair follicle are several sebaceous glands which excrete, through the pores, an oily material called sebum, and it is this that controls the degree of oiliness of the skin. The composition of sebum is approximately 50 percent fats, 20 percent waxes, and about 5 percent free fatty acids which give the fluid a slightly acidic pH, helping a little to combat bacteria. This acidity would normally be neutralised by excess soap. Blackheads are formed when sebum dries in the skin ducts and blackens on reaction with the air. Pimples are inflammations caused by the irritation of sebum escaping into surrounding tissue; they are not initially due to infection, although secondary infection can occur and make them worse.

Under normal conditions the water content of the skin is higher than that of the surrounding air, so that evaporation occurs. If the water is not replaced then the skin becomes dry. However, direct application of water to the skin surface does not replace the water in the skin—an oily vehicle is required to hold the water in contact with the skin, and to hinder evaporation of the water.

Skin types

Cosmeticians and dermatologists disagree about the validity of classifying skins into distinct types.[1] Dermatologists think in terms of a normal distribution about an average skin, with most people showing minor variations—some having more oil and others less oil than the average. For the cosmetics industry the greater the degree of classification, the greater the variety of products that can be offered. Cosmeticians divide skins into:

normal—although 90 percent of children have this ideal skin, very few adults can boast of a skin that is smooth, soft, moist, and of healthy appearance

oily—shiny, with enlarged pores, a tendency to blemishes and coarse texture, and sometimes a flakiness due to the accumulation of dried out oils

dry—fine textured, flaky and taut, expression lines around eyes, mouth, and throat, with ageing loses elasticity and develops pronounced wrinkles

combination—areas of both dryness and oiliness

sensitive—florid, with tiny broken capillaries, usually fine textured and with many of the characteristics of dry skin (a rather different definition from that used by dermatologists)

blemished—excessively oily, with blemishes such as pimples and blackheads.

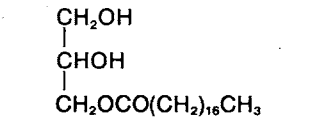
Ageing

With age the skin loses its elasticity and becomes thinner and drier; folds appear and wrinkles fail to vanish. Sometimes colour changes occur. The process is universal and irreversible, yet there are some people who look younger at fifty than others do at forty. Although ageing is partly determined by factors such as heredity, dermatological research has shown that exposure to sunlight, i.e. to ultraviolet light, makes an important contribution. This is evidenced by the sometimes striking contrast between the leathery skin that is normally exposed and the soft smooth skin that is usually covered, especially of outdoor workers and elderly people. Persistent and repeated exposure to sunlight is also a factor in skin cancer—the incidence of skin cancer is much higher in Australia than in Britain for people of comparable heredity.

The most obvious signs of ageing are wrinkles. Their cause is not known, but it is probable that they are the result of changes in the dermis or in the subcutaneous tissue—the dermis becomes thinner and less elastic, and the sebaceous glands are less active, leading to dryness.

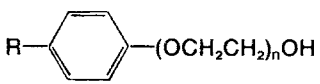
Emulsions[2,3]

The basis of most cosmetic products is an *emulsion*, which is the combination of two materials that do not normally dissolve in each other; because they do not mix the components are called phases. The emulsion system provides a convenient means of applying both an oily material and water simultaneously to the skin and hair.



glycerol monostearate

a 'fat' with two of the fatty acids missing; a *mono*glyceride.



polyoxyethylene alkyl phenol

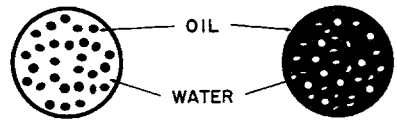
a non-ionic detergent
e.g. triton X-100, teric X10

4.1 Typical emulsifiers used in cosmetics

In order to allow oil and water to form as emulsion an *emulsifier* must be added. The purpose of the emulsifier is to reduce the difference in surface tension (i.e. the mutual repulsion) between the two phases—for example, in

making mayonnaise from oil and vinegar, egg yolk acts as an emulsifier. The emulsifiers reduce the interfacial tension between the two immiscible phases, i.e. they allow the oil and water to 'wet' each other.

The selection of the correct emulsifier is very critical. Emulsifiers are characterised on a scale called HLB, the Hydrophilic–Lipophilic Balance (hydrophilic = water loving; lipophilic = oil loving); in this system the relative affinity of an emulsifier for the oil phase is expressed as a number ranging from 1 to 20. Propylene glycol monostearate has a low HLB number—it is more at home in the oil phase, while polyoxyethylene monostearate $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nH$ which has a long polyoxyethylene chain with lots of polar oxygen atoms, has a high HLB value and is quite at home in water. In general, emulsifiers with HLB value of 3–6 will produce emulsions of water dispersed in oil, while HLB values of 7–17 give emulsions of oil in water. Cosmetic emulsions can be either dispersions of oil in water—o/w—or water in oil—w/o—see Figure 4.2.



4.2 Oil in water and water in oil emulsions

The effect of the two different types of emulsions is quite different. Water evaporates from an o/w emulsion and this causes cooling and leaves a film of the oily ingredients, e.g. oils, waxes, emulsifiers, humectants, etc. On the other hand a w/o emulsion permits direct immediate contact of the oil phase with the skin. No cooling effects occur because of the evaporation of the emulsified water is much more gradual. These are 'warm' emulsions in the sense of their apparent effect on skin temperature. As most cosmetic ingredients (perfume etc.) are in the oil phases, there are greater formulating difficulties for w/o systems than in o/w types. The minimum concentration of the outer phase must be at least 26 percent. (How does this value arise?)

In an emulsion, the finer the particle size the more stable is the emulsion and the higher is the *viscosity* (resistance to flow—low viscosity = runniness). Large particle size increases the tendency for the particles to coalesce and hence finally for the emulsion to separate into the two phases.

The easiest way to test for which type of emulsion is present is based on the fact that most oils have a much higher electrical resistance than aqueous solutions.[4] The w/o type are relatively non-conducting compared to the o/w. A simple resistance meter is often all that is required for this test or else a neon glow lamp and two electrodes can be used with a mains supply. Another test is to use an oil-soluble dye, e.g. fuchsin, which will spread and colour the surface only if the oil is in the continuous phase (i.e. w/o). Conversely

water-soluble dyes, e.g. food colours or methyl orange, will colour only o/w emulsions. Oil/water emulsions are used in 'vanishing creams' to assist penetration into the skin and to conceal the oily nature of the preparation.

Skin Care Cosmetics

Moisturisers

Moisturisers are preparations which replace water lost from the skin, and both o/w and w/o emulsion types are used. The dryness and reduced flexibility of the skin cannot be corrected by adding oily materials, but the skin will become more flexible when water is replaced, even in the absence of oily vehicles. The skin can be protected and skin dryness prevented or relieved by emollient creams and lotions, which slow the evaporation of water from the outer layer of the skin. Detergents cause dry and chapped skin because they dissolve away some of the water-attracting components of the skin, which are reduced in concentration anyway with increasing age.[2,5,6]

Cleansing creams and lotions

Even though adequate washings with soap and soft water will achieve the same result, there are possible advantages in using a cleansing cream for the removal of facial make-up, surface grime, and oil from the face and throat. The specific chemical design of a cleansing cream allows it to dissolve or lift away more easily the greasy binding materials that hold pigments and grime on the skin. Although physically a cold cream has heavier body and application, most emulsified cleansing creams can be considered as cold creams which have been modified to enhance their ability to remove make-up and grime.[2,7]

The increased use of eye cosmetics has created a need for a means of removal. Mineral oil, alone, is a safe effective agent.

Cleansers for oily skin

For the usual type of oily skin where there is no associated acne, the use of ethyl alcohol or isopropyl alcohol can provide a temporary relief from excessive oil flow and the resulting shiny skin. The concentration of alcohol should not exceed 60 percent and preferably should be below 50 percent, otherwise it could be too drying or irritating. Other modifying ingredients should also be included in the formula to balance the harshness of the alcohol.[2]

Toothpaste

In toothpaste a solid phase (a polishing agent or blend of agents) is suspended

in aqueous glycerol, sorbitol, or propylene glycol (all polyalcohols) by means of a suspending agent, e.g. sodium carboxymethyl cellulose (see Chapter 2). (A similar philosophy is used in the 'froth flotation' method of separating finely ground minerals of lead and zinc ores.) The mixing is done in a vacuum to avoid unpleasant effects on appearance and consistency of the resulting paste. Air bubbles can also lead to undesirable deterioration in flavour. If the emulsion is destroyed (the enzyme cellulase can degrade cellulose products) the product becomes watery. A few percent of anionic detergent (sodium lauryl sulphate) is added as a foaming agent.

Because of consumer concern about the abrasive action of toothpaste, the abrasive is 'hidden' in the translucent toothpastes by an optical 'illusion'. If the abrasive and the surrounding medium have approximately the same *refractive index* (ability to bend light rays—e.g. high in diamond but lower in glass and water) then the solid will not scatter light and so not appear white but remain translucent.

Baby Care Products[2,8]

The skin of a baby is much less effective as a barrier than that of older children (from age 3) and of adults. Because it is thinner and softer and contains more water, material can pass through it both ways more easily. Because of the concentration of moisture and soil in the nappy area, bacteria breed quickly and irritants remain in contact with the skin. This is the major cause of nappy rash. In 1921 it was proved conclusively that ammonia, liberated from urinary urea by the action of an enzyme present in a bacterium (*Bacillus ammoniagenes*) inhabiting the colon, was a cause of nappy rash:

$$(NH_2)_2CO + 2H_2O \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2$$

These bacteria are present in the faeces under normal conditions. When the intestinal contents are of a low acidity, the number of such organisms is greatly increased, and consequently the nappy region becomes infected with the bacteria. They grow most rapidly on the skin and in the nappy under neutral to alkaline conditions, whereas there is practically no growth at pH 6. Other bacterial organisms act similarly on urea.

Nappy rash can be a frightening condition to a young mother. It happens only rarely during the baby's first months but later it can be very severe. Fortunately in most cases nappy rash responds readily to treatment but it can persist or occur again. To avoid the problem the following rules should be obeyed:[9]

1. Plastic pants are great from mum's point of view—but they also suit the bacteria which form the ammonia and the nappy rash—so they generally make things worse.
2. The more often nappies are changed obviously the less the problem will

be. The skin should be bathed with water in between. Do not wipe it with the unsoiled part of the nappy. Pat dry with a fresh towel or nappy.

3. After scraping off the nappies, launder in *hot* water (above 60°C) in which most of the relevant bacteria will not survive.
4. Rinse nappies *very* thoroughly to remove all chemicals—the (cationic) nappy washes do give softer nappies but their bacteria killing ability in *practice* has been disputed in *Choice* (vol. 16, no. 2, 1975).
5. Sun drying is far preferable to other methods because of the sanitising effect of sunlight.

Manufacturers provide nappy conditioners, nappy sterilisers, nappy washes, etc., to assist in combating the condition. Some claim to sterilise, others to sanitise, some to soften. The compositions of two typical nappy sanitisers are given in Table 4.1. These are approximate ingredients only, true at the time of analysis.

TABLE 4.1

Napisan	*Nursil*
sodium tripolyphosphate (see Chapter 2) sodium chloride(common salt) potassium persulphate surfactant fluorescers	sodium perborate sodium tripolyphosphate sodium bicarbonate sodium chloride surfactant optical brightener, perfume and paraffin
This product operates on the principal that potassium persulphate and salt are stable as a mixed powder but on dissolving in water react to form chlorine bleach, which is constantly generated.	This is similar to a built laundry detergent but with extra perborate bleach and less surfactant.

The complete nappy treatments were all found to be totally ineffective in the laboratory tests reported by *Choice*. The easy-to-kill golden staph (*Staphylococcus aureus*) were demolished, but tougher bugs such as *Pseudomonas aeruginosa*, which is often used to test disinfectants, survived quite nicely. On the other hand the nappy softeners (cationic detergents added in the final rinse) while not being very effective as bacteria destroyers, do remain absorbed on the nappy and when the nappy is used next time they may inhibit the bacteria from forming ammonia in the wet nappy.

The standard commercial disposable nappy consists of two main components: highly absorbent pulp on the inside and an outer cover of non-woven fabric. Washable nappy liners generally consist of a fabric measuring 15×40 cm,

specifically knitted, not woven, from a specially prepared type of polypropylene yarn (see Chapter 6). The non-absorbency and water repellency of the polyolefin accelerates the absorbent action of the cotton nappy, draining the urine through the interstices of the knitted plastic.

Baby oils are generally based on a mineral oil. They may also contain some vegetable oil, lanolin, antioxidants, and germicides. Products such as pH-iso-Derm are emulsions and lather like soap. Their pH is slightly acid to match that of the skin. pH-iso-Hex contains hexachlorophene which is no longer recommended for continuous use on infants since a large number of babies died when a sample talc used in France had a many-fold excess of this material included by mistake. It is difficult to ascertain from the technical literature just how baby cosmetics actually differ from those made for adults.

The United States FDA announced that all labels affixed to cosmetic and toiletry products after April 15 1977 must list the ingredients in descending order of predominance. The ingredient list will permit shoppers to make comparisons and will help consumers avoid ingredients to which they are allergic or sensitive.

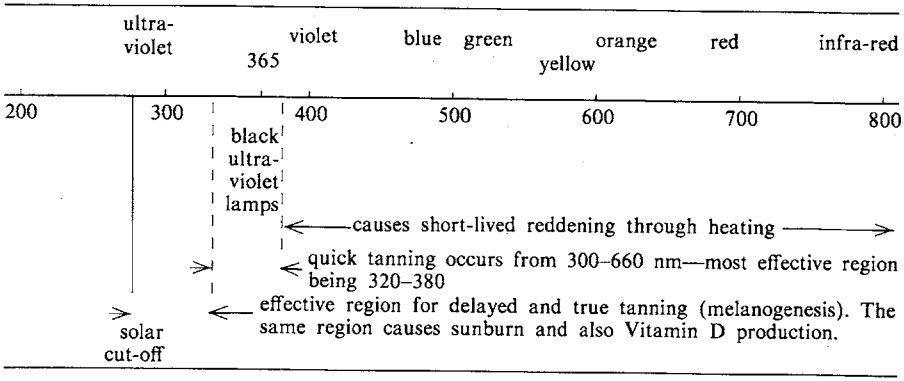
Sunscreens[2,10]

The sun irradiates the surface of the earth in the wavelength range from 290 nm (nanometres—1nm=10^{-9}m) in the ultraviolet through the visible into the infra-red or heat end of the spectrum. The amount of ultraviolet radiation reaching us is limited by its absorption by ozone in the upper atmosphere. Hence the concern about the emissions from supersonic high flying commercial and military aircraft and the effects of fluorocarbon propellants in aerosols as to their possible role in destroying the ozone layer.

> Ultraviolet light damages the hereditary material in the cell (DNA) by causing two pyrimidine bases, usually, but not always, on the same strand, to become covalently linked as a dimer. In ultraviolet-sensitive bacteria this linkage inhibits DNA replication and thereby stops further growth. It appears that normal human skin cells have an enzyme system for the repair of ultraviolet damage which excises the dimers and repairs the gap. A rare genetic disease where this enzyme is lacking makes its sufferers very liable to skin cancer.

The natural skin colour of man evolved to match the intensity of sunlight according to the region of the earth that he inhabited. However, with migration and colonisation, this neat balance has been upset and Caucasians in hot climates suffer from sunburn and increased skin cancer while Negroes in cold climates

have problems caused by insufficient vitamin D synthesis in the skin. Tanning is the negative feedback system developed by nature to control the level of sunlight activity on the skin. On exposure to sunlight the ultraviolet rays cause a pigment in the skin, melanin, to darken at the surface. More melanin is produced in the lower layer and this darkens and moves to the surface. The skin also tends to thicken. The processes of tanning, sunburn, and vitamin D production are closely linked, as a glance at the diagram below shows.



Sunlight in the wavelength range 300–660 nm gives a quick tan through the darkening of the melanin already at the surface of the skin; this is a photochemical process and occurs in corpses as well as in living people. The colour reaches a maximum about one hour after exposure and usually begins to fade within two or three hours after exposure. In the more restricted range of the ultraviolet 290–320 nm, delayed tanning is initiated in which the lower-lying melanin is oxidised (and hence darkened) and migrates to the surface, and this shows up between one and several days later. The actual formation of new melanin is also triggered by sunlight in this restricted range and starts about two days after exposure and reaches a maximum after two or three weeks. This particular wavelength range is the active one for sunburn, for triggering skin cancer, and for vitamin D production in the skin—which takes place through a photochemical reaction.

It follows that, except for the immediate short-lived tanning response, it is not possible to screen selectively for true tanning while protecting against sunburn and susceptibility towards skin cancer. Pigmentation requires preceding sunburn (which can be kept at a low level) to trigger the process. Sunscreens are used to lower the dose of light received by the skin to the point where tanning has a chance to catch up. The amount by which the dose must be lowered will depend on the intensity of the light and the susceptibility of the skin. Sunscreens which are formulated to give a quick tanning response but to supress sunburn (and true tanning) will absorb more strongly in the

290–320 nm range than in the longer wavelength range. This can be checked through measuring an absorption spectrum; for the suppression of sunburn it is only the absorption in the 290–320 range which is of interest. Table 4.2 gives some results, and reveals that the *p*-aminobenzoates show an optimum rate of quick tanning transmission and sunburn suppression. Sunscreens have been reviewed by the United States Food and Drug Administration Over the Counter (FDA–OTC) Review Panel with respect to safety and effectiveness. Among those accepted are those in Table 4.2.

TABLE 4.2 *Tanning range transmission of commercial sunscreening compounds*

Sunscreen	Percentage of screen required to reduce sunburn transmission to 7%	Percentage quick tanning transmission of such a screen
A. *p*-(dimethyl)-aminobenzoates (PABA) derivatives	2.0	87.0
B. isoamyl and amyl *N,N*-dimethyl *p*-aminobenzoate (Escalol 506)	1.3	71.0
C. phenyl salicylates	11.0	68.0
D. 2-ethoxyethyl *p*-methoxycinnamate (Giv-tan F)	1.4	51.0

Some examples of sunscreens with these active ingredients

Pabafilm:	B—2.5%	Phiasol A.S. lotion:	B—n.a.
Pabagel:	A—5.0% (dimethyl)	UV filter cream:	D—5.0%
Phiasol:	D—1.5%	UV filter lotion:	D—3.6%
UVosan:	B—25 %	UVistick:	A—2.0% (methyl ester) C—5.0%

Sources: See references 2 and 11

Of interest is the fact that glass does not transmit much light with wavelength below 350 nm—all that happens to skin behind a glass window is reddening due to heating. Perspex on the other hand does transmit light with shorter wavelengths. It is also important to take reflected light into account. Typical reflection values for 300 nm radiation from specific surfaces are: snow 0.85, dry sand 0.17, water 0.05, grass 0.025.

A unit that is used to measure the time-intensity of exposure is the MED —minimum erythemal dose—the time of exposure to a particular source required to produce reddening after six hours and which is still visible after twenty-four hours (on a standard white untanned skin).[2] Thus if the MED turns out to be fifteen minutes in the middle of a summer's day then a suntan preparation which reduces the intensity of the radiation by four or eight times will increase the time of exposure for MED to one or two hours.

There are many parameters which are important in a sunscreen. The ability to absorb or reflect radiation is perhaps the easiest parameter to measure and is quoted in Appendix 4.3 for a large number of commercial products. A sunscreen must be chemically and photochemically stable otherwise its absorption ability changes with time. It must be soluble in the cosmetic base but insoluble in water or perspiration. The present (1977) breed of compounds, given in Table 4.2, are modified versions of older compounds which reacted with and stained fabrics and towels. The self-plasticising properties of commercial compound A allow the formation of a continuous plastic layer on the skin. The benzophenones are optically more efficient than the aminobenzoates—i.e. they screen against sunburn more efficiently—but they crystallise easily and hence do not form a film and adhere so well to the skin.

> The story is told of Alexander the Great that he made use of the fact that some colours are photochemically unstable and bleach rapidly in sunlight. Because his commanders didn't have watches to synchronise their attacks, he gave them bleachable coloured rags to put around their arms so they could measure time during the day. Thus came into being Alexander's rag time-band.

Another problem is absorption of chemicals through the skin. Solutions containing some benzoate or salicylates (~5 percent) can be detected within thirty minutes in the urine. For those avoiding salicylates in food (see Chapter 12), absorption from sunscreens must also be avoided.

Evaluation of Screening

The amount of light which a material will let through (at a given wavelength) depends on the thickness of the layer of material, d cm, the concentration of the materials, c g per litre, and a property of the material called the absorption coefficient, a. The relationship between the light transmitted I, and the light falling on the surface I_o, is given by an expression called Beer's Law:

$$\log \frac{I}{I_o} = -a.c.d$$

Note the logarithmic relation. The percentage transmission (% T) given in the table in Appendix 4.3 is related to Beer's Law by

$$\frac{I}{I_o} = 0.01 \times [\%T].$$

Thus a 1 percent transmission requires I/I_o to be 0.01, log $I/I_o = -2$ and *a.c.d.* $= +2$. For a thickness of 0.01 mm, *a.c* $= 2000$. Thus knowing the characteristic value of a for a material allows c, the necessary concentration, to be determined. Because the relationship is logarithmic a 0.1 percent transmission requires not 10 times the concentration but 1½ times, while halving the concentration increases the transmission to 10 percent. What we have said about concentration is equally applicable to path length (thickness), d—these two parameters occupy equivalent positions in the equation. The percentage of light transmitted grows and falls exponentially with both variables. It should be remembered that in actual use the volatile material in a sunscreen is lost and the residual film on the skin is composed of the non-volatile film components mixed with skin secretions.

Actual patch testing on skin exposed to sunlight could be expected to be a much more realistic approach than simply using the figures given in Appendix 4.3. Areas of the back or abdomen are best, and should not have been recently exposed to sunlight. Adhesive tape can be used to delineate the field, or aluminium foil with holes 2 cm in cross-section. Great care must be taken to standardise the method of application to ensure equal thickness. The effect of swimming can be ascertained—a short swim removes at least 90 percent of sunscreen from the skin, more or less independent of the nature of the product.[10]

There are few other cosmetic preparations which are used as extensively as sunscreens and which cover such a large area of skin. If one estimates the total skin area of an adult (which is about the same as the area to be covered) to be about a square metre and uses a sunscreen lotion with an active concentration of 1.5 percent, then it will deposit about 0.3 gram on the square metre. This increases to 2.2 grams for an 11 percent active ingredient screen.[2]

Photo-allergies

The Adelaide dermatologist, Dr J.N. Burry, has published numerous papers on photocontact dermatitis.[12] This form of dermatitis occurs in those areas which are exposed to sunlight, such as the face, neck and hands. Tribromosalicylanilide (TBS) has been used as an antiseptic in soap in Australia since 1964 and cases of photosensitivity have been recognised since 1967. This material can cross-react with other antiseptics, including hexachlorophene. This is perhaps not really surprising since a study of the properties of photochromic materials (chemicals which change colour reversibly on

exposure to light because they undergo a simple reaction) have shown that the halogenated salicylanilides (see Appendix 4.2, Annex 11, Nos. 348-51) are a particularly effective set of compounds! They can, however, be modified so as to be inert in sunlight.

LEGAL ASPECTS

New South Wales seems to have more advanced legislation controlling therapeutic goods and cosmetics than the other states. The Therapeutic Goods and Cosmetics Act, 1972 and the regulations thereto allow scope to regulate the manufacture, sale, and advertising of cosmetics, although these powers have yet to be exercised to any noticeable extent. *Therapeutic use* is defined but *cosmetic use* is not and reliance is placed upon dictionary meaning or everyday usage or, as a last resort, the Minister of Health can issue an Order declaring that goods are or are not therapeutic or cosmetic.

Goods declared to be therapeutic substances include: acne treatment preparations; antiperspirants; antiseptics and disinfectants; contact lens cleaning and soaking solutions; dandruff treatment preparations; fluoride toothpaste containing more than 0.5 percent fluoride ion; medicated dressings; medicated shampoos; medicated soaps; overweight preparations; sunburn treatment preparations; throat lozenges; and vitamin preparations other than food.

Goods declared to be cosmetics include: deodorant preparations for dermal application; hair dyes and colourants; mouthwashes for which cleaning or refreshing claims *only* are made (if more, the product is classed as a therapeutic); moisturisers; soaps other than medicated soaps; suntanning and sunscreening preparations; toothpastes (unless fluoride ion content exceeds 0.5 percent).

In 1977 the Standards Association of Australia set up a committee (CS 42) to develop standards for sunscreens.

APPENDIX 4.1

ESTIMATED U.S. PRODUCTION OF MAJOR COSMETICS AND TOILETRIES (1968 AND 1971)

	Million lb.		Avg. increase
	1968	1971	Percent per year
Toilet soaps	550	600	2.8
Women's hair sprays	350	420	6.3
Mouthwashes	200	250	4.8
Dentrifices	150	175	5.2
Shampoos	125	160	8.6
Face creams	100	130	9.2
Deodorants	60	95	16.4
Shaving creams	43	50	5.0
Hand lotions and creams	40	45	4.0
Shaving lotions and colognes	36	58	10.0
Baby powder	40	45	4.0
Hair colourings	35	40	4.5
Men's hair dressings	29	30	1.5
Men's hair sprays	—	30	—
Denture products	20	25	7.6
Talcum powder	15	17	4.2
Cream rinses	13	17	9.5
Face powder	13	14	2.5
Women's fragrances	8	11	11.2
Women's hair dressings	7	10	12.7
Suntan preparations	7	10	12.7
Bath oils and salts	6	9	14.6
Nail and cuticle removers	8	9	4.0
Makeup bases	6	7	5.2
Feminine hygiene sprays	—	7	—
Permanent wave kits	6	5	(9.4)
Lipstick	4	5	7.5
Nail polish	4	5	7.5
Eye products	1	2	26.0
Depilatories and other	3	4	10.0
Total	1879	2285	6.7

ROUGHLY ESTIMATED U.S. SALES OF PRINCIPAL COSMETIC RAW MATERIALS IN 1971

	Millions of Dollars
Perfume oils	$170
Fluorocarbon propellants	90
Tallow	40
Coconut oil	30
Alcohol, denatured	25
Surfactants	25
Flavours	15
Glycerine	15
Mineral oil	10
Fatty acids	10
Fatty esters	8
Sorbitol	8
Antiperspirants	7
Bacteriostats	7
Calcium phosphates	7
Dyes	7
Hair polymers—proteins	7
Lanolin and derivatives	5
Caustic soda	4
Pigments	4
Thickeners and gums	4
Sunscreen agents	2
Talc	2
Thioglycolic acid and salts	2
Miscellaneous inorganic chemicals	4
Miscellaneous organic chemicals	7
All other materials	5
Total	$520

Source: The President's Science Advisory Committee. *Chemicals and Health.* Science and Technology Policy Office, National Science Foundation. September 1973, p.75.

APPENDIX 4.2

European Economic Community—Council Directive 27 July 1976

on the approximation of the laws of the Member States relating to cosmetic products (76/768/EEC).

ANNEX I

Illustrative list by category of cosmetic products.

Creams, emulsions, lotions, gels, and oils for the skin (hands, face, feet, etc.)
Face masks (with the exception of peeling products)
Tinted bases (liquids, pastes, powders)
Make-up powders, after-bath powders, hygienic powders, etc.
Toilet soaps, deodorant soaps, etc.
Perfumes, toilet waters, and eau de Cologne
Bath and shower preparations (salts, foams, oils, gels, etc.)
Depilatories
Deodorants and antiperspirants
Hair care products:
- hair tints and bleaches
- products for waving, straightening, and fixing
- setting products
- cleansing products (lotions, powders, shampoos)
- conditioning products (lotions, creams, oils)
- hairdressing products (lotions, lacquers, brilliantines)

Shaving products (creams, foams, lotions, etc.)
Products for making up and removing make-up from the face and the eyes
Products intended for application to the lips
Products for care of the teeth and the mouth
Products for nail care and make-up
Products for external intimate hygiene
Sunbathing products
Products for tanning without sun
Skin-whitening products
Antiwrinkle products

ANNEX II

List of substances which cosmetics products must not contain (compared here to those covered by Australian NHMRC Poison Schedules)

LIST OF SUBSTANCES WHICH COSMETIC PRODUCTS MUST NOT CONTAIN

		NHMRC Schedule (1976)
1.	N-5-Chlorobenzoxazol-2-ylacetamide	
2.	β-Acetoxyethyl trimethyl ammonium hydroxide (acetylcholine and its salts)	S4
3.	Deanol aceglumate*	S4—Deanol
4.	Spironolactone*	S4
5.	[4-(4-Hydroxy-3-iodophenoxy)-3,5-diiodopheny1] acetic acid and its salts	
6.	Methotrexate*	
7.	Aminocaproic acid* and its salts	
8.	Cinchophen*, its salts, derivatives and salts of these derivatives	
9.	Thyropropic acid* and its salts	
10.	Trichloroacetic acid	
11.	*Aconitum napellus L.*, (leaves, roots, and galenical preparations)	S1—Aconite (roots of *Aconitum napellus*)
12.	Aconitine (principal alkaloid of *Aconitum Napellus L.*) and its salts	S1
13.	*Adonis vernalis L.* and its preparations	
14.	Epinephrine*	
15.	*Rauwolfia serpentina*, alkaloids and their salts	S4
16.	Alkyne alcohols, their esters, ethers, and salts	
17.	Isoprenaline*	S3
18.	Allyl isothiocyanate	
19.	Alloclamide* and its salts	
20.	Nalorphine*, its salts and ethers	
21.	Sympathicomimetic amines acting on the central nervous system: any substance contained in the first list of medicaments which are subject to medical prescription and are referred to in resolution AP(69) 2 of the Council of Europe	
22.	Aniline, its salts, and its halogenated and sulphonated derivatives.	S6—excluding its salts and derivatives—1% ≤ of aniline
23.	Betoxycaine* and its salts	
24.	Zoxazolamine*	
25.	Procainamide*, its salts and derivatives	S4 (alone)
26.	Benzidine	
27.	Tuaminoheptane*, its isomers and salts	
28.	Octodrine* and its salts	
29.	2-Amino-1,2-bis(4-methoxyphenyl)ethanol and its salts	
30.	1,3-Dimethylpentylamine and its salts	

*In this Directive, names followed by an asterisk are those published in Computer printout 1975 International Non-proprietary Names (INN) for pharmaceutical products, Lists 1-33 of proposed INN, WHO, Geneva, August 1975.

NHMRC Schedule (1976)

31.	4-Aminosalicyclic acid and its salts	
32.	Toluidines, their isomers, salts, and halogenated and sulphonated derivatives	
33.	Xylidines, their isomers, salts, and halogenated and sulphonated derivatives	
34.	Imperatorin (9-(3-methoxylbut-2-enyloxy)furo-[3,2-g] chromen-7-one)	
35.	*Ammi majus* and its galenical preparations	
36.	2,3-Dichloro-2-methylbutane	
37.	Substances with androgenic effect	
38.	Anthracene oil	
39.	Antibiotics, with the exception of that given in Annex IV	
40.	Antimony and its compounds	S1 and S2 (S4 organic preps)
41.	*Apocynum cannabinum L.* and its preparations	
42.	Apomorphine (5,6,6a,7-tetrahydro-6-methyl-4H-dibenzo[de,g] = quinoline-10,11-dihydric alcohol) and its salts	S3 alone
43.	Arsenic and its compounds	S4 org. compounds for therapeutic use (S5 ⩽ 3% arsenic)
44.	*Atropa Belladonna L.* and its preparations	Belladonna S1 and S2
45.	Atropine, its salts and derivatives	S1 and S2 (Atropine methonitrate S4) (Atropine sulphate S6 0.5mg tablets)
46.	Barium salts with the exception of barium sulphate lakes prepared from barium sulphate and pigments prepared from the colouring agents listed in Annex III, Part 2 and Annex IV, Parts 2 and 3 and marked Ba	(Ba silicofluoride S5) (Barium salts S6)
47.	Benzene	S7 (1% v/v)
48.	4,5-Dihydrobenzimidazol-4-one	
49.	Benzazepines and benzadiazepines, their salts and derivatives	
50.	1-Dimethylaminomethyl-1 methylpropyl benzoate and its salts (amylocaine)	
51.	2,2,6-Trimethyl-4-piperidyl benzoate and its salts (benzamine)	
52.	Isocarboxazide*	
53.	Bendroflumethiazide* and its derivatives	
54.	Beryllium and its compounds	S6 (alone)
55.	Bromine, elemental	S1
56.	Bretylium tosilate*	Bretylium S4
57.	Carbromal*	S4
58.	Bromisoval*	
59.	Brompheniramine* and its salts	Bromodiphenhydramine S4
60.	Benzilonium bromide*	Benzilonium S4
61.	Tetrylammonium bromide*	
62.	Brucine	S1 except where <0.2% & S2
63.	Tetracaine* and its salts	
64.	Mofebutazone*	
65.	Tolbutamide*	S4
66.	Carbutamide*	
67.	Phenylbutazone*	S4
68.	Cadmium and its compounds	Cd sulphide S5 ⩽ 2.5% & S6
69.	Cantharides, *Cantharis vesicatoria*	Cantharidin S2 ⩽ 0.01% & S4

		NHMRC Schedule (1976)
70.	(IR,2S)-Hexahydro-1,2-dimethyl-3,6-epoxyphthalic anhydride (cantharidin)	S2/S4
71.	Phenprobamate*	
72.	Nitroderivatives of carbazol	
73.	Carbon disulphide	S6
74.	Catalase	
75.	Cephaeline and its salts	
76.	*Chenopodium ambrosioides* (essential oil)	
77.	2,2,2-Trichloroethane-1,1-diol	
78.	Chlorine	S7
79.	Chlorpropamide*	S4
80.	Diphenoxylate* (hydrochloride)	S4
81.	4-Phenylazophenylene-1,3-diamine citrate hydrochloride (chrysoidine citrate hydrochloride)	
82.	Chlorzoxazone*	S4
83.	2-Chloro-6-methylpyrimidin-4-yldimethylamine (crimidine-ISO)	
84.	Chlorprothixene* and its salts	
85.	Clofenamide*	S4
86	*N,N*-bis (2-chloroethyl)methylamine *N*-oxide and its salts	
87.	Chlormethine* and its salts	
88.	Cyclophosphamide* and its salts	
89.	Mannomustine* and its salts	
90.	Butanilicaine* and its salts	
91.	Chloromezanone*	S4
92.	Triparanol*	
93.	2-[2(4-Chlorophenyl)-2-phenylacetyl]indane-1,3-dione (chlorophacinone-ISO)	S6
94.	Chlorphenoxamine*	S4
95.	Phenagylcodol*	
96.	Chloroethane	
97.	Chromium; chromic acid and its salts	S6 Chromates and dichromates
98.	*Claviceps purpurea Tul.*, its alkaloids and galenical preparations	
99.	*Conium maculatum L.* (fruit, powder, galenical preparations)	
100.	Glycyclamide*	
101.	Cobalt benzenesulphonate	
102.	Colchicine, its salts and derivatives	S1 (alone $\leqslant$ 0.5%)/S2
103.	Colchicoside and its derivatives	
104.	*Colchicum autuminale L.* and its galenical preparations	
105.	Convallatoxin	
106.	*Anamirta cocculus L.* (fruit)	
107.	*Croton Tiglium* (oil)	S1
108.	1-Butyl-3-(*N*-crotonoylsulphanilyl)urea	
109.	Curare and curarine	S4
110.	Synthetic curarizants	
111.	Hydrogen cyanide and its salts	S1/S2
112.	2-*a*-Cyclohexylbenzyl(*N,N,N'N'*-tetraethyl)trimethylenediamine (phenetamine)	
113.	Cyclomenol* and its salts	
114.	Sodium hexacyclonate*	
115.	Hexapropymate*	
116.	Dextropropoxyphene*	S2/S4
117.	*O,O*-Diacetyl-*N*-allyl-*N*-normorphine	

NHMRC Schedule (1976)

118.	Pipazetate* and its salts	
119.	5-(α,β-dibromo-phenethyl)-5-methylhydantoin	
120.	*N,N*-Pentamethylenebis (trimethylammonium salts), e.g. Pentamethonium bromide*	Pentamethonium S4
121.	*N,N'*-[Methylimino) diethylene] bis-(ethyldimethyl-ammonium) salts, e.g. azamethonium bromide*	
122.	Cyclarbamate*	
123.	Clofenotane*; DDT (ISO)	
124.	Hexamethylenebis (trimethylammonium salts) e.g. hexamethonium bromide*	Hexamethonium S4
125.	Dichloroethanes (ethylene chlorides)	ethylene dichlorides S6
126.	Dichloroethylenes (acetylene chlorides)	
127.	Lysergide* and its salts	S7
128.	2-Diethylaminoethyl-3-hydroxy-4-phenylbenzoate and its salts	
129.	Cinchocaine* and its salts	
130.	3-Diethylaminopropyl cinnamate	
131.	*O,O*-Diethyl *O*-4-nitrophenyl phosphorothioate (parathion-ISO)	S7
132.	[Oxalybis(iminoethylene)]bis[*o*-chlorobenzyl) diethylammonium salts], e.g. ambenomium chloride*	Ambenomium S4
133.	Methyprylon* and its salts	S4
134.	Digitaline and all heterosides of *Digitalis purpurea L*	S4
135.	7-[2-Hydroxy-3-(2-hydroxyethyl-*N*-methylamino) propyl]theophylline (xanthinol)	Xanthinol nicotinate S4
136.	Dioxethedrin* and its salts	
137.	Piprocurarium*	
138.	Propyphenazone*	S3
139.	Tetrabenazine* and its salts	
140.	Captodiame*	S4
141.	Mefeclorazine* and its salts	
142.	Dimethylamine	S2
143.	1,1-Bis(dimethylaminomethyl)propyl benzoate and its salts (amydricaine, alypine)	
144.	Methapyrilene* and its salts	S3/S4
145.	Metamfepramone* and its salts	
146.	Amitriptyline* and its salts	S4
147.	Metformin* and its salts	S4
148.	Isosorbide dinitrate*	
149.	Malononitrile	
150.	Succinonitrile	
151.	Dinitrophenol isomers	S4
152.	Inproquone*	
153.	Dimevamide* and its salts	
154.	Diphenylpyraline* and its salts	S4
155.	Sulfinpyrazone*	S4
156.	*N*-(3-Carbamoyl-3, 3-diphenylpropyl)-*N,N*-disiopropylmethylammonium salts, e.g. isopropamide iodide*	S4 Isopropamide
157.	Benzactyzine*	S4
158.	Benzatropine* and its salts	
159.	Cyclizine* and its salts	S4 Cyclizine
160.	5,5-Diphenyl-4 imidazolidone	
161.	Probenecid*	S4

		NHMRC Schedule (1976)
162.	Disulfiram*; thiram (ISO)	Disulfiram except for therapeutic use S6/thiram S6
163.	Emetine, its salts and derivatives	S4
164.	Ephedrine and its salts	S3
165.	Oxanamide* and its derivatives	
166.	Eserine or physostigmine and its salts	
167.	Esters of 4-aminobenzoic acid, with the free amino group, with the exception of that given in Annex IV, Part 1	
168.	Choline salts and their esters, e.g. choline chloride	
169.	Caramiphen* and its salts	S4
170.	Diethyl 4-nitrophenyl phosphate	
171.	Metethoheptazine* and its salts	
172.	Oxpheneridine* and its salts	
173.	Ethoheptazine* and its salts	S2/S4
174.	Metheptazine* and its salts	
175.	Methylphenidate* and its salts	S8 (alone)
176.	Doxylamine* and its salts	S4
177.	Tolboxane*	
178.	Monobenzone*	S4
179.	Parethoxycaine* and its salts	
180.	Fenozolone*	
181.	Glutethimide* and its salts	S4 (alone)
182.	Ethylene oxide	S6
183.	Bemegride* and its salts	S4 (alone)
184.	Valnoctamide*	S4
185.	Haloperidol*	S4
186.	Paramethasone*	
187.	Fluanisone*	
188.	Trifluperidol*	
189.	Fluoresone*	
190.	Fluorouracil*	S4
191.	Hydrofluoric acid, its normal salts, its complexes and hydrofluorides with the exception of those given in Annex IV, Part 1	S6
192.	Furfuryltrimethylammonium salts, e.g. furtrethonium iodide*	
193.	Galantamine*	S4
194.	Progestogens, with the exceptions of those listed in Annex V	
195.	1,2,3,4,5,6-Hexachlorocyclohexane (BHC-ISO)	S6
196.	(1*R*,4*S*,5*R*,8*S*)-1,2,3,4,10,10-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4:5,8-dimethanonaphthalene (endrin-ISO)	
197.	Hexachloroethane	
198.	(1*R*,4*S*,5*R*,8*S*)-1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene (isodrin-ISO)	
199.	Hydrastine, hydrastinine and their salts	
200.	Hydrazides and their salts	
201.	Hydrazine, its derivatives and their salts	
202.	Octamoxin* and its salts	
203.	Warfarin* and its salts	Except for therapeutic use S6
204.	Ethyl bis(4-hydroxy-2-oxo-1-benzopyran-3-yl) acetate and salts of the acid	
205.	Methocarbamol*	S4

		NHMRC Schedule (1976)
206.	Propatylnitrate*	
207.	4,4′-Dihydroxy-3,3′-(3-methylthiopropylidene) dicoumarin	
208.	Fenadiazole*	
209.	Nitroxoline* and its salts	
210.	Hyoscyamine, its salts and derivatives	S1
211.	*Hyoscyamus niger L.* (leaves, seeds, powder, and galenical preparations)	S1
212.	Pemoline* and its salts	
213.	Iodine	S2/S6
214.	Decamethylenebis (trimethylammonium salts), e.g. decamethonium bromide*	
215.	Ipecacuanha (*Cephaelis ipecacuanna Brot.* and related species) (roots, powder, and galenical preparations)	
216.	(2-Isopropylpent-4-enoyl)urea (apronalide)	
217.	*a*-Santonin(3*S*,5a*R*,9b*S*)3,3a,4,5,5a,9b-hexahydro-3,5a,9-trimethyl naphto [1,2-b] furan-2,8-dione	
218.	*Lobelia inflata L.* and its galenical preparations	S1/S2
219.	Lobeline* and its salts	
220.	Barbiturates	S4 and derivatives
221.	Mercury and its compounds, excluding the exceptions listed in Annex IV and Annex V	covers range S1 to S7
222.	3,4,5-Trimethoxyphenethylamine and its salts	
223.	Metaldehyde	S5/S6
224.	2-(4-Allyl-2-methoxyphenoxy)-*N,N*-diethylacetamide and its salts	
225.	Coumetarol*	
226.	Dextromethorphan* and its salts	S3
227.	2-Methylheptylamine and its salts	
228.	Isometheptene* and its salts	
229.	Mecamylamine*	S4
230.	Guaifenesin*	S3
231.	Dicoumarol*	
232.	Phenmetrazine*, its derivatives and salts	S8
233.	Thiamazole*	
234.	3,4-Dihydro-2-methoxy-2-methyl-4-phenyl-2*H*,5*H*-pyrano [3,2-c]-[1] benzopyran-5-one (cyclocoumarol)	
235.	Carisoprodol*	
236.	Meprobamate*	S4
237.	Tefazoline* and its salts	
238.	Arecoline	S4
239.	Poldine metilsulfate*	
240.	Hydroxyzine*	S4
241.	2-Naphthol	
242.	1- and 2-Naphthylamines and their salts	
243.	3-(1-Naphtylmethyl)-2-imidazoline	
244.	Naphazoline* and its salts	S3 (alone)
245.	Neostigmine and its salts (e.g. neostigmine bromide*)	
246.	Nicotine and its salts	S6/S7
247.	Amyl nitrites	S3
248.	Inorganic nitrites, with the exception of sodium nitrite	
249.	Nitrobenzene	S6
250.	Nitrocresols and their alkali metal salts	
251.	Nitrofurantoin*	Nitrofuran S4

		NHMRC Schedule (1976)
252.	Furazolidone*	
253.	Propane-1,2,3-triyl trinitrate	
254.	Acenocoumarol*	
255.	Alkali pentacyanonitrosylferrate (2-)	
256.	Nitrostilbenes, their homologues and their derivatives	
257.	Noradrenaline and its salts	S3/S4
258.	Noscapine* and its salts	S3 (alone)
259.	Guanethidine* and its salts	S4 (alone)
260.	Oestrogens, with the exception of those listed in Annex V	
261.	Oleandrin	
262.	Chlortalidone*	S4
263.	Pelletierine and its salts	
264.	Pentachloroethane	
265.	Pentaerithrityl tetranitrate*	
266.	Petrichloral*	
267.	Octamylamine* and its salts	S4 (alone)
268.	Phenol and its alkali salts, excluding the exceptions listed in Annex III	
269.	Phenacemide*	S4
270.	Difencloxazine*	
271.	2-Phenylindane-1,3-dione (phenindione)	
272.	Ethylphenacemide*	
273.	Phenprocoumon*	
274.	Fenyramidol*	
275.	Triamterene* and its salts	S4 (alone)
276.	Tetraethylpyrophosphate; TEPP (ISO)	S7
277.	Tritolyl phosphate	
278.	Psilocybine*	S7
279.	Phosphorus and metal phosphides	Phosphorus yellow S1/S6
280.	Thalidomide* and its salts	Prohibited substance
281.	*Physostigma venenosum Balf.*	(Physostigmine S4)
282.	Picrotoxin	S4
283.	Pilocarpine and its salts	S4 (alone)
284.	*a*-Piperidin-2-yl benzyl acetate laevorotatory form (Levophacetoperane) and its salts	
285.	Pipradrol* and its salts	S4 (alone)
286.	Azacyclonal* and its salts	
287.	Bietamiverine*	
288.	Butopiprine* and its salts	
289.	Lead and its compounds, with the exception of that mentioned in Annex V	(Lead salts S2)
290.	Coiine	S1/S2
291.	*Prunus laurocerasus L.* ('cherry laurel water')	
292.	Metyrapone*	S4
293.	Radioactive substances†	
294.	*Juniperus sabina L.* (Leaves, essential oil and galenical preparations)	

†The presence of natural radioactive substances and of radioactive substances caused by artificial contamination from the environment is permitted, provided that the radioactive substances are not enriched for the manufacture of cosmetic products and that their concentration falls within the limits set in the Directive laying down the basic standards for the protection of the health of workers and the general public against the dangers arising from ionising radiations (OJ No. 11, 20.2.1959, p.221/59)

	NHMRC Schedule (1976)
295. Hyoscine, its salts and derivatives	S1/S2
296. Gold salts	
297. Selenium and its compounds	S4/S6 (selenium sulphide S5)
298. *Solanum nigrum L.* and its galenical preparations	
299. Sparteine and its salts	S4 (alone)
300. Glucocorticoids	
301. *Datura Stramonium L.* and its galenical preparations	
302. Strophantines, their aglucones and their respective derivatives	
302. *Strophantus* species and their galenical preparations	S4
304. Strychnine and its salts	S1
305. *Strychnos* species and their galenical preparations	
306. Narcotics, natural and synthetic: all substances listed in Tables I and II of the single Convention on narcotic drugs signed in New York on 30 March 1961	
307. Sulphonamides (sulphanylamide and its derivatives obtained by substitution of one or more H-atoms of the $-NH_2$ groups) and their salts	S4/S6
308. Sultiame*	(Sulthiame? S4)
309. Neodymium and its salts	
310. Thiotepa*	S4
311. *Pilocarpus jaborandi Holmes* and its galenical preparations	(Pilocarpine S4)
312. Tellurium and its compounds	
313. Xylometazoline and its salts	S3 (alone)
314. Tetrachloroethylene	S6
315. Carbon tetrachloride	S7
316. Hexaethyl tetraphosphate	
317. Thallium and its compounds	S7 (alone)
318. *Thevetia neriifolia Juss.*, glycoside extract	
319. Ethionamide*	(Ethion S7)
320. Phenothiazine* and its compounds	
321. Thiourea and its derivatives, with the exception of those listed in Annex IV, Part I	S4
322. Mephenesin* and its esters	S4 (alone)
323. Vaccines, toxins, or serums listed in the Annex to the second Council Directive of May 1975 on the approximation of provisions laid down by law, regulation or administrative action relating to proprietary medicinal products (OJ No. L 147, 9.6.1975, p.13)	
324. Tranylcypromine* and its salts	
325. Trichloronitromethane (chloropicrine)	S6
326. 2,2,2-Tribromoethanol (tribromoethyl alcohol)	
327. Trichlormethine* and its salts	
328. Tretamine*	S4
329. Gallamine triethiodide*	gallamine S4
330. *Urginea scilla Stern.* and its galenical preparations	
331. Veratrine, its salts and galenical preparations	
332. *Schoenocaulon officinale Lind.* (seeds and galenical preparations)	
333. *Veratrum album L.* (roots and galenical preparations)	(Veratrum S1/S4)
334. Vinyl chloride monomer	S7
335. Ergocalciferol* and cholecalciferol (vitamins D_2 and D_3)	

		NHMRC Schedule (1976)
336.	Salts of O-alkyldithiocarbonic acids	
337.	Yohimbine and its salts	S4
338.	Dimethyl sulfoxide*	S4
339.	Diphenhydramine* and its salts	S4 (alone)
340.	4-tert-Butylphenol	
341.	4-tert-Butylpyrocatechol	
342.	Dihydrotachysterol*	
343.	Dioxane	
344.	Morpholine and its salts	
345.	*Pyrethrum album L.* and its galenical preparations	(pyrethrins S5)
346.	2-[4-Methoxybenzyl-*N*-(2-pyridyl)amino]ethyldimethylamine	
347.	Tripelennamine*	S4
348.	Tetrachlorosalicylanilides	
349.	Dichlorosalicylanilides	
350.	Tetrabromosalicylanilides	
351.	Dibromosalicylanilides, e.g. metabromsalan*, dibromsalan*	
352.	Bithionol*	S6
353.	Thiuram monosulphides	
354.	Thiuram disulphides	
355.	Dimethylformamide	S6
356.	4-Phenylbut-3-en-2-one	
357.	Benzoates of 4-hydroxy-3-methoxycinnamyl alcohol except for normal content in natural essences used	
358.	Furo [3,2-g) chromen-7-one and its alkyl-substituted derivatives (e.g. trioxysalan* and 8-methoxypsoralen), except for normal content in natural essences used	trioxysalan S4
359.	Oil from the seeds of *Laurus nobilis L*	
360.	*Sassafras officinale Nees* oil containing safrole	
361.	5,5′-Di-isopropyl-2,2′-dimethylbiphenyl-4,4′-diyl dihypoiodite	

ANNEX III

Part I

List of substances which cosmetic products must not contain except subject to the restrictions and conditions laid down.

Ref. No.	Substance	Restrictions			Conditions of use and warnings which must be printed on the label
		Field of application and/or use	Maximum authorised concentration in the finished cosmetic product	Other limitations and requirements	
1	Boric acid	(a) Talcs	(a) 5%	(a) Not to be used in products for children under three years old	(a) Not to be used for babies
		(b) Products for oral hygiene	(b) 0.5%		
		(c) Other products	(c) 3%		
2	Mercaptoacetic acid and its salts and esters	(a) Hair waving or straightening products:			
		—home use	(a) —8% ready for use pH≤9.5		
		—professional use	—11% ready for use pH≤9.5		
		(b) Depilatories	(b) 5% pH≤12.65		
		(c) Other hair care products which are removed after application	(c) 2%—percentages calculated as mercaptoacetic acid		
3	Oxalic acid, its esters and alkaline salts	Hair treatment products	5%		For hairdressing only
4	Chlorobutanol	Preservative	0.5%	Prohibited in aerosols	Contains chlorobutanol
5	Ammonia		6% calculated as NH_3		Above 2%: contains ammonia

Ref. No.	Substance	Restrictions			
		Field of application and/or use	Maximum authorised concentration in the finished cosmetic product	Other limitations and requirements	Conditions of use and warnings which must be printed on the label
6	Tosylchloramide sodium		0.2%		
7	Chlorates of the alkali metals	(a) Toothpaste (b) Other uses	(a) 5% (b) 3%		
8	Dichloromethane		35% (when mixed with 1,1,1-trichloroethane, total concentration must not exceed 35%)	0.2% as maximum impurity content	For preparations in aerosol dispensers; do not spray on a naked flame or any incandescent material
9	*o*- and *m*-Phenylenediamines their N-substituted derivatives and their salts; N-substituted derivatives of *p*-phenylenediamines[1]	Oxidising colouring agents for hair dyeing	6% calculated as free base		Can cause an allergic reaction: sensitivity test advisable before use; contains phenylenediamines: do not use to dye eyelashes or eyebrows
10	Methylphenylene-diamines, their N-substituted derivatives and their salts[1]	Oxidising colouring agents for hair dyeing	10% calculated as free base		Can cause an allergic reaction: sensitivity test advisable before use; contains phenylene-diamines: do not use to dye eyelashes or eyebrows
11	Diaminophenols[2]	Oxidizing colouring agents for hair dyeing	10% calculated as free base		Can cause an allergic reaction: sensitivity test advisable before use; contains diaminophenols: do not use to dye eyelashes or eyebrows

12 Dichlorophen		0.5% maximum		Contains Dichlorophen
13 Hydrogen peroxide	Oxidation colouring agents for hair dyeing	40% volume, i.e. 12% H_2O_2		Contains x% hydrogen peroxide
14 Formaldehyde	(a) Nail hardeners	(a) 5%		(a) Protect cuticles with grease or oil; contains x% formaldehyde
	(b) Use as a preservative	(b) 0.2% calculated as formaldehyde	(b) Prohibited as a preservative in aerosol dispensers and in mouth hygiene products	(b) Contains formaldehyde
	(c) For mouth hygiene products	(c) 0.1%		
15 Hexachlorophene	Preservative	0.1%	Not to be used in products for children or personal hygiene products	Not to be used for babies: contains hexachlorophene
16 Hydroquinone[3]		2%		Do not use to dye eyelashes or eyebrows; rinse eyes immediately if product comes into contact with them; contains hydroquinone

[1]These substances may be used singly or in combination provided that the sum of the ratios of the levels of each of them in the cosmetic product at the maximum level authorised for each of them does not exceed 2
[2]These substances may be used singly or in combination provided that the sum of the ratios of the levels of each of them in the cosmetic product at the maximum level authorised for each of them does not exceed 1
[3]These substances may be used singly or in combination provided that the sum of the levels of each of them in the cosmetic product at the maximum level authorised for each of them does not exceed 2

Cont. next page

Ref. No.	Substance	Restrictions			Conditions of use and warnings which must be printed on the label
		Field of application and/or use	Maximum authorised concentration in the finished cosmetic product	Other limitations and requirements	
17	Potassium or sodium hydroxide	(a) Nail cuticle solvent	(a) 5% by weight[4]		(a) Avoid contact with eyes: can cause blindness; keep away from children
		(b) Hair straightener	(b) 2% by weight[4]		(b) Avoid contact with eyes: can cause blindness; keep away from children
		(c) Other uses as a neutraliser	(c) up to pH 11		
18	Lanolin				Contains lanolin
19	α-Naphthol	Hair dye	0.5%		Contains α-naphthol
20	Sodium nitrite	Only as rust inhibitor	0.2%	Do not use with secondary amines	
21	Nitromethane	Only as rust inhibitor	0.3%		
22	Phenol	Soaps and shampoos	1%		Contains phenol
23	Picric acid	Only as rust inhibitor	1%		Contains picric acid
24	Pyrogallol[5]	For dyeing hair only	5%		Do not use to dye eyelashes or eyebrows; rinse eyes immediately if product comes into contact with them: contains pyrogallol
25	Quinine and its salts	(a) Shampoos	(a) 0.5% calculated as quinine base		

		(b) Hair lotions	(b) 0.2% calculated as quinine base	
26	Resorcinol[6]	(a) Hair dyes	(a) 5%	(a) Can cause an allergic reaction: contains resorcinol: rinse hair well after application; do not use to dye eyelashes or eyebrows; rinse eyes immediately if product comes into contact with them
		(b) Hair lotions	(b) 0.5%	(b) Can cause an allergic reaction: contains resorcinol
		(c) Shampoos	(c) 0.5%	(c) Can cause an allergic reaction: contains resorcinol; rinse hair well after application
27	Ammonium sulphides, alkali and alkaline earth sulphides		2% in pastes 20% for monosulphides in aqueous solution without additive	
28	Zinc chloride and sulphate		1% calculated as zinc	
29	Zinc 4-hydroxybenzenesulphonate	(a) Astringent	(a) 6% calculated as the anhydrous substance	(a) Avoid contact with eyes
		(b) Deodorant	(b) 6% calculated as the anhydrous substance	(b) Do not spray into eyes

[4]The sum of the two hydroxides expressed by weight as sodium hydroxide

[5]These substances may be used singly or in combination provided that the sum of the ratios of the levels of the content of each of them in the cosmetic product at the maximum level authorised for each of them does not exceed 2

[6]These substances may be used singly or in combination provided that the sum of the ratios of the levels of the content of each of them in the cosmetic product at the maximum level authorised for each of them does not exceed 2

ANNEX IV
Part I

LIST OF SUBSTANCES PROVISIONALLY ALLOWED

Ref. No.	Substance	Restrictions			Conditions of use and warnings which must be printed on the label
		Field of application and/or use	Maximum authorised concentration in the finished cosmetic product	Other limitations and requirements	
a	b	c	d	e	f
1	Methanol	Denaturant for ethanol and isopropyl alcohol	5% Calculated as a % of ethanol and isopropyl alcohol		
2	Thiomersal	Solely as a preservative in eye make-up	0.007% Calculated as Hg; when mixed with other mercury compounds permitted under this Directive, total Hg concentration must not exceed 0.007%		Contains thiomersal
3	Phenylmercuric compounds	Ditto	Ditto		Contains phenyl-mercuric compounds
4	Chloroform	Toothpaste	4%		
5	2,3-Dihydroxypropyl 4-aminobenzoate		5%		Contains 2,3-dihydroxy-propyl 4-aminobenzoate
6	Quinolin-8-ol and bis (8-hydroxyquinolinium) sulphate		0.3% in base	Not to be used in products applied after sunbathing; not to be used in talcum powder for babies	Not to be used for babies

7	Ammonium monofluorophosphate	Oral hygiene products		Contains ammonium monofluorophosphate
8	Sodium monofluorophosphate	Oral hygiene products		Contains sodium monofluorophosphate
9	Potassium monofluorophosphate	Ditto		Contains potassium monofluorophosphate
10	Calcium monofluorophosphate	Ditto		Contains calcium monofluorophosphate
11	Calcium fluoride	Ditto		Contains calcium fluoride
12	Sodium fluoride	Ditto		Contains sodium fluoride
13	Potassium fluoride	Ditto	0.15% Calculated as F; when mixed	Contains potassium fluoride
14	Ammonium fluoride	Ditto	with other fluorine compounds permitted under this Annex, total	Contains ammonium fluoride
15	Aluminium fluoride	Ditto	F concentration must not exceed 0.15%	Contains aluminium fluoride
16	Stannous fluoride	Ditto		Contains stannous fluoride
17	Hexadecyl-trimethyl-ammonium fluoride	Ditto		Contains hexadecyl-trimethyl-ammonium fluoride
18	3-(N-Hexadecyl-N-2-hydroxylammonio) propyl bis (2-hydroxyethyl) ammonium difluoride	Ditto		Contains 3-N-Hexadecyl-N-2-hydroxyethylammonio) propyl bis (2-hydroxethyl) ammonium difluoride
19	N,N′,N′-tris (polyoxyethylene)-N-hexadecyl-propylenediamine dihydrofluoride	Ditto		Contains N,N′,N′-tris (polyoxyethylene)-N-hexadecyl-propylenediamine dihydrofluoride

a	b	c	d	e	f
20	Octadecyl-ammonium fluoride	Oral hygiene products	0.15% Calculated as F; when mixed with other fluorine compounds permitted under this Annex, total F concentration must not exceed 0.15%		Contains octadecyl-ammonium fluoride
21	Sodium fluorosilicate	Ditto			Contains sodium fluorosilicate
22	Potassium fluorosilicate	Ditto			Contains potassium fluorosilicate
23	Ammonium fluorosilicate	Ditto			Contains ammonium fluorosilicate
24	Magnesium fluorosilicate	Ditto			Contains magnesium fluorosilicate
25	Safrole		100 ppm		
26	1,3-bis (hydroxy-methyl) imidazolidine-2-thione	Hair care preparations	(a) Up to 2% (b) from 2 to 8%	(a) Prohibited in aerosol dispensers (b) Ditto	(a) Contains 1,3-bis (hydroxymethyl) imidazolidine-2-thione (b) Rinse hair thoroughly after use: contains 1,3-bis (hydroxymethyl) imidazolidine-2-thione
27	1,3-bis (hydroxymethyl)-3-thiourea	Ditto	6%		Rinse hair thoroughly after use: contains 1,3-bis (hydroxymethyl)-2-thiourea
28	Hydroxymethyl-2-thiourea	Ditto	6%	Ditto	Rinse hair thoroughly after use: contains hydroxymethyl-2-thiourea

29	1-Hydroxymethylimidazolidine-2-thione	Hair care products	6%	(a) Prohibited in aerosol dispensers	Rinse hair thoroughly after use: contains 1-hydroxymethylimidazolidine-2-thione
30	1-Monomorpholinomethyl-2-thiourea	Ditto	6%	Ditto	Rinse hair thoroughly after use: contains 1-morpholinomethyl-2-thiourea
31	1,3-bis (morpholinomethyl)-2-thiourea	Ditto	6%	Ditto	Rinse hair thoroughly after use: contains 1,3-bis(morpholinomethyl)-2-thiourea
32	1,1,1-Trichloroethane (methyl chloroform)	Solvent for aerosol dispensers	35% When mixed with dichloromethane, total concentration must not exceed 35%		Do not spray on a naked flame or any incandescent material
33	Tribromosalicylanilides (e.g. tribromsalan*)	Soap	1%		Contains tribromosalicylanilides

ANNEX V

List of Substances excluded from the scope of the Directive

1. Lead acetate (for use in hair treatment products only)
2. Hexachlorophene (for all uses other than that stated in Part 1 of Annex III)
3. Hormones
   (a) —oestrone
   —oestradiol and its esters
   —oestriol and its esters
   (b) —progesterone
   —ethisterone
4. *p*-Phenylenediamine and its salts
5. Strontium and its salts, with the exception of those used in the colouring agents listed in Part 2 of Annex III and Parts 2 and 3 of Annex IV
6. Zirconium and its derivatives
7. Thiomersal and phenylmercuric compounds (for use as preservatives in concentrated shampoos and creams containing non-ionic emulsifiers which render other preservatives ineffective; maximum concentration 0.003% calculated as Hg)
8. Lidocaine
9. Tyrothricin

APPENDIX 4.3

Australian and State Cancer Councils: Ultraviolet absorption of sunscreens at 305 nm for 0.01 mm thickness of screen (Australian Government Analytical Laboratories, 1976)

The protection decreases from Group 1 to Group 7. The table does not take into account the ability of the screen to stay on the skin—the figures are simply for a layer of $^{1}/_{100}$ of a millimetre. The various cancer societies should be consulted for updated lists.

Group 1

Over 99% protection (up to 1% transmitted)

Ambre Solaire	Sunblock 305
Avon	Lip Dew
Biokosma	Tibetan Sun Oil 'Forte'
Bonne Bell	High Altitude Cream
Bonne Bell	Kristi Lip-Cote
Bonne Bell	Lip Gloss
Bonne Bell	Weatherproofer
C.F.C.	Uvistik
Charles of the Ritz	Sun Bronze Protective Creme
Charles of the Ritz	Sun Bronze Extra Protective Creme
Charles of the Ritz	Sun Protective Stick
Coppertone	Eclipse
Coppertone	Lipscreen
Coppertone	Nosekote Clear
Craigston	Ultraviolet Sunscreen
Cyclax	Ultra Tan Sun Spray

Elizabeth Arden	Ardena Covering Cream (all four shades)
Estee Lauder	Sun Block
Gilda	Superscreen
Glenell	Butter Tan Nose and Lip Screen
Glenell	Butter Tan Sunscreen Oil
Hamilton	Sola Stick
Hamilton	Sun-Proof Lotion
Harriet Hubbard Ayer	Altitude Cream
Harriet Hubbard Ayer	Bronze Tahitien Super Protection
Heather Laboratories	Surf Ski
Heather Laboratories	Surf Ski Sunshield Lotion
Heather Laboratories	U.V. Filter Cream
ICI	Sun Filter Lotion
Innoxa	Kerodex 12W Total Sun Deflectant Cream
Juvena	Sun Fluid Bronze
Juvena	Sun Gel
Juvena	Sun Protection Cream
Juvena	Sun Protection Fluid
Key-Sun	Pinke Zinke
Mary Quant	Sunshine Oil
Natra	Sunfilter Gel
Nyal	Sunscreen Lotion
Nyal	Sunskreen
Nyal	Sunskreen Nose and Face Gel
Owen	Pabafilm
Owen	Pabagel
Piz Buin	Broad Spectrum U.V. Creme
Piz Buin	Broad Spectrum U.V. Lotion
Piz Buin	Exclusiv Creme
Piz Buin	Exclusiv Lip and Nose Protector
Piz Buin	Exclusiv Lotion
Piz Buin	Exclusiv Milk
Piz Buin	Extreme Creme
Piz Buin	Extreme Creme for Children
Piz Buin	Extreme Lotion
Piz Buin	Extreme Milk
WQ.R.I.	Sun Protection Cream
Revlon	Bronze Lustre Protective Face Colour Cream
Revlon	Bronze Lustre Sunblock Stick
Robins	Phiasol A.S.
Roche	Eversun 7 Sun-Cream
Roche	Eversun Sunstick
Sea and Ski	Block Out
Sea and Ski	Crazie Zinc
Stanhome	Sun Chum Sun Block
Theta	Bonza Bronza Sun Filter
Theta	Burn Free Sun Filter
Tiki	Vitamin E Sun-Tan Oil
Uvistat	Sunscreen for Lips
Uvosan	Ultraviolet Barrier Lotion

Uvosan	Ultraviolet Barrier Spray
Virax	Uvicone Barrier Spray

Group 2

97–99% protection (1 to 3% transmitted)

Avon	Bronze Glory Sun Safe
Bonne Bell	Sun Bloc
Bonne Bell	Sure Tan for Dry Skin
Charles of the Ritz	Sun Bronze Tanning Glow (Medium Filter)
Coppertone	Tropical Blend
Gilda	Tan 'n' Ban Gel
Gilseal	Sun Protection
Harriet Hubbard Ayer	Bronze Tahitien Normal Protection
Harriet Hubbard Ayer	Sun Milk
Juvena	Sun Cream
Key-Sun	White Zinke
Natra	Sunburn Relief
Natra	Sunfilter
Nyal	Bronze, Zinc
Orlane	Tan A Sol Liquide
Piz Buin	Exclusive Creme Spray
Revlon	Bronze Lustre Sun Stick
Revlon	Bronze Lustre Tanning Gelee Normal Skin
Revlon	Bronze Lustre Tanning Gelee Sensitive Skin
Revson	Ultima II Deep Deep Tanning Gel
Robins	Chap Stick
Sea and Ski	Lipsaver (all four flavours)
Stanhome	Sun Chum Suntan Lotion
Uvosan	Total Block Cream
Vanda	Vandatan Shadow
Vitaplex	Vitamin E Healing Cream with P.A.B.A.

Group 3

91–97% protection (3 to 9% transmitted)

Abbott	Sola-Screen
Ambre Solaire	Mousse
Ambre Solaire	Oil Free Suntan Lotion
Ambre Solaire	Suntan Oil
Avon	Bronze Glory Tanning Oil
Charles of the Ritz	Sun Bronze Tanning Glow (Low Filter)
Coppertone	Baby
Coppertone	Dark Tanning Oil
Coppertone	Sudden Tan Foam

Dorothy Gray	Satura Sunfilter Cream
Estee Lauder	Sun Bathing Milk (Tinted)
Estee Lauder	Ultraviolet Screening Creme
Faberge	Sun Tan Mousse
Harriet Hubbard Ayer	Sun Cream
Hawaiian Tropic	Sun's Screen
ICI	UV Sun Filter Cream (tube and jar)
Johnson and Johnson	Tanfast Cream Lotion
Johnson and Johnson	Tanfast Suntan Oil
Juvena	Sun Foam
Nyal	Kwiktan Sun Oil
Nyal	Zinc Cream
Orlane	Maqui-Sol (all four shades)
Orlane	Suntan Milk
Piz Buin	Oil
Reckitts	TanNatural Tanning Lotion
Reckitts	TanNatural U.V. Sunscreen Lotion
Revlon	Bronze Lustre Tanning Lotion for Sun-Sensitive Skins
Revson	Ultima II Highly Protective Tanning Lotion
Roche	Eversun 2 Sun-Lotion
Roche	Eversun 3 Sun-Cream
Roche	Eversun 5 Sun-Lotion
Rosken	Lip-Sed Jel
Sigma	Zinc Cream
Skol	Blockade
Uvosan	UV Ultraviolet Filter Cream
Vanda	Vandatan Sun Lotion
Virax	Uvicone Cream

Group 4

80–91% protection (9 to 20% transmitted)

Ambre Solaire	Sun Tan Lotion
Avon	Bronze Glory Tanning Cream
Avon	Bronze Glory Tanning Lotion
Biokosma	Tibetan Sun Cream "Forte"
Bonne Bell	Suretan for Skiers
Coppertone	Tanning Lotion
Dorothy Gray	Satura Sunfilter Lotion
Elizabeth Arden	Sun Gelee
Estee Lauder	Sun Bathing Milk
Gilda	Sunbronzer
Hawaiian Tropic	Sun's Screen Protective Gel

Innoxa	Sunplay
Maria Read	Maria Sun Block
Nyal	Kwiktan Cream
Pistache	Over Exposure
Q.R.I.	Sun Screen Cream
Reckitts	TanNatural Dark Tanning Oil
Revlon	Bronze Lustre Sun Colour Cream
Revlon	Bronze Lustre Tanning Lotion for Normal Skin
Revlon	Ultima II Sun Creme for the Face
Sea and Ski	Dark Tanning Oil
Sea and Ski	Golden Tan
Sea and Ski	Indoor Outdoor
Sea and Ski	Suntan Lotion
Skol	Anti-Burn Coconut Oil
Skol	Quick Tanning Creme
Skol	Sun Tan
Skol	Suntan Lotion
Sundowner	Suntan Oil

Group 5, 6 and 7

60–80% protection (20 to 40% transmitted)

Alba	Baby's Outdoor Lotion
Ambre Solaire	Bronz Up
Ambre Solaire	Creme
Bonne Bell	Sure Tan Non-Greasy
Con-Stan	Nutri-Tan
Coppertone	Shade
Coppertone	Sudden Tan Lotion
Cyclax	Moisture Bronze for Sun-Sensitive Skin
Elizabeth Arden	Sun-Pruf Cream Regular
Gilda	Sunlike
Glenell	Butter Tan Sunscreen Lotion
Mary Quant	Topspeed Tan
Nivea	Sun Screen Filter
Nivea	Suntan Lotion
Nyal	Kwiktan Suntan Lotion
Orlane	Bronzilane
Orlane	Bronze Orlane
Parke Davis	Filtrosol Suntan Cream
Sea and Ski	Dark Tanning Lotion
Skol	Suntan Creme
Skol	Suntan Lotion Non-Oily
Souls	Suntan Lotion
Uvistat	Ultraviolet Filter Sun Cream

30–60% protection (40 to 70% transmitted)

Biokosma	Tibetan Sun Milk 'Forte'
Coppertone	QT Lotion
Cyclax	Moisture Bronze for Easy-to-tan Skin
Elizabeth Arden	Sun-Pruf Cream Dark
Elizabeth Arden	Sun-Tan Cream
Hamilton	Suncream
Hamilton	Sun Sport Suntan Lotion
Hawaiian Tropic	Dark Tanning Lotion
Orlane	Creme Astrale Solaire
Pistache	Decent Exposure
Pistache	Double Exposure
Pistache	Under Exposure
Robins	Phaisol Lotion

Less than 30% protection (over 70% transmitted)

Coppertone	Swim Tan
Hawaiian Tropic	Dark Tanning Oil
Johnson and Johnson	Baby Oil
Orlane	Tan Orlane
Prosana	Coconut Oil

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Chapter 5

CHEMISTRY IN THE GARDEN

PESTICIDES AND PREFERABLE ALTERNATIVES[1]

Insects may be small in *size* but that's all! Insects represent about 76 percent of the total animal mass in the world today and probably always have been the major form of animal life. Egyptian hieroglyphics mention the frightening effect of locust swarms, which can have a mass of the order of 15,000 tonnes/swarm. Locust swarms are highly visible but most insects are much more inconspicuous. If you examine a few square metres of typical sheep grazing soil and count all the grass grubs, the chances are that the weight of the grubs eating the grass from below will be greater than the weight of the sheep eating it from above! Man's developing agriculture, the concentration

PLATE 5.I *If swallowed . . .*

of growing plants, was a marvellous step forward—for insects. It concentrated their feeding and breeding. The storing of produce and the keeping of reservoirs of water for domestic use also helped insects. Apart from these primary effects of agriculture, there were also secondary effects due to man's new sedentary nature. Thus in contrast to other primates man has fleas because he has a permanent residence, one of the requirements in the life cycle of the flea. It is no wonder that the battle against the insect is waged with vigour. Pesticides were the first weapons of mass insect destruction but they are failing rapidly and there is no longer any idea of complete elimination since it is neither practical nor economical. The concept of pest management has been adopted in its place. Management entails the acceptance of a certain level of damage.[1]

The consumer is still presented with a bewildering array of dangerous chemicals in the garden section of the retail store. Little bottles with even littler instructions. There are also reassuring warnings, such as *Keep out of reach of children and if swallowed seek medical advice.* This appears on so many products that it is difficult to assess an order of dangerousness. Scheduling of chemicals is discussed in Chapter 9.

If you are intent on following the advice of your gardening books and the helpful hints in the gardening section of your newspaper and wish to continue the chemical warfare in the garden, then perhaps this chapter will help you understand what you are using and help to ensure that it is the insect rather than you that ends up knocked out.

A *pesticide* is a material capable of a degree of selectivity in killing a pest in a biological community. Perhaps the first usage of pesticides was recorded in 1763 when nicotine extract was used to kill aphids. Since then the number of pesticides has increased tremendously and there are many varieties now in use. Pesticides are classed depending on the particular use intended. Insecticides, fungicides, herbicides (weed killers), rodenticides, acaricides (mites, ticks, spiders, etc.). This by no means exhausts the list, nor are the individual groups non-overlapping. Within these major divisions there are many further subdivisions according to chemical type (generic group), or mode of action, or specificity etc., and these groups are again not mutually exclusive.

INSECTICIDES

Insecticides are sometimes divided *functionally* as:

1. stomach poisons (require ingestion)
2. contact poisons (absorbed through the cuticle)
3. fumigants (gases).

Chemically the more important groups of insecticides are:—

1. inorganic group
2. organo-chlorine compounds (chlorinated hydrocarbons), e.g. DDT, aldrin

3. organo-phosphorus compounds, e.g. parathion
4. nitrogenous compounds and carbamates, e.g. sevin
5. plant extracts (botanical), e.g. pyrethrums, rotenoids

The inorganic group are almost exclusively stomach poisons, which are active only after ingestion and are thus restricted mainly to chewing insects; they are not very effective against sucking insects such as aphids and mosquitoes. Inorganic pesticides are the most persistent.

Other classes of chemicals used either alone or in relation to insecticides are attractants and repellents and synergists.

Inorganic insecticides

Typical inorganic insecticides are usually heavy metal compounds particularly of lead, mercury, arsenic, and antimony although some others, such as fluoride salts (e.g. NaF), sulphur and polysulphides, and borax, have limited applicability.

$PbHAsO_4$ *(lead arsenate)*—A typical heavy metal compound. Being water-insoluble it is not readily absorbed by plants on contact and is effective only by ingestion. The lead ties up essential sites on enzymes and is thus non-specific and toxic to all living systems as well as being extremely persistent. Sodium arsenite was used as a cattle dip against the tick but has been superseded.

NaF and Na_3AlF_6 *(cryolite)*—These compounds liberate fluoride ion which precipitates Mg^{++} as fluorophosphate and upsets magnesium-dependent enzymes. It is non-specific and toxic to mammals.

$Na_2B_4O_7$ *(borax)*—Used as a cockroach and ant poison but is not very toxic to mammals.

S *(elemental sulphur) and* CaS_n *(lime sulphur, $n \sim 5$)*—Lime sulphur is a solubilised form of sulphur (a polysulphide); its mode of action is through aerial oxidation to SO_2 which is an effective fungicide and acaricide but of limited use as an insecticide. It is one of the safer fungicides.

Copper compounds—Two copper compounds are widely used by home gardeners: bordeaux mixture is a combination of copper sulphate and lime; paris green is copper aceto-arsenite. Copper sulphate causes vomiting and promotes its own elimination. Timber for garden use is impregnated by the pressure pot method with copper chrome arsenate. Exhaust ventilation should be provided when sanding or finishing treated timber, and the urine of regular workers should be analysed for arsenic content. Dermatitis can result from chronic skin contamination. Such timber should not be burnt for barbeques, etc.

Natural insecticides

There are several well known insecticides of plant origin such as rotenoids (sold as Derris Dust—it is not persistent and must be sprayed every three

days; it is primarily rotenone which is also used in poisoning fish), and nicotine. Even garlic oil has been shown to be effective against the larvae of mosquitoes, houseflies, and other pests. One of the oldest and best known of the natural insecticides is the class of compound known as pyrethrines which are extracted from the pyrethrum flower, a daisy-like member of the *Chrysanthemum* genus originally grown in Caucasian Mountains. Most of the present crop comes from East Africa. Pyrethrins act by paralysing insects and have a low toxicity to animals. They are expensive, subject to crop failure, and thus commercially unreliable. Synthetic pyrethrins are now produced.

TOXICITY

At this stage it is worth explaining a few of the terms used to measure the properties of insecticides.

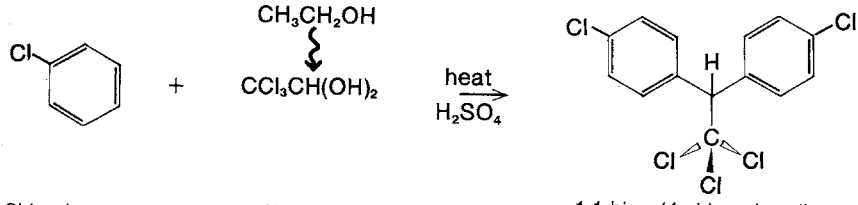
The usual measure for acute oral *toxicity* of a substance is the dose necessary to kill, on the average, 50 percent of a group of test animals (usually rats). This dose is known as LD_{50} and is expressed as milligrams of substance per kilogram of body weight. The *lower* the figure, the *more toxic* is the substance. The dermal or skin value is obtained by applying the material to the animal's back.

Organo-chlorine compounds

These are organic compounds which contain chlorine. DDT is shorthand for dichlorodiphenyltrichloroethane. (Actually the correct nomenclature is 1,1-bis[4-chlorophenyl]-2,2,2-trichloroethane.) It was first made in 1874 but it was not used for the first time until near the end of World War II. After World War I thousands of homeless and hungry people fell victim to louse-borne typhus and died miserably. After World War II, because of the dusting of people with DDT, this problem did not arise. The most widespread killing and debilitating disease in the world is malaria. The female mosquito carries the parasite, needs blood, and likes to hunt at night. DDT brought the death rate from malaria in Ceylon down by 34 percent in just one year. By 1963 endemic malaria had virtually disappeared but when, for a variety of reasons, insecticide spraying came to a halt, there was a malaria flare-up. During 1968–9 there were more than two million cases.

The discovery of the insecticidal properties of DDT in the Swiss laboratories of the Geigy company in 1939 was an event of major importance. Before this discovery the main insecticides available were naturally occurring products.

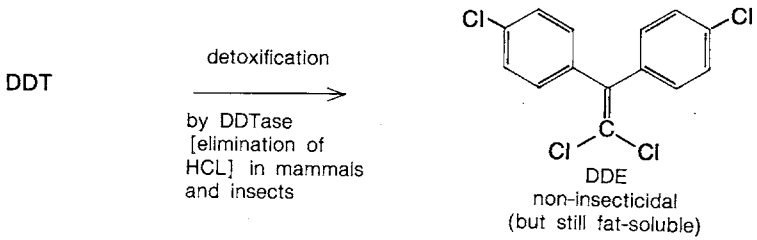
DDT is a highly effective insecticide both by contact and by ingestion and is of very low toxicity to mammals. It is practically odourless and tasteless; and it is chemically stable, although this is now seen as a major disadvantage. It is made in a one step reaction (Figure 5.1) from low-cost raw materials and therefore is cheap.



Chlorobenzene Chloral 1,1-bis- (4-chlorophenyl) - 2,2,2-trichloroethane DDT

5.1 Preparation of DDT. Oral LD_{50}—300–500 mg/kg; dermal LD_{50}—2500 mg/kg

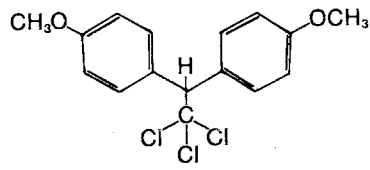
Increasingly many insects are developing resistance to DDT by the natural selection of surviving members whose enzymes can detoxify the DDT to a substance known as DDE (Figure 5.2). DDE is flatter than DDT and the change in shape alters the toxicity. The chemically stable DDT and its metabolic breakdown product DDE tend to accumulate in the fat of birds and fish because these creatures are at the end of the biological chains. The mosquito eradication campaign on Long Island, New York, showed levels of DDT in the sea water of 3×10^{-6} ppm (non-toxic); in the fat of plankton of 0.04 ppm; in the fat of minnows of 0.5 ppm; in the fat of needlefish of 2 ppm; in the fat of cormorants, osprey, etc. of 25 ppm. This progression is called biological magnification. The level in the birds is biologically active and is believed to upset the metabolism of the female hormone oestrogen; it is alleged that this has resulted in eggs being produced with very thin shells which consequently break.



5.2 Detoxification of DDT

Development of biodegradable analogues is well advanced. The method is to include groups on the molecule which can be metabolised to polar groups, thus giving water-solubility and allowing excretion. An example is the

insecticide *methoxychlor*, a biodegradable analogue of DDT, illustrated in Figure 5.3. This method is the basis of ***building-in*** biodegradability. Non-polar compounds stay dissolved in the fat of the body while polar substances are water-soluble and can be excreted and also can be further attacked by other organisms.



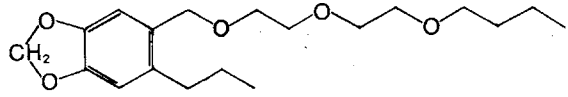
oral LD_{50} 5000–7000 mg/kg

5.3 Methoxychlor

The mode of action of DDT is that it fits into the nerve cell wall and alters its structure allowing sodium and potassium ions to leak out. This effects transmission of nerve impulses and the insect dies of paralysis. DDT-like action is clearly related to a specific size and shape of the molecule because the same effects can be elicited by an analogue of DDT where methyl groups replace the chlorines (Figure 5.5).

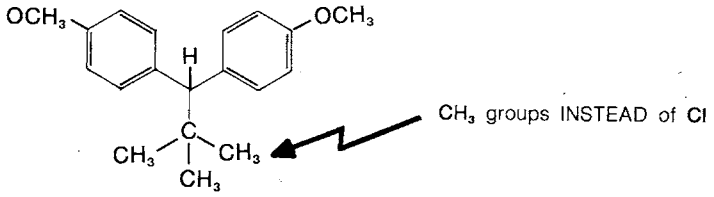
SYNERGISM

DDT, methoxychlor, and particularly the pyrethrines are much more efficient in the presence of piperonyl butoxide (Figure 5.5). This is called a *synergistic* effect. Synergism differs from a similar effect discussed in detergents—namely potentiation (Figure 2.7)—because



5.4 Piperonyl butoxide (common name)

in this case the additive is not itself an insecticide. The piperonyl butoxide helps to *deactivate* certain enzymes (oxidases) which are important for detoxification of the pesticide in the insect.

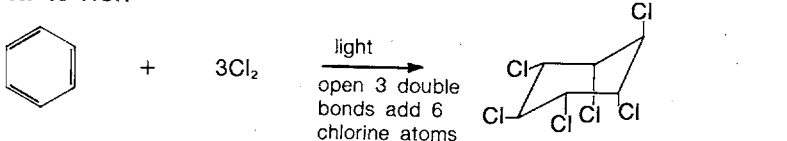


5.5 The methyl analogue of methoxychlor

This methyl analogue is even more persistent than DDT (because it cannot be detoxified by the elimination of HCl)—but it can be destroyed by oxidation.

Lindane, gammexane, or BHC (benzene hexachloride)

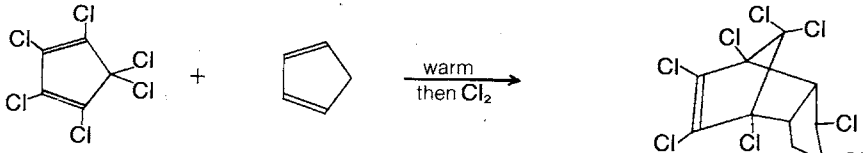
This substance was first discovered in 1825 by Faraday and involves a simple synthesis by addition of chlorine to benzene in the presence of light. A mixture of nine isomers is formed, and of these only one, the γ-isomer, is active and it forms only 13–18 percent of the mixture. The insecticidal properties of the γ-isomer were discovered in 1943. Detoxification is again accomplished by elimination of HCl.



there are 9 isomers of
1,2,3,4,5,6-hexachlorocyclohexane
oral LD_{50} 230 mg/kg
dermal LD_{50} 500–1000 mg/kg

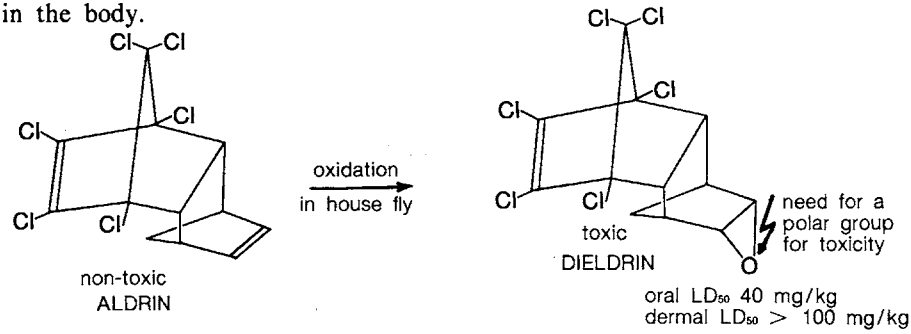
Aldrin, chlordane, dieldrin, heptachlor, endrin

These compounds form a closely related group of insecticides (made from a common starting material, hexachlorocyclopentadiene, by Diels-Alder reaction with certain alkenes). Chlordane is very easy to make and is toxic to insects and people. It is less toxic than dieldrin or aldrin. CSIRO was given the task of protecting telephone cables from termites which would 'eat' through lead sheath. Dieldrin spread around the cable proved satisfactory.



chlordane
oral LD_{50} 280 mg/kg
dermal LD_{50} > 1600 mg/kg

These compounds are all broad spectrum insecticides, are highly toxic to both insects and mammals, and have a high persistence. Like DDT they accumulate in body fats and act on the central nervous system. In some cases the actual compound is itself non-toxic but is converted to a toxic material in the body.



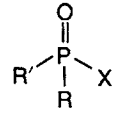
Tests for chlorinated hydrocarbons

There is no simple and generally applicable method of testing to determine whether excessive chlorinated hydrocarbon absorption has occurred. When absorbed into the body, such pesticides enter the blood stream and remain there for varying periods (measured as a half residence time). This varies from only a few hours in the case of endrin (which is one of the most toxic chlorinated hydrocarbons) to approximately 80 days for dieldrin and to 100 days in the case of DDT. This group of pesticides is detoxified in the liver and excreted by the kidneys; however a certain amount is retained and stored for long periods in the body fat and is released in times of illness and stress. It is also released into maternal milk. One story goes that mother's milk in the United States at one stage would not be allowed for sale (if it were sold) because of the high DDT levels.[2]

The high persistence of the chlorinated pesticides has led to increased restriction of their use and they are being increasingly replaced by the *organo-phosphorus* group which is now the fastest growing group of insecticides. As each new class of broad spectrum chemical insecticide is introduced the safety margin between insect toxicity and human toxicity diminishes.

Organo-phosphorus insecticides

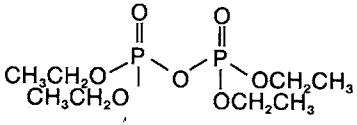
These are a wide variety of compounds with tremendous range of activity, persistence, specificity, function. All have the general formula (RR'X)P=O,



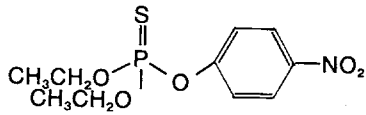
P has valencies 3 or 5; it is the five-valent state that is of importance for insecticides

5.6 Organo-phosphates

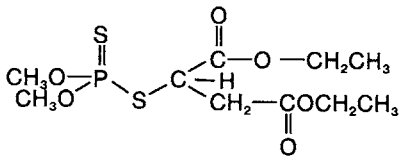
where R and R′ are short-chain groups and X is a group especially selected so that it is easily removed from the molecule either directly or after a reaction in the body. This group is built in so that the persistence of the substance is reduced.



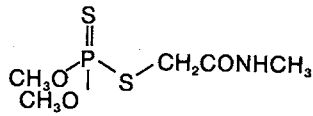
TEPP
(tetraethylpyrophosphate)
oral LD_{50} rat 1 mg/kg



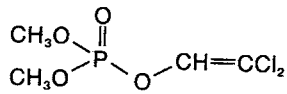
parathion (code number E 605)
oral LD_{50} 3–6 mg/kg
dermal LD_{50} 4–35 mg/kg



maldison
(Malathion)
oral LD_{50} 1400–1900 mg/kg
dermal LD_{50} > 4000 mg/kg
toxicity ratio for
insect:man is about 100, i.e. the
LD_{50} value for man
is × 100 that for insects.
Insects are × 100 more susceptible.



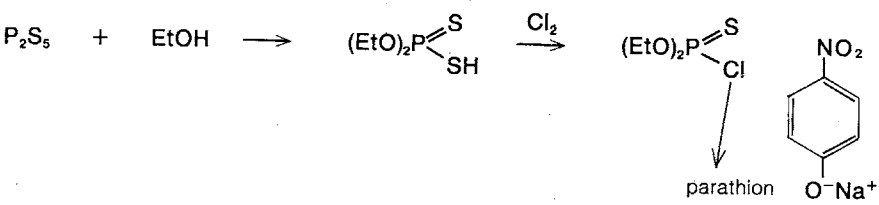
dimethoate (Rogor)
oral LD_{50} 200–300 mg/kg
dermal LD_{50} 700–1150 mg/kg



dichlorvos (Shelltox strips)
oral LD_{50} 25–30 mg/kg
dermal LD_{50} 75–900 mg/kg

5.7 Some organo-phosphate insecticides

The five compounds in Figure 5.7 are perhaps the best known organo-phosphorus insecticides. They are very easily and cheaply made. An example is the production of parathion:



The other important characteristic apart from ease and cheapness of production is persistence—how long the material stays around. For crop dusting insecticides this is specified by a withholding period—the number of days between application and harvesting. While the exact period varies with the climate and the time of the year, the average value generally offers a good guide to the persistence of a substance. Sometimes a time is specified for a certain fraction of the material to have disappeared.

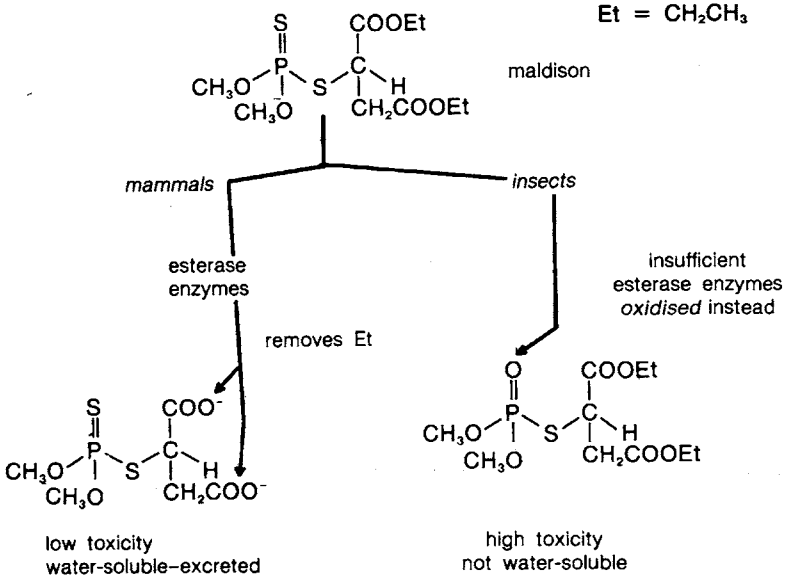
$t_{½}$ = time for half the material to go
$t_{99\%}$ = time for 99 percent of the material to go

Thus for *TEPP*, LD_{50} oral/rat = 1 mg/kg—highly toxic
$t_{½}$ (25°) = 6.8 hours
$t_{99\%}$ (25°) = 45 hours—quickly detoxified

Parathion, LD_{50} oral/rat 10 mg/kg—highly toxic
$t_{½}$(28°) in water 120 days—very persistent

Parathion is used as both methyl and ethyl ester. It has probably been responsible for more deaths than any other pesticide. The methyl ester (MSO) has not caused many deaths but this is probably because of lower usage.[2]

Maldison—like parathion is persistent but has low *mammalian* toxicity, LD_{50} oral/rat = 1300 mg/kg, due to the fact that mammals and insects detoxify it differently and with very different efficiency (see Figure 5.8).



5.8 Detoxification of maldison

Dichlorvos—(DDVP) Dimethyl dichlorovinyl phosphate. This is relatively volatile (low molecular weight), broad spectrum, but rather toxic to mammals, LD_{50} oral/rat 30 mg/kg. It is not very persistent, $t_{½}$ (25° in water, pH 7) 8 hours. This compound is used in the Shelltox pest strip in a slow release formulation. A Shelltox strip weighs 21.3 g and is stated to contain 18.6 percent by weight of Dichlorvos. This means that a strip contains 4 g of insecticide. Using the LD_{50} value of 30 mg/kg, the dose for which, on the average, half of a group of 10 kg children could be expected to die would be $10 \times 30/1000$ or 0.3 g, equivalent to the contents of less than one-tenth of a strip. This is how the LD_{50} values are used.

Unlike aerosol insecticides which kill flies with a quickly dispersed spray the strips continuously saturate the domestic atmosphere with DDVP vapour. The concentration of this vapour is lethal to insects; whether breathing the same concentration for hours on end is also harmful to human health has been a matter of dispute since the strips were first marketed in the mid-1960s. The strips were banned in Holland in January 1974 and are under study in the United States (where the EPA—the Environmental Protection Agency—has made no decision as yet) as a result of pressure from the Consumers' Union. The argument for the ban is based on failure to list all the insecticidal components in the strips, which were alleged to include two known human mutagens[3] (the specification has improved substantially over recent years and the typical active component is said to be now 99 percent pure); on the habit of hanging the strips from light fittings where heat can cause an increase in vapour release; on surveys showing that the strips are being used where they should not be—in spite of printed warnings on the labels—domestic kitchens, dining rooms, sick rooms; they should not be used in restaurants or other areas where food is prepared or served.

The Shell Company's own results showed no evidence of carcinogenic properties. When used according to instructions in the houses of their own employees the average concentrations were higher than necessary. Note that these instructions include only one strip to be used per 30 cubic metres of room (say $4m \times 3m \times 2.5m$). The concentrations are very sensitive to humidity because water destroys the DVVP. In dry areas the level can be very high. Certain groups in the community—such as asthmatics—could be particularly sensitive because of the effect of DDVP vapour on airway resistance.

In most countries like Australia flies are an aesthetic rather than a medical problem in most areas and so 'blanketing our homes with a 24-hour nerve gas which may well be causing mutations, altering our chemistry, and reducing the breathing ability of people with severe lung disorders' should be considered carefully (noting at the same time that the quoted statement shows the *New Scientist*[3] in one of its more vindictive moods—it has had a long history of non-cooperation from Shell.

All these organo-phosphorus insecticides are contact poisons which are rapidly absorbed through the insect cuticle. This however causes problems with spraying and absorption through human skin. One approach to this problem is the use of *systemics*—compounds which affect the body as a whole. They are absorbed by plants and animals and move throughout the host; they are equally effective against both chewing and sucking insects; they are administered as a spray, or to the plant roots as granules, or injected into the plant trunk. Two typical organo-phosphorus systemics are demeton and dimethoate.

Demeton (Systox) is a mixture of two components:

$(EtO)_2P(=S)—OCH_2CH_2SEt$ (Demeton O) and
$(EtO)_2P(=O)—SCH_2CH_2SEt$ (Demeton S).

It is a broad spectrum persistent systemic, very toxic to mammals, LD_{50} oral/rat = 9 mg/kg. It is commonly used by the home gardener; cases of poisoning have resulted from absorption through intact skin.

Dimethoate (Rogor) is also broad spectrum but much less persistent than demeton—it is detoxified by the plant fairly rapidly; it is best applied as a spray. It is formed by the reaction

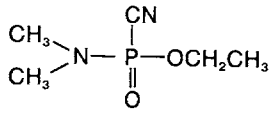
$$(MeO)_2P(=S)S^-Na^+ + ClCH_2CONHMe \longrightarrow (MeO)_2P(=S)S—CH_2CONHMe + Na^+Cl^-$$

dimethoate

Absorption of organo-phosphates may occur through either the lungs or the skin, or on swallowing. The first symptoms of poisoning come on within minutes or at the most hours after exposure. They are usually headache, fatigue, giddiness, saliva formation, sweating, blurred vision, pin point pupils, chest tightness, nausea, abdominal cramps and diarrhoea. Development of such symptoms in an exposed person is an indication to seek urgent medical aid.[2] When absorbed these pesticides inactivate two enzymes in the body called *cholinesterase*. These enzymes are normally responsible for returning to normal a compound (acetylcholine) used to activate muscles. With the enzymes inactivated, muscular spasms in involuntary muscles occur first, and overactivity of certain glands can take place. After exposure several days can be needed to restore normality in one enzyme while the other requires regeneration of red blood cells and this occurs at 1 percent of the normal value per day. Treatment involves the inducement of vomiting (for swallowed poison) and the removal of clothing and thorough washing of skin—seek urgent medical aid.

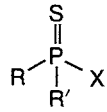
In 1937, while carrying out research on organo-phosphorus insecticides, Schroder, in Germany, discovered the nerve gases. The first of these nerve

gases, illustrated in Figure 5.9, was called Tabun. These compounds are effective on humans as well as insects. A 0.2 mg splash on the skin is fatal; in fact every accident the workers had was fatal.



5.9 Tabun

The persistent organo-phosphorus insecticides are mostly thiophosphates (Figure 5.10) (thio = sulphur). The presence of sulphur makes them more resistant to decomposition by water and lengthens their shelf life as well as their persistence. But these thiophosphates are not reactive enough to be toxic —most living organisms however have general enzymes which can convert the thiophosphates to their toxic reactive phosphate analogues which are the active insecticides. This is an example of *biological priming* or activation of an inactive precursor.



5.10 Organo-thiophosphates

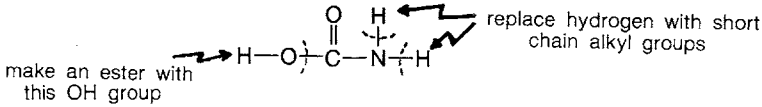
A systemic insecticide is one that is absorbed into the plant through the leaves and ingested by the sap-sucking insect along with the plant juices. Sarin and the related Tabun completely eliminate phylloxera in vines in one week when a 0.1 percent solution is spread in the ground near the vine root.

Water-solubility for most of the contact organo-phosphorus insecticides is very low—typically 0.00001 percent, but the water-solubility is improved by selecting a suitable group X which will allow the compound to become water-soluble after a while.

Systemics are necessarily fairly persistent to allow time for the slow plant transportation process.

Carbamates

These act in a similar way to the organo-phosphates. They are based on carbamic acid. Some common carbamate insecticides are given in Table 5.1.



5.11 Carbamic acid and derivatives

TABLE 5.1 *Carbamate Insecticides*

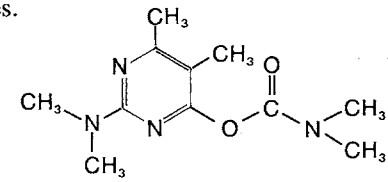
Name	Uses	Toxicity LD_{50} rat Oral	Dermal
Isolan*	baits for house flies, fruit flies, aphids	50 mg/kg	
Dimetilan	house and fruit flies	60 mg/kg	
Carbaryl (Sevin*)	general purpose crop spray	400 mg/kg toxic to bees	>500 mg/kg
Mexacarbate (Zectran*)	snails, slugs	60 mg/kg	
Aminocarb (Matacil*)	snails, slugs	30–40 mg/kg	275–280 mg/kg
Aldicarb (Temik)	seed and soil treatment	1 mg/kg	
Propoxur (Arprocarb, Baygon*)	flies, mosquitoes, cockroaches, ants	80 mg/kg	>2400 mg/kg
Methomyl (Lannate*)		27 mg/kg	>1600 mg/kg

*Trade Name

Source: New South Wales Health Commission[2]

The chemical compounds in commercial use as pesticides number about 350. At first everybody was looking for broad spectrum chemicals that could be used extensively and marketed economically, e.g. lindane, DDT, aldrin, etc. This increased the hazard of undesirable side effects. Then, since rapid penetration of the living cell was desirable, the chemist turned more and more to designing compounds of high fat/oil solubility, and these tended to accumulate in fatty tissues and hence become concentrated in the last links of a food chain.

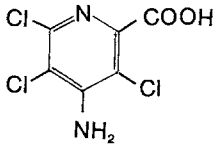
The pesticide industry is moving towards the pharmaceutical industry—there is a steadily increasing number of products, each catering for a smaller and more select market, and requiring lower dosages, stricter quality control, and higher purity. An example of such developments is Pirimicarb (a carbamate), a selective and systemic insecticide for aphids. It has a very low toxicity to predators which do not suck the sap; for example, it has no effect on ladybirds, lacewings or bees. It is rapidly metabolised and leaves no lasting residues in plant materials. It is an expensive, highly specialised chemical. Its synthesis is complex and involves five or six steps, including sophisticated plant and handling procedures.



5.12 Pirimicarb (ICI)

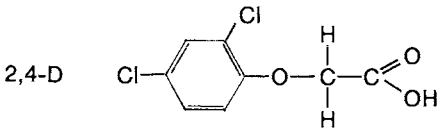
HERBICIDES

A group of compounds known as chlorophenoxy (or just phenoxy) herbicides became infamous during their use in defoliating forests in Vietnam; an example is picrolam, illustrated in Figure 5.13, which is not allowed in the United States because it is hazardous, but was used in Vietnam.

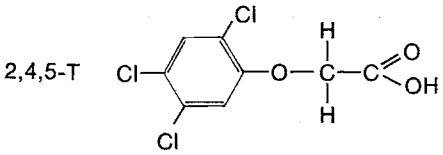


5.13 Picrolam

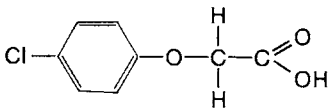
The compounds in Figure 5.14 are only three examples of a wide range of related products, which may involve the use of salts (sodium, potassium, and ethanolamine) of the acid to lower the volatility. Esters are another useful formulation because they are more soluble in the waxy leaf cover (cuticle) and more biologically active. These herbicides act to mimic natural plant growth hormones, causing excessive growth of stems with little or no root growth, and leaves that are deficient in chlorophyll, causing the plant to die.



2,4-dichlorophenoxy-acetic acid
oral LD_{50} 400–500 mg/kg
dermal LD_{50} 1500 mg/kg



2,4,5-trichlorophenoxy-acetic acid

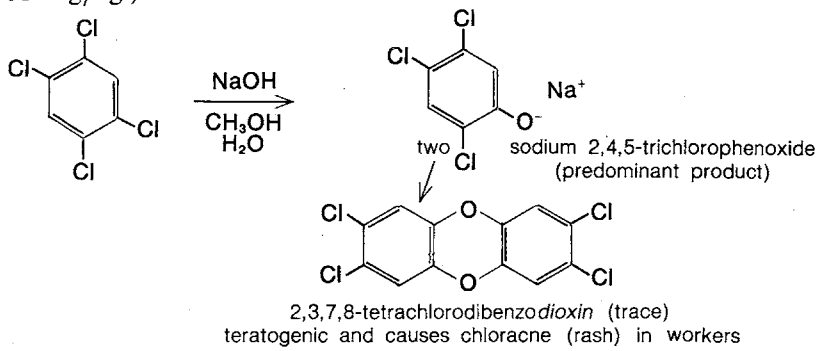


MCPA
Methox, Methoxone, Tuloxone
oral LD_{50} 800 mg/kg
dermal LD_{50} > 1000 mg/kg

5.14 Some chlorophenoxy herbicides

The compound 2,4,5-T was implicated in causing birth anomalies in animals. It turned out that the cause of the problem was a small quantity of impurity —a dioxin formed during manufacture (Figure 5.15) for which LD_{50} guinea pig is 0.0006 mg/kg. It is fat-soluble and may be concentrated like DDT. Adequate manufacturing control can keep the level of this impurity below 0.1

mg/kg of 2,4,5-T, which is considered to be acceptable. (In 1965 it was 5–32 mg/kg.)



5.15 2, 3, 7, 8-tetrachlorodibenzo*dioxin* (trace)

I noticed that a sample of 2,4,5-T, which I purchased to control some overactive raspberry, was labelled:

> *XXXX's Blackberry and Brush Killer. Buyer assumes all risk of use and handling whether or not product is used in accordance with directions given.*

Perhaps it would be wise to let the vines take over after all. I made an application to the Trade Practices Commission to have such exclusion clauses deleted.

On 10 July 1976 a cloud of gas escaped after an explosion at the Swiss-owned Icmeas chemical plant at Seveso in northern Italy. The cloud contained dioxin which is reported to have been formed because of a sudden rise in temperature within a reactor producing trichlorphenol. [*The Times* (London) 3 August]. Professor Fritz Mori, who designed the plant, stated that the poison could not have been created in his plant without enormous and highly improbable errors. The development of the tragedy could be followed in the (British) press over the next six months.

1 August (Sunday Times): *Doomwatch—Italian style*
A full page coverage on the history of the disaster (on page 13!)—the social and chemical history of the production process. In all the other main production centres for 2,4,5 trichlorophenol, in the United Kingdom, Germany, Holland, and the United States—accidents have occurred. In each case dioxin had escaped although until the Italian disaster the poison had been confined to the factory.

1 August (Observer): *Gas more potent than thalidomide*
Records should be kept of all pregnant women in the area of the accident so that possible malformation of their offspring can be controlled. US Food and Drug Admin. studies suggest that in chickens dioxin is a million times

more potent as a teratogen than the drug thalidomide. Reports of several previous industrial accidents are given—e.g. one at Bolsover in Derbyshire in April 1968. The temperature of the reactor increased to 250°C and then exploded killing the supervising chemist. The whole factory was contaminated and seventy-nine men later complained of chloracne. Even three years later material from the factory—cleaned and re-used—caused chloracne.

5 August (Guardian): *German experts say poisoned land may be barren for ever—page 2*
Another similar accident was reported from Ludwigshafen at the Badische Anilin und Soda Fabarik (BASF) factory in 1953. Fifty-five men contracted chloracne; twenty-one with severe poisoning including damage to liver, kidney, and spleen. BASF were unable to clean the site and the building was finally demolished. The amount of dioxin released in this accident was small compared to the estimated 4 kg released at Seveso.

5 August (Guardian): *The poison cloud over civilisation's future—page 11*
Discussed the lack of knowledge in this area of toxicology. Polychlorinated biphenyls have recently been shown to contain impurities similar to dioxin. Organic chemists realise that chemical processes produce small amounts of side products (e.g. see azo food colours) but they are considered insignificant until their *potency* is taken into account.

9 August (Daily Telegraph): *Poison in the air: is enough being done?*
Discussed the only source of information, from a large report of the American Academy of Science on the effects of the use of herbicides in Vietnam. Without this report (which would not exist except for that war) nothing would be known.

Roche (the Swiss firm responsible) has provided $100,000 to assist with evacuation and decontamination [burning vegetation, removing topsoil to a depth of 20 cm in area of a kilometre or so around the plant;] and finally killing all domestic animals and wildlife. *Reason*: dioxin is very insoluble in water, not biodegradable, thermally stable to 800°C. Wind and rain have already put such plans into jeopardy.

15 September (Times): *Indemnity talks begin*

13 October (Times): An investigator (chemist) was himself a victim of a previous accident being exposed while working with only milligram quantities of the material. He developed chloracne (*British Journal of Industrial Medicine*, 1975)—huge blackheads giving off a rancid odour developed all over his face and neck. Under treatment the chloracne gradually disappeared after a year's time only to be replaced with other troublesome symptoms: continual stomach upsets, bowel disturbances, excessive flatulence, etc. He started

growing long coarse black hairs on his shoulders, back, eyebrows and hands. He and other exposées have enormous cholesterol levels without apparent reason.

17 October (Observer): *Bureaucrats block antidote for poisoned Italian town*
A mixture of olive oil and cyclohexanone was poured over the ground. The idea was to dissolve the dioxin and allow the ultraviolet radiation of the sun to begin the process of breaking down. Unfortunately the weather turned cloudy and started to rain. Because of the danger that the dissolved dioxin would be washed into the rivers or penetrate to the watertable, the method was abandoned. A second approach was suggested using a product Phenobac which had been shown by U.S. Air Force tests to successfully degrade the herbicides, 2,4-D and 2,4,5-T. It consists of a mixture of more than a dozen strains of micro-organisms selected from nature and improved by breeding to feed on unusual chemical substrates. The report suggested 'it is reasonable to assume that microbial degradation of the dioxin is [also] occurring in the cultures'. The rest of the article describes the interaction of this idea with the Italian bureaucracy. In spite of success in a laboratory run on sample of soil, a rival Italian product had to be tested as well. It failed, allegedly because someone, deliberately or by accident, cut the wires leading to a gas chromatograph used to test the soil samples!

17 October (Sunday Times): *The new spectres that haunt Seveso*
Checks on the children's blood and on the local water supply are raising disturbing new fears about the long term effects of the Seveso chemical factory disaster. The check showed a decrease in lymphocytes, the white cells which fight disease, in *every* child tested from Zone A (the area nearest the factory). In spite of its insolubility, the dioxin *had* been moved down by rain water to a depth of nearly ten inches (25 cm) and traces were being found in local rivers.

7 November (Sunday Times)—the rate of spontaneous miscarriage was double the normal for pregnant women in the district.

Dioxin, like DDT, is stored in the fat. Future pregnancies will be affected. The birth deforming (teratogenic) effects will soon be known.

ALTERNATIVE METHODS—BIOLOGICAL CONTROL

Probably the best known and most successful application of using a pest's natural or imported enemies was against a plant—the prickly pear in southern Queensland. During the late 1920s caterpillars brought in from Argentina

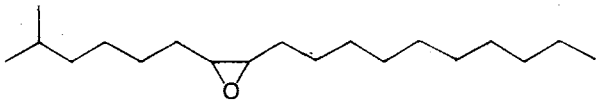
literally ate their way through some 25 million hectares of prickly-pear infested country. The Cactoblastis Memorial Hall near Chinchilla in central Queensland, on the Warrego Highway, commemorates the little grub's feat.

From the time they were introduced by the First Fleet, cattle have been upsetting the ecological balance in Australia with their dung, which gives bushflies, and the blood-sucking buffalo flies, copious breeding places. Australia has native beetles that bury dung, but they evolved to cope with the pellet-like droppings of the native marsupials, not the massive and sloppy offerings of cattle. Dung beetles from Africa have lived with large plant eating animal droppings for millenia and appear to be finding the local drop quite digestible; they were introduced into Australia in the early 1970s.

Insects have been used to control lantana, a fungus has been found effective against skeleton-weed, and a bacterium is being used commercially to control caterpillars.[4]

Sex attractants

One of the most fascinating approaches to insect control involves *pheromones*. These are chemicals excreted externally and may serve to mark a trail, to send an alarm, or to attract a mate. The latter, the sex attractants, are usually excreted by the female to attract males. These compounds are detectable in extremely low concentration by males and can be used to lure males into traps or to disorient them. Field tests have shown that the sex attractant of the gypsy moth is effective at amounts of 0.00000000000001 g (10^{-13}g) in the field. It is interesting that the first claim, in 1961, for having discovered the structure of the attractant was wrong! Research in this area is difficult. In 1967 researchers used the abdominal tips—which contain the glands that produce the sex attractant—of hundreds of thousands of female gypsy moths to isolate a minute amount of attractant, and it was synthesised three years later (see Figure 5.16).



5.16 Sex attractant for the gypsy moth

Some sex attractants are simple—others are complex or even complex mixtures where the *ratio* of chemicals is important. The sex attractant for the common house fly is now known to be (at least) a two-component system; one component is

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3,$$

which is fairly easy to make. This approach to control looks promising for the mobile stages of insect pests.

Juvenile hormones

Juvenile hormones control the rate of development of the larval stage of insects and are switched off to allow development of the adult. Application of a mosquito juvenile hormone will keep mosquitoes in the harmless larval stage. Synthetic hormones have been produced which are much more potent than the natural compounds. This technique is mainly effective for insects which are pests in the adult stage.

Sterilised male

In this method males are sterilised by irradiation from a radioactive source and then let loose in the insect populations. The females of many insect species mate only once so it is statistically possible to wipe out a species in an area quickly. This technique has been successful against the fruit fly in an *isolated* area. The biggest control program is the one in Texas against the screw-worm (a fly) but here the aim, at the moment, is to erect a 'barrier' to prevent the screw-worm moving north out of Mexico.

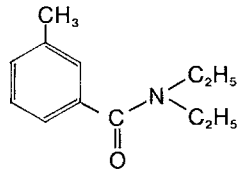
Resistance

The main reason for the development of new insecticides and the search for biological control measures is the development of resistance by insects to present methods. Some insects are resistant to organo-chlorine, organo-phosphorus, and carbamate compounds—at least at levels which do not at the same time give problems of residues in crops. One mechanism for the development of resistance is due to the Darwinian concept of the survival of the fittest. If an insecticide wipes out 99 percent of a population of insects then the 1 percent that survive contain those best suited to deal with the poison and it is these that breed the next generation of insect. So insecticides carefully breed resistant insects! (See also Chapter 10—the use of antibiotics in medicine.)

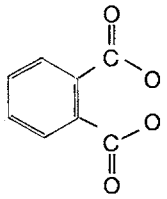
INSECT REPELLENTS[5,6]

On a less drastic level there are several products which will keep insects away, at least from you. In the past, insect repellents contained strong smelling oils such as citronella. These products kept away friends as well as the insects. It was later found that *contact* with the product was needed, not smell. In a study of more than 7000 chemicals, the United States Department of Agriculture found only a few really effective repellents. *N*,*N*-diethyl-*m*-toluamide, deet (Figure 5.17), was found to last twice as long as any other. Dimethylphthalate (DMP) is also very effective, but it is a rather good solvent

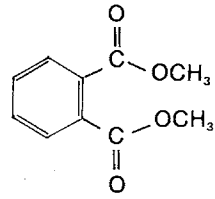
for plastics as well (see Chapter 6). Other compounds found by the study to be effective were ethyl hexanediol (E-Hex) and Indalone (registered trade name for butyl 3,4-dihydro-2,2-dimethyl-4-oxo-2H-pyran-6-carboxylate).



5.17 Deet



a phthalic symbol!



5.18 Dimethylphthalate

Choice found that the concentration of deet and/or ethyl hexanediol determined the *duration* of repellent action. Deet has somewhat better stay-put ability than the other preferred chemicals. On fabric, repellents are not rubbed off as quickly as they are from skin and will last for days instead of hours, but they can stain permanently and damage some synthetics and plastics (such as spectacle frames, watch 'glass').

One point which is not adequately emphasised is that you should be clear in your mind what insect you are intent on repelling.[7] The Australian bush fly *Musca vetustissima* is a notorious nuisance to man throughout Australia (a rumour that the CSIRO breeds them in the wilds around Canberra is hotly denied!). It has been known since 1947 that effective mosquito repellents such as DMP are of no avail and that deet, which is one of the best mosquito repellents, is of little value. An aerosol with an effective repellent was introduced to the Australian market in 1961 (Scram—David Gray Co.). It contains 5 percent of di-*n*-propyl isocinchomeronate, the persistency of which is extended by the addition of the pyrethrum synergist *N*-octyl bicycloheptenedicarboximide. The use of such aerosols a few times a day prevents the flies from *settling* but not from momentary contact to test the site—although that is reduced. Other Australian manufacturers now market aerosols containing this repellent along with the others to repel mosquitoes, sand flies, etc. If it's bush flies you're after (or not after!) then 'isocinch' plus synergist is what to look for on the can.

SWIMMING POOLS

The view of any Australian city from the air presents a myriad of blue spots, mostly round but many oblong and rectangular. These are the backyard swimming pools which have reached plague proportions in recent years because of the use of cheap systems of construction, e.g. fibreglass or PVC liners with iron retaining wall.[8]

Along with every pool there comes a test kit for measuring pH and, above all, the level of chlorine. The test for chlorine has been taken over commercially from the accepted method of analytical chemists without any thought as to whether the two situations are comparable. The accepted analytical method involves the use of *o*-tolidine (4,4′-diamino-3,3′-dimethylbiphenyl) reagent. *o*-tolidine is controlled in the United Kingdom by the Carcinogenic Substances Regulations 1967 (N:897). Even though alternative dyes are available (diethyl paraphenylenediamine), they are not always used.

An analytical test must be sensitive, accurate, reproducible, and immune as far as possible from interference. The *o*-tolidine test was selected by analytical chemists on this basis. In the home swimming pool situation however, interference from cyanide and thiocyanate could well be considered unlikely. In addition to a much lower problem of interference a home test must involve safe chemicals, be easy to use, and be unambiguous. The distinguishability between free chlorine and chloroamines (formed in the pool from reaction of chlorine with nitrogenous waste materials) is critical. With the *o*-tolidine test the skill of a good analyst is required and there is no evidence that any meaningful results are obtained by home users with this test. Anyway, it appears that the chemical is shipped here commercially from the United States as a concentrated (0.1M) solution. As the solution must be checked every six months, it could have deteriorated before repackaging and sale and surely between seasons. If a test involves a hazard and also gives the wrong answer there is really very little left to commend it.

Three years after I submitted a paper to the Australian National Health and Medical Research Council (followed by a little subtle external pressure) *o*-tolidine was placed in Schedule 7 of the Uniform Poisons Standard Act, 1975 (see Chapter 9). This should mean that the States (and Territories) will make this classification mandatory. Included in the submission was an alternative test method. The method, based on a recognised (but not standard) method for testing for chlorine, has been found over a period of three years to work very well in unskilled hands.

Theory:

Free chlorine *bleaches* methyl orange solution quantitatively. At pH value 2 the rate of reaction with chloroamines is very slow and so only the free chlorine

is measured. (The reaction was tested by preparing standard solutions and calibrating them iodometrically immediately before use. A spectrophotometric analysis of the change in absorbance of methyl orange at 510 nm was checked against a calibration curve. This is of course not convenient for home use.)

Method:

A *stock* solution is prepared as follows: 0.50 g methyl orange is dissolved in 100 ml of water. A *standard* solution is made by diluting 10 ml of stock to 100 ml after adding 0.2 g NaCl. The reagent appears to be stable in the dark for years. A *test* solution consists of 24 ml of standard methyl orange to which is added 3 ml of 6M hydrochloric acid (to lower the pH of the solution to 2 after the addition of pool water).

Procedure:

It is essential that all samples from swimming pools be tested *immediately*.

Place 0.25 ml of test solution in a test tube. Add 10 ml of pool water.

A It decolorises instantly. There is at least 1 mg/kg chlorine present, which is sufficient. If you like, proceed.

B It does not decolorise instantly. There is insufficient chlorine present; add more chlorine to pool and repeat test.

Repeat test but use 0.5 ml of test solution.

A It decolorises instantly. There is at least 1.5 mg/kg chlorine present. If you like, proceed.

B It does not decolorise instantly. You have between 1.0 and 1.5 mg/kg of chlorine. This is ideal.

Repeat test but use 0.75 ml of test solution.

A It decolorises instantly. There is at least 1.75 mg/kg of chlorine present. This is too high.

B It does not decolorise instantly. You have between 1.5 and 1.75 mg/kg of chlorine. This is high.

It is simple to organise this test to be performed in a convenient manner. If it is desired to test for chloramines as well, the addition of sodium bromide allows the two to be measured together.

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Chapter 6

THE CHEMISTRY OF HARD- AND SOFT-WARE I

PLASTICS

The common characteristic of the many chemical materials in the synthetic plastic, fibre, and elastomer categories is the presence of molecular frameworks which are extended in one or three dimensions, seldom two. These structures are built up by the repeated joining of small basic building blocks called *monomers*; the resulting compound is called a *polymer*. Differences in the chemical constitution of the monomers, in the structure of the polymer chains, and in the interrelation of the chains, determine the different properties of the various polymeric materials.

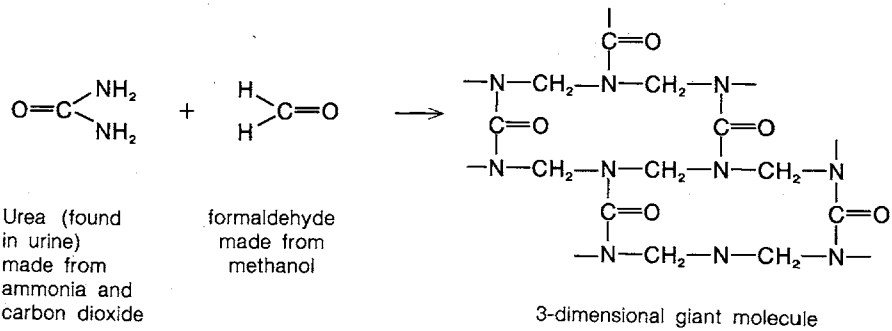
There are many ways of classifying plastics.[1] One method is by division into two groups: those polymers which extend only in one dimension, i.e. they consist of linear chains; and those polymers which have links between the chains, so that the material is really one giant molecule—an example is given in Figure 6.1. The first group of plastics are called *linear polymers*, and are *thermoplastic*, i.e. they gradually soften with increasing temperature and finally melt because the molecular chains can move independently. An example is polythene which softens at about 85°C. The second group are the *cross-linked polymers* which are *thermosetting*: they do not melt on heating but finally blister due to the release of gases, and char; an example is bakelite.

One readily available linear polymer is made from milk. The milk protein casein is separated out (using rennet from calves' stomachs, or acid) and moulded and then cross-linked (hardened) with formalin. Casein plastic is used to make buttons and knitting needles.

In 1907 when Leo Baekeland, a Belgian working in the United States, was looking for a shellac substitute he discovered the first man-made plastic—bakelite—by mixing phenol and formaldehyde. Bakelite is a good electrical insulator and is still used today for power plugs, points, and switches, and

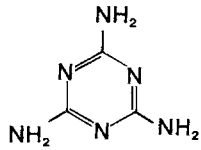
for electric jug lids, etc. It is still the most important cross-linked plastic because it is cheap and rigid (but available only in dark colours—white double-adapters were originally more expensive than brown).

Plastics related to bakelite are made from a combination of urea and formaldehyde—see Figure 6.1. This mixture is also widely used for adhesives that are not water-soluble.



6.1 3-dimensional giant molecule

In melamineware (used for dinnerware) the compound melamine (Figure 6.2) is used instead of urea. Laminated plastics and veneers, e.g. Formica, are made by impregnating several sheets of materials (usually paper or cloth) with plastic, then pressing the sheets together and hardening them in an oven. (Other laminated plastics are made from other materials, e.g. fibreglass is glass cloth plus polyester.)



6.2 Melamine

ADDITION POLYMERISATION

The *linear* polymers can be made by joining together a sequence of monomers but here the possibility for cross-linking in two or three dimensions does not exist. The simplest and most widely used is polyethylene, . . . $-CH_2-CH_2-CH_2-$ . . . . When the chain length exceeds about a thousand units, the material becomes relatively rigid and can be used in a variety of ways. It appears that the linear molecular chains are partly tangled with each other forming amorphous (without structure) regions and are partly packed in an organised way to give very small crystalline regions which impart strength and a higher melting point to the material. Polyethylene (polythene) is made by joining

together monomers of ethylene in a process called *additional polymerisation*, according to the reaction

$$R{-}O{-}O^{\cdot} + CH_2{=}CH_2 \longrightarrow R{-}OOCH_2{-}CH_2^{\cdot}$$

$$+ \text{ next } CH_2{=}CH_2 \longrightarrow R{-}OOCH_2{-}CH_2{-}CH_2{-}CH_2^{\cdot} \quad \text{etc}$$

where $R{-}O{-}O^{\cdot}$ is a free *radical* and acts as an *initiator*. (When a molecule has an odd electon it is called a radical, and is indicated by a dot at the point where the electron is expected to be.) The final product of the reaction is polyethylene, $(CH_2)_n{-}CH{=}CH_2$, termination of the chain often occurring by a reverse of the initiation step. About every tenth unit has a CH_3 branch. Polythene is fairly inert but biodegradability can be built in by increasing the number of double bonds, which gives microbes somewhere to chew (see Chaper 3).

Under normal conditions with the usual catalysts, the spatial arrangements of the branches in the polymer products is random; such polymers are called *atactic*, and an example is given in Figure 6.3.

Ionic polymerisation

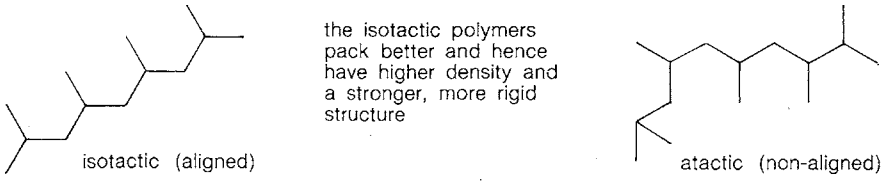
However, when a suitable acid A is used to initiate the reaction, the process becomes a particular type of addition polymerisation called *ionic polymerisation*, the reaction proceeding as follows:

$$A + CH_2{=}CH_2 \longrightarrow \bar{A}{-}CH_2{-}\overset{+}{C}H_2$$

$$\downarrow \quad + CH_2{=}CH_2$$

$$\bar{A}{-}CH_2{-}CH_2{-}CH_2{-}\overset{+}{C}H_2$$

This process allows the use of suitable catalysts to give products in which the branches are arranged in an orderly manner—*isotactic* polymers, illustrated in Figure 6.3 for polypropylene. For polyethylene this form of polymerisation has the advantage of reducing the number of branches that are formed. The process uses lower temperatures and pressures than non-ionic polymerisation and consequently little cross-linking or branching occurs. The truly linear chains pack together to give a *high density* high melting polymer. By use of anionic catalysts mounted on a crystalline solid the geometry (stereochemistry) and shape of the product can thus be determined.



6.3 Polypropylene

The molecules in linear isotactic polyethylene can line up with one another very easily, yielding a tough high density compound which is useful for making toys, bottles, etc. The polyethylene with irregular branches is less dense, more flexible, and not nearly as tough as the linear polymer since the molecules are further apart. Polyethylene is the most widely used of all plastics. It was discovered in the early 1930s and gained prominence during World War II as an insulator for high frequency cables used in radar installations.

As well as variations in density which affect the rigidity of the polymer, a second basic parameter is the *molecular weight*—the number of monomer units combined to give a polymer. With increasing molecular weight there is a corresponding increase in strength, toughness, and chemical resistance. A third basic parameter is molecular weight *distribution*. Because of the statistical nature of polymerisation, polymer molecules show a variation in weight. If most of the molecules fall within a very narrow weight range, products made from the resin will have better mechanical properties (in contrast to chemical properties, which stay much the same regardless of weight range) compared with materials having a mixture of molecules with a broad range in weight. It is the balance in these characteristics that provides the variation in properties of the different plastics formed from the same basic monomer.

Certain properties can also be controlled by adding small amounts of other monomers to the ethylene monomer. Vinyl acetate or ethyl acrylate in low density resins, and hexene or butene in high density resins, will increase branching—thus increasing flexibility and elasticity. Finally, polyethylene can be changed from a linear polymer to a cross-linked polymer by the incorporation of particular reagents. Additives are used in polyethylene and these include slip agents (to decrease frictional properties), anti-block agents (to prevent sheets of molecules from sticking together), and antioxidants.[2]

Most polymers undergo oxidation and photo-initiated degradation and this can be retarded by antioxidants. Low density polythene requires only a very small amount of antioxidant. High density polyethylene, polystyrene, and particularly polypropylene are much more sensitive, both during processing and on exposure to the environment. The result of oxidation is (1) chain breaking which means lower molecular weight and loss of toughness, and (2) cross-linking which means higher molecular weight (but not toughness) and a tendency to be brittle. To combat this a variety of materials are used: primary antioxidants—BHT and BHA (see Chapter 3)—other phenols and amines, peroxide decomposers—thioesters and phosphites. Polypropylene used in, for example, washing machine agitators, requires antioxidants capable of withstanding hot detergent; high molecular weight (>800) derivatives of BHT and BHA are used.

Both high and low density polyethylenes have the same density in the molten

state, so that in a mould the high density polymer shrinks much more than the low density one. The consequent warping of the high density material has been a problem. Shrink wrapping of products is achieved by allowing polyethylene to shrink on heat treatment. A paper-like film resembling parchment is blown from high density polyethylene. Corrugated agricultural drainage pipe with small slits is made from a continuous extrusion blow-moulding process from polyethylene. Polyethylene has replaced wax on the inside of cardboard milk cartons. Blow-moulded polythene bottles and plastic bags are now in use.

Vinyl polymers

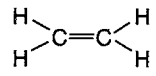
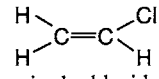
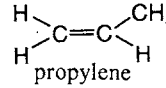
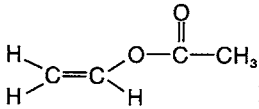
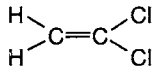
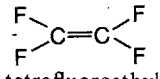
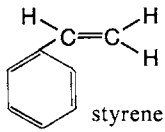
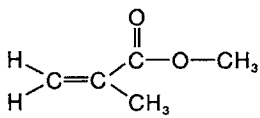
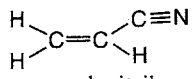
If one of the hydrogens in ethylene is replaced by chlorine, we have *vinyl chloride*. If two hydrogens on the same carbon atom are replaced we have *vinylidene chloride*. If instead we replace a hydrogen in ethylene with acetate (from acetic acid) we have *vinyl acetate*. These monomers can all be readily polymerised. Their molecular structures are given in Table 6.1.

Vinyl polymers and copolymers make up one of the most important and diversified groups of linear polymers. This is because PVC (polyvinyl chloride) can be *compounded* to produce a wide spectrum of physical properties. PVC is used in exterior guttering and water pipes and also the very thin flexible surgeon's inspection gloves.

There are three main processes for polymerising PVC. In the *suspension* process, droplets of monomer are dispersed in water and polymerised. In the *mass* process special agitation is used to polymerise liquid vinyl chloride monomer without water present. The commonest method of making PVC is to disperse vinyl chloride in water as an *emulsion* (using surfactants) with catalysts and heat. The monomer is polymerised to solid particles of polymer which emerge as a suspension in water. This is centrifuged and dried. The important parameters here are the average molecular weight (i.e. length of polymer molecule) and chemical purity. A large molecular weight means a stronger and more rigid polymer but this is more difficult to work. PVC which is to be used as an electrical insulator is generally not made by this method, which is known as *emulsion polymerisation*, because the soap that remains in the polymer as an impurity decreases the insulating properties. However vinyl acetate is generally polymerised by emulsion polymerisation since most PVA (polyvinyl acetate) is used in making emulsion (latex or water-base) paints. Plasticiser and pigment are added. When the paint is applied to a surface, the water evaporates and leaves a polymer film containing pigment and plasticiser.

A wide variety of additives are added to PVC resin depending on the processing required and the end-use (see later this chapter). For example, rigid

TABLE 6.1 *Vinyl polymers*

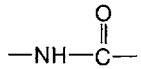
Monomer	Polymer	Main uses
	Common Polymers	
 ethylene	polythene (i) low density (ii) high density	bottles, tubing, sheets, and other moulded objects
 vinyl chloride	Polyvinyl chloride 'PVC'	raincoats, shower curtains, gramophone records, garden hose, rigid clear bottles, swimming pool liners
 propylene	polypropylene	as for polythene, and carpets (isotactic)
	Specialised Polymers	
 vinyl acetate	polyvinylacetate 'PVA'	adhesives, latex paints
 vinylidene chloride	polyvinylidene chloride, copolymer with PVC in Saran	some clinging wraps, some freezer bags
 tetrafluoroethylene	polytetrafluoroethylene PTFE—Teflon	bearings, gaskets, non-stick pan lining, chemical resistant films
 styrene	polystyrene	'rigid foams', moulded objects, electrical insulation
 methylmethacrylate	polymethylmethacrylate perspex, lucite, plexiglas'	'safety glass' but PV Butyral is the adhesive in Triplex and Pilkingtons windscreen glass
 acrylonitrile	polyacrylonitrile	orlon, acrilan textile fibres
	Mixed Polymers	
styrene and acrylonitrile	SAN	latex paints, plastic plates, etc.
acrylonitrile, butadiene, and styrene	ABS	rigid: telephone sets, shoe soles, automobile parts

products contain no plasticiser as they increase malleability, flexible products do not require impact modifiers to improve resistance to impact, and transparent compounds contain no filler, which when used increase cheapness and rigidity. The plasticisers used (and about 80 percent of all plasticisers are used in PVC) are organic liquids of low volatility which facilitate internal movement of the molecular chains. The esters of phthalic acid are most commonly used, particularly di(2-ethylhexyl)phthalate(DEHP), also called dioctylphthalate (DOP), when the composition is a mixture. Combinations of different compounds are used as plasticisers and the amount can vary up to 50 percent of total weight. Because plasticisers are not bound chemically they tend to migrate to the surface where they are lost by abrasion, solution, or slow evaporation, leaving a more brittle, stiff product. The use of non-compatible plasticisers results in the appearance of a 'spew', an oily exudate, on a vinyl product surface.

PVC is used industrially for piping, and for building products (panels, window sashes, gutters, downpipes, conduit). The automobile industry is a large user of flexible PVC—wire insulation, injection moulded knobs, and upholstery (you end up with a partly opaque film of plasticiser on your windscreen and rear window because the plasticiser distils out in hot weather and condenses on the window and the film is hard to remove). Bottles produced from rigid PVC are particularly useful for holding alcoholic or oily products (polythene is permeable to oil).

Mixed polymers of the ABS type (see Table 6.1) are used in trim and bumper strips. These polymers can be electroplated, e.g. chrome plated. This is handy for articles such as coffin handles destined for cremation because the handles are completely combustible—except for a little chromium oxide ash. The ABS polymers are also used for children's toy building blocks (see Chapter 13).

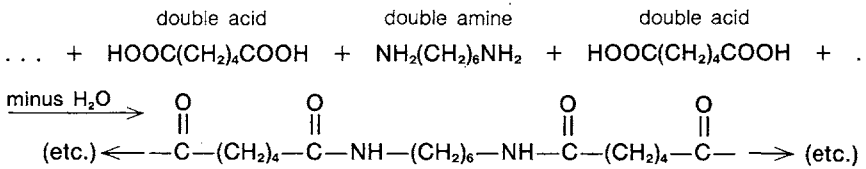
CONDENSATION POLYMERISATION



6.4 The amide bond

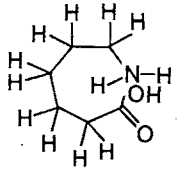
Another form of polymerisation involves the joining together of monomers by removing a small molecule in the joining process. This is called *condensation polymerisation.* An example of such a process is the formation of a *polyamide.* The amide bond is illustrated in Figure 6.4. The original polyamide was

6,6-nylon (Carothers, DuPont 1934) which was developed as a replacement for silk in parachutes. The reaction is:



Stretching aligns the chains and additional weak (hydrogen) bonds between the chains strengthen the fibre. The two different monomers each have six carbon atoms—hence the polymer is called 6,6-nylon.

Why not have *one* monomer with *two different* functional (or end) groups? Why not! Using $H_2N—(CH_2)_5COOH$, which is illustrated in Figure 6.5, the product is 6-nylon.

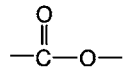


6.5 6-nylon monomer

The amide bond is similar to that formed when (the polymer) protein is formed from individual (but not identical) amino acids. The shorter the $—CH_2—$ chain the more hygroscopic is the nylon. For industrial applications (nylon bearings, etc.) long $—CH_2—$ chains are used to reduce the water absorption—nylons are amongst the toughest plastics, particularly in regard to repeated blows, and they also have the advantage of low frictional properties. Nylons resist many solvents, but they are soluble in formic acid and phenols.

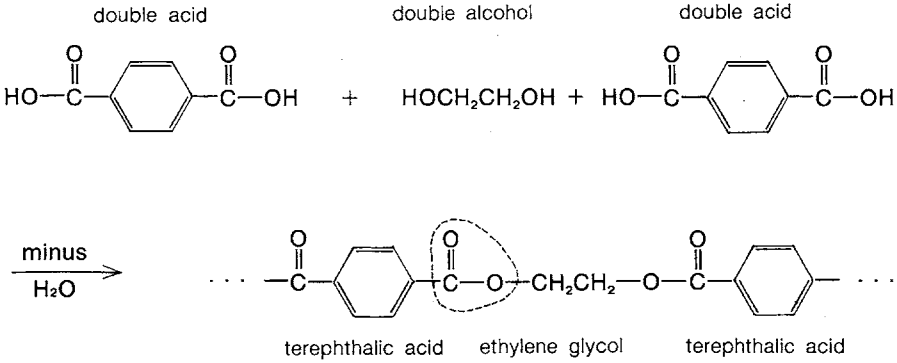
Bags for cooking poultry, roasts, etc. are made from cross-linked nylon as well as from polyester. (I once used a polyethylene bag by mistake—providing a dinner of shrink-wrapped chicken with little gastronomic appeal.) Although the two different bags look the same to a hungry cook, the cross-linked plastic has a higher melting point. It is an interesting exercise to do a dummy run without any food in the cooking bag, and to smell what comes out of the bag by itself.

A *polyester* can be obtained by forming an ester bond (see Chapter 3) instead of an amide bond.



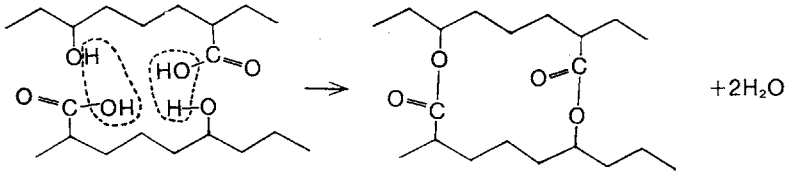
6.6 The ester bond

Compare the ester bond in Figure 6.6 with the amide bond in Figure 6.4. The reaction is:

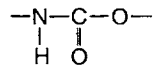


The polyester product of this reaction has numerous trade names—examples are Terylene and Crimplene in the United Kingdom, Dacron in the United States, and Trevira in West Germany. The polyester film material has unusual strength and electrical resistance (mylar film, magnetic recording tape, frozen food packaging). Polyesters are used in fibreglass.

If each monomer has only two functional groups, the resulting polymer is a linear chain. If there are more than two functional groups on the monomers then cross-linkage can occur and result in a much more rigid lattice. An example is the reaction:



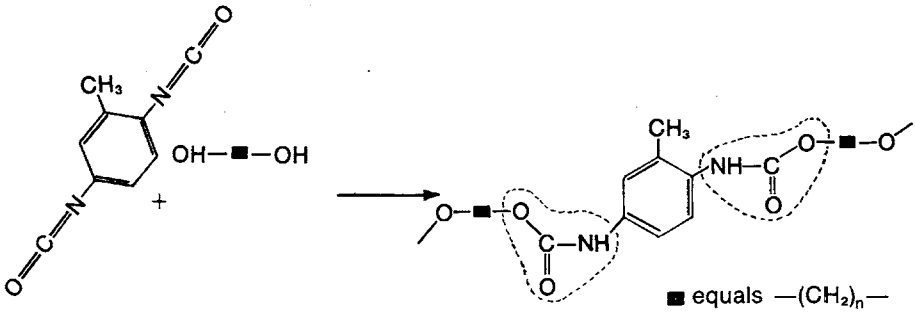
Cross-linked polymers of this type are known as *alkyd* resins and find uses in paint enamels and in the manufacture of false teeth.



6.7 The urethane linkage (cf. Fig. 5.11)

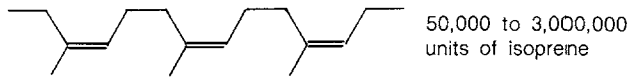
Molecules containing the isocyanate group —NCO, will react with other molecules containing, say, an —OH group to give a *urethane* linkage—shown in Figure 6.7—which is similar to the amide bond in nylons. Polyurethanes can be formed by using bifunctional molecules. Because the isocyanate monomer decomposes with water to form gaseous CO_2, judicious amounts of

water can be added during polymerisation to form polyurethane foam rubber. Heating polyurethanes (in a limited supply of air) can produce HCN (hydrogen cyanide) and even in sufficient air unpleasant vapours containing nitric acid, HNO_3, and NO_2 are formed. Polyurethanes form copious vapours—a burning pillow can fill a room with fumes very quickly.



ELASTOMERS

Natural rubber contains a linear polymer of isoprene, $CH_2{=}C(CH_3)CH{=}CH_2$, in which all the —CH=CH— groups are *cis* (see Figure 3.1) as shown in Figure 6.8.



6.8 Natural rubber

The 'elastic' properties are a result of the degree of extension of the polymer chains which can occur without severe chain breaking. The 'wear' properties are improved by cross-linking using sulphur (as discovered by Goodyear), which produces *vulcanised* rubber.

Synthetic rubbers are produced from related monomers. *But*adiene,

$$CH_2{=}CH{-}CH{=}CH_2,$$

with a sodium, *Na*, catalyst produces *Buna* rubber.

Chloroprene,

$$CH_2{=}C(Cl){-}CH{=}CH_2$$

gives neoprene, an oil-resistant rubber. Copolymers such as SBR (styrene-butadiene rubber) are produced in even greater quantities for vehicle tyres (90 percent of local tyres). To produce all *cis* polymers (which have much higher elasticity than those which are not entirely *cis*) a special stereoregulating catalyst must be used. (The *trans*-isoprene polymer also occurs in nature and is called gutta-percha.)

IMPORTANT PACKAGING PLASTICS—FURTHER TECHNICAL DETAILS

In this section several of the most important polymers currently used in packaging will be described in further detail. The most important properties affecting the safety and efficacy relate to the potential for interaction between the container and its contents.

Polyethylene

The molecular weight distribution has been shown to affect certain of the physical and mechanical properties of polyethylene. The existence of both crystalline and amorphous zones in the polymer is well known and the ratio of these structures can be of critical importance for particular applications. With increasing crystallinity, hardness and chemical resistance increase, while permeability and firm toughness decrease. In Table 6.2 are some of the properties of the polyethylenes which are of interest in the estimation of the potential for interaction with contents.

TABLE 6.2 *Properties of polyethylene*

Property	Low density polyethylene	Medium density polyethylene	High density polyethylene
Density, g/cm^3	0.910–0.925	0.926–0.940	0.941–0.965
Maximum usable temperature, °C	80–100	105–120	120
Clarity	translucent	translucent	opaque
Effect of strong acids	attacked by oxidising acids	slower attack by oxidising acids	even slower attack by oxidising acids
Effect of strong alkalis	resistant	very resistant	very resistant
Effect of organic solvents	resistant below 60°C	resistant below 60°C	resistant below 60°C
Effect of sunlight	darkens	yellows	yellows

Polypropylene

Polypropylene evolved from the discovery of stereospecific catalysts which permitted the production of geometrically regular polymers from olefins. The degree of crystallinity of the polymer can be controlled by varying the catalyst system or the polymerisation conditions. The polymer is a colourless, odourless, thermoplastic material with excellent rigidity even at high temperatures. The resistance of polypropylene to strong acids and alkalis is excellent and the polymer therefore finds applications in the chemical industry. Unlike

polyethylene it does not exhibit cracking phenomena in the presence of polar solvents. Extruded films have good transparency and possess tough tear-resistant qualities. Aromatic or chlorinated hydrocarbon solvents tend to cause swelling. The resistance to continuous heat permits sterilisation of articles fabricated from this polymer. Table 6.3 illustrates some of the properties of polypropylene of interest in packaging. (The copolymer contains other monomers as well as propylene.)

TABLE 6.3 *Properties of polypropylene*

Property	Unmodified	Copolymer
Density, g/cm^3	0.902–0.906	
Maximum temperature, °C	110–150	85–115
Clarity	transparent, translucent, opaque	
Effect of organic solvents	resistant below 80°C	
Effect of sunlight	crazes rapidly unless protected	

Polyvinyl chloride

The instability of unmodified PVC in particular makes it necessary to add heat stabilisers and various other additives prior to its use in manufacturing consumer products. The stabilisers used are generally the salts of tin, lead, cadmium, barium, calcium, or zinc, along with epoxides and organic phosphites, and must be carefully selected for non-toxic applications. As previously discussed, plasticisers are almost always added in varying proportions to impart flexibility. Lubricants such as waxes, metallic stearates, paraffin waxes, or mineral oil represent processing aids. It is not unusual for fillers to be included in the composition.

The popularity of PVC as a packaging material is a consequence of its glass-like clarity and superior chemical resistance. Recent approval by the United States Food and Drug Administration of certain octyl tin compounds for use in stabilising PVC during blow-moulding of containers will probably expand the use of this polymer for food and drug packaging, provided the amount of residual vinyl chloride monomer present in the polymer resin or formed during blow-moulding of containers can be kept within the legal limits set in Australia. Rigid PVC compounds contain less than 5 percent of plasticiser with many formulations containing only small quantities of epoxidised soya-bean oil or none at all. Such containers resist chemical attack by most acids and by alkalis, salts, moisture, oils, and aliphatic hydrocarbons. However, they are attacked by esters, ketones, and aromatic or chlorinated hydrocarbons.

The properties of polyvinyl chloride are set out in Table 6.4.

TABLE 6.4 *Properties of polyvinyl chloride*

Property	Rigid	Flexible unfilled
Density, g/cm³	1.35–1.45	1.16–1.35
Maximum temperature, °C	65–80	65–80
Clarity	Transparent to opaque	
Effect of organic solvents	Resists alcohols, aliphatic hydrocarbons and oils; soluble or swells in ketones and esters; swells in aromatic hydrocarbons	
Effect of sunlight		slight

Cellulosics

Cellulose plastics are prepared by the chemical modification of *cellulose*, a natural polymer common to all plants. As a starting material α-cellulose of high purity is required, each molecule consisting of as many as 3000 anhydroglucose units which are structural (monomer) units similar to glucose. Each unit of the cellulose chain consists of a joined pair of anhydroglucose units oriented in opposite directions.

Direct nitration of cellulose using sulphuric acid as catalyst and camphor as plasticiser yields cellulose nitrate—the first commercial plastic. Although it is a tough thermoplastic with some excellent mechanical properties, its flammability and poor stability to heat and sunlight restrict its use.

An important subgroup of cellulose derivatives is represented by organic cellulose esters such as acetate, butyrate, and propionate. Although available in several grades the cellulose ester plastics are generally characterised by toughness, transparency, and resistance to water and most aqueous solutions. Films made from butyrate are particularly suitable for blister packs.

Some properties of the cellulose ester plastics are given in Table 6.5, which includes data on cellulose acetate sheets and cellulose propionate moulding powder.

TABLE 6.5 *Properties of cellulose esters*

Property	Cellulose acetate sheet	Cellulose propionate moulding
Density, g/cm³	1.28–1.32	1.17–1.24
Maximum temperature, °C	60–105	70–105
Clarity	Transparent, translucent, opaque	
Effects of strong acids	decomposes	decomposes
Effect of strong alkalis	swells	decomposes
Effect of organic solvents	soluble in liquid ketones and esters of lower alcohols; softened or dissolved by chlorinated or aromatic hydrocarbons, little affected by aliphatic hydrocarbons	
Effect of sunlight	slight	slight

More packaging technicalities

Of the wide variety of commercial organic polymers, several major types occupy a commanding position in packaging. Low density polyethylene is fairly flexible, and is outstanding for extensibility, toughness, chemical resistance, and low cost. Its limitations are low strength, inability to recover after stretching, low melting point, translucency, and sensitivity to oxidation—it requires the addition of hindered phenolic antioxidants (see Chapter 3) for stability during processing. It is particularly useful as film packaging, for tubing, and for squeeze bottles.

In contrast, high density polyethylene is more rigid, stronger, less extensible and less tough, higher melting, and more opaque, and finds major use in blown bottles. Polypropylene is stronger still, and even more rigid, less tough, higher melting, and is much more sensitive to oxidation, requiring multi-component antioxidant systems to stabilise it during processing and use. These multi-component antioxidant systems generally include hindered phenols and organic sulphides such as dilauryl thiodipropionate, along with a variety of other synergists. Polypropylene is finding growing use in packaging films, fibres, and moulded forms such as caps for bottles and jars.

Clear unmodified 'crystal' polystyrene has found wide use as vials for solid pharmaceutical tablets. Oriented polystyrene foam is used in packaging of fresh produce. Rubber-modified polystyrene, generally called 'impact styrene' or even just 'polystyrene' is the most widely used plastic for moulded and heat-pressed food packaging, based upon its combination of reasonable rigidity, strength, toughness, chemical stability, and low cost.

Polyvinyl chloride is noteworthy for its compatibility with high-boiling point liquid plasticisers, permitting the plastics manufacturer to use it in a wide range of formulations from rigid strong products such as clear bottles to soft flexible tubing and film. The rigid unplasticised product, generally blended with rubbery polymers for toughness, requires careful stabilisation to prevent liberation of hydrochloric acid and discolouration during melt processing. The most effective stabilisers are: (1) lead compounds, which present serious toxicological problems; and (2) organo-tin compounds of which the dioctyl tins have received hesitant toxicological approval, while the more common dibutyl tins and the newer dimethyl tins raise more serious questions. The safest stabilisers, based on calcium and zinc, are only moderately effective, and relatively unreliable in production. Rigid polyvinyl chloride is characterised by its high density, low softening temperature, and good chemical resistance.

Soft flexible polyvinyl chloride is produced by the addition of liquid plasticisers in the proportion of 30–120 parts of plasticiser per hundred of resin (the polymer before formulation with additives). The most common plasticisers are esters of phthalic, phosphoric, and adipic acids, all of which tend to be extracted from the plastic and migrate into adjacent materials. Some

have found fairly wide acceptance in food and drug packaging, but questions concerning their safety still remain. The ester-type plasticisers can be replaced by polymeric plasticisers—polycaprolactone, nitrile rubber—which entirely eliminate the problem of migration, but this practice is less common than it might be. (These latter are used in plastic pilchers where the product has to withstand repeated extraction by laundry detergent—even then the pilchers become brittle and tear after a number of washing cycles.) The problem of thermal stability is reduced by the lower processing temperature of the plasticised polymer, permitting use of less harmful stabilisers such as calcium and zinc soaps, epoxidised soyabean oil, and organic phosphite esters. Plasticisers also markedly increase permeability, which is undesirable in certain types of packaging. Unlike polyethylene, plasticised polyvinyl chloride combines high extensibility with fairly complete retractability, giving better form stability in film packaging. However when plasticised PVC is used in, say, car upholstery, the plasticiser distils out in hot weather and condenses on the windows in a film which is difficult to remove.

Cellophane—regenerated cellulose in plasticised film form—is of course the original man-made packaging film, and still enjoys wide usage because of its strength, clarity, non-toxicity, and moderate cost. Cellulose ester plastics, such as the acetate and butyrate, generally plasticised by phthalic esters, are outstanding for their toughness, clarity, and gloss, but are considerably higher in price, restricting their use in packaging to those applications in which a glistening appearance is important for marketing. They find considerable application in blister packaging, and see-through windows for boxes.

While the plastics that have been discussed are the most common that are currently used in packaging, other speciality polymers, such as polyvinylidene fluoride, polyester, polyurethane, and polyamide films, are already in limited use and may find growing application as time goes on. Many newer plastics materials are also bidding for their share of the growing packaging and medical markets. It should be remembered that each new polymeric material, along with its positive qualities, may introduce unforeseen problems which will require unforeseen tests and specifications to make it safe for use in food and pharmaceutical packaging. The development of new packaging should never be content to rest secure in meeting the present specifications drawn simply for the present materials and their present problems.

SUMMARY

BASIC PLASTICS MATERIALS USED FOR FOOD PACKAGING APPLICATIONS

reprinted from 'Plastics Technology—Materials' in *Plastics and Food Packaging in Australia*[3]

Polyethylene

This material is available in a variety of grades ranging from low to high density. The *low density* material is tough and flexible and can readily be processed into low-cost film, sheets, and moulded containers. It is probably the most easily heat-sealed of all the plastic packaging films. It is quite unaffected by water at normal temperatures and is widely used for packaging wet commodities such as fruit juices, which are packed in thick-walled bottles. Thin films are relatively permeable to air and essential flavours and their use is therefore largely confined to stable food products such as bread, sugar, and other dry groceries. Being flexible at freezing temperatures polyethylene is widely used for packaging frozen and chilled foods, either by itself or in combination with other materials which provide improved gas barrier properties.

The intermediate and high density polyethylenes are physically stronger materials with reduced permeability to gases. A typical use is for large containers of fluid products such as fruit juices and flavoured cordials. Their greater resistance to heat makes them less suitable for heat sealing operations and they are frequently used in conjunction with other film materials as laminates.

Polyvinyl chloride (PVC)

This material, like polyethylene, is very inert in its chemical behaviour but it is more resistant than polyethylene to oils and fats. The basic polymer is a hard tough material and is usually mixed with varying amounts of plasticiser to increase flexibility and to make processing into useful shapes easier. The amount and type of plasticiser dictates largely the gas transmission properties of films, and a range of permeabilities is available for bakery products requiring the good moisture retention of rigid PVC to fresh meat where the oxygen permeability and transparency of plasticised film is desired. Rigid PVC bottles are popular for packaging vegetable oils and fruit juices. PVC plastisols are used for casting into gaskets for container lids and liners for crown seals.

Polyvinylidene chloride (PVDC)

Copolymers of PVDC with polyvinyl chloride (PVC) can be processed into films processing excellent water-vapour barrier properties and very low permeability to oxygen and most other gases. These good protective properties together with the ability to shrink when heated makes the material suitable for packaging ham, poultry, and other meat products. It is used to improve the gas transmission properties of other packaging films as coatings and as a laminate layer, particularly with cellulose materials.

Nylon

The term *nylon* has become a generic name for a range of polyamide materials

characterised by toughness and good thermal stability. In film form nylons are capable of withstanding sterilisation and they retain their flexibility well at low temperatures. Their chemical resistance is good against all types of foodstuffs except those appreciably acid. The permeabilities to water vapour and gases vary between the different types of nylon. In general they are used as laminates with polyethylene which provides easier heat-sealing abilities for foods such as processed meats and freeze-dried products.

Acrylonitrile

The three monomers which are the basis for the family of ABS plastics can be used in different proportions to give a wide range of properties in the plastic polymer. Various grades are available which have different combinations of physical strength, transparency, resistance to food chemicals and ease of processing. In general the ABS plastics have good all round resistance to food products and they are used widely for containers, particularly margarine. Mixtures of PVC with ABS have excellent processing characteristics and are used for producing low-cost bottles for cooking oils and other foods where transparency and impact strength are prime requirements.

Polystyrene

This material has a tendency to be brittle and is frequently blended with rubber to improve flexibility and impact resistance. It is readily processed into low-cost sheeting which is frequently heat-formed into containers for dairy foods, chocolate, and other fat-containing foods. Material made from foamed polystyrene is very light and low in cost. It is used widely for the trays used for holding cuts of fresh meat in supermarkets, and for drinking cups with insulating properties.

Polypropylene

This polymer is a close relative of polyethylene but is more resistant to a wide variety of foods containing oils and fats, and has a higher resistance to heat, making it suitable for the boil-in-the-bag type of package. It is more rigid than polyethylene and is used for a variety of food containers and for plastic drinking straws. It is relatively free from taste and odour problems when in contact with foods and perhaps its best known application is for large ice-cream tubs.

Potential problems of plastic containers

Desorption

Desorption, or the leaching of plastic components into the contents of the container, has received a great deal of attention. Naturally enough it is the potential toxicity of extractives that has been of concern and has led to the adoption of various tests and specifications by regulatory authorities. The design of extraction procedures which yield data suitable for extrapolation to

the variety of compositions existing in foods or pharmaceutical preparations is an exercise to be undertaken with caution.

Nevertheless a great deal of work has been undertaken in connection with the biological effects of extracted materials, and several pharmacopoeias describe specific tests and specifications. The important role of the extractant in such methodology has often been pointed out. For example one research worker quotes that after six hours of recirculation of physiological saline solution in polyvinyl chloride tubing no di(2-ethylhexyl)-phthalate (DEHP) was extracted. On the other hand whole human blood stored at 4°C for twenty-one days in DEHP-plasticised blood bags *contained 5–7 mg of plasticiser per 100 ml of blood*, almost all of it associated with the lipo-protein portion of plasma. A 4 percent bovine serum albumin was able to extract DEHP from PVC tubing. Significant quantities of DEHP were found in the spleen and abdominal fat of two patients who had received blood transfusions from blood bags of this type.[4]

Photodegradation

Most plastics exhibit varying degrees of degradation upon prolonged outdoor exposure. Polymethylmethacrylate (Perspex) is one of the few exceptions. The ultraviolet and blue parts of sunlight are sufficiently energetic to cause polymer bonds to break. One way of retarding this effect is to add a compound that will absorb the radiation and convert it efficiently to heat. Derivatives of benzophenone are used (particularly in polypropylene) because of their high absorbance of light in the 290–400 nm range (see Chapter 4). Substituted benzotriazoles are also used.

Stress cracking

Polyethylene and polystyrene are examples of plastics subject to environmental stress cracking. Crack resistance tests have shown that alcohols, organic acids, vegetable and mineral oils, ethers, and surface active agents provide an active environment for stress cracking of polyethylene.

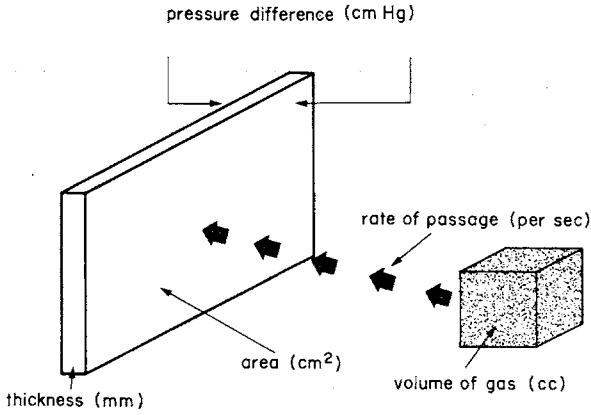
Permeability

One of the important properties of plastics when used as flexible films is their permeability to various gases. This is particularly true when they are used for wrapping food for which permeability of oxygen from the air into the food will hasten spoilage. Table 6.6 gives gas permeabilities for a number of compounds.

TABLE 6.6 *Gas permeability of plastics—after Sacharow*[5]

Name	Permeability to			
	Oxygen	CO_2	Water 90% R.H. 25°C	Nitrogen
Cellulose (PVDC-coated)	0.06	0.4	20	0.09
Cellulose acetate	7.8	68	75,000	2.8
Rubber hydrochloride	0.3	1.7	240	0.8
Polyethylene (low density)	55	352	800	19
Polyethylene (high density)	10.6	35	130	2.7
Polypropylene	23.0	92	680	
Polyvinyl alcohol	0.3	low	soluble	
Polyvinyl chloride (PVC)	1.2	10	1,560	0.40
Polyvinylidene chloride (PVDC)	0.053	0.29	14	0.0094
Polystyrene	11.0	88	12,000	2.9
Polyamide (nylon)	0.38	1.6	7,000	0.10
Polyester	0.3	1.53	1,300	0.5
Chlorotrifluoroethylene	0.10	0.72	2.9	0.03

The permeability P is the volume of gas in cc which passes through a square centimetre of plastic surface 1 mm thick in 1 sec for a pressure difference of 1 cm height of mercury—i.e. the lower the number the slower the gas moves through the plastic film. Figures given are $P \times 10^{10}$ cc cm^{-2} mm^{-1} sec^{-1} $(cm\ Hg)^{-1}$



6.9 Schematic representation of gas permeability of plastics

It is interesting to note that the diffusion rates of O_2:N_2 and CO_2:N_2 are about 4 and 25 respectively in most films. The best oxygen barrier is provided by

polyvinylidene chloride, PVDC, while for water vapour chlorotrifluoroethylene is best. Another set of data is given in Table 6.7, but take care!—the units are different from those in Table 6.6.

TABLE 6.7 *Gas permeability of plastics—after Shell*[6]

Name	Permeability to		
	Oxygen	CO_2	Water Vapour
Cellulose acetate	3–4	27–28	29000–47000
Ethylene vinyl acetate	60	130	2800
Nylon 6	0.12	0.5	2800
Nylon 11	1.6	7	166
Nylon 12	2.4	10	36
Polyethylene			
low density	15	55	420
high density	3	13	60
Polypropylene	4	12	160
Polystyrene			
conventional	4	35	4700
toughened	7	50	
Rigid PVC	0.7	0.4	630

Figures given are $P \times 10^8$ cc cm^{-2} mil^{-1} sec^{-1} $(cm\ Hg)^{-1}$ at 25°C. (1 mil = 0.001 inch.) In fact the SI system of units requires pressure in Pascals. 1 cm Hg = 1.333 kPa.

It is no wonder that CSIRO, in its guide to food storage: *Handling Food in the Home*, recommends flexible film coated with polyvinylidene chloride rather than the common cling wraps or bags made from polyethylene. Note that for the nylons, the permeability for water decreases while that for O_2 and CO_2 increases from nylon 6 to nylon 12. The reason is that there is a change from one polar group for every six non-polar CH_2 groups to one for every twelve. So, overall, nylon 6 is more polar than nylon 12, and hence for polar water the permeability is greater in the more polar nylon 6, but the opposite is true for the non-polar O_2 and CO_2

The gas permeability problem is not restricted to film packaging but applies to thicker bottles as well. For a research chemist the storage of standard reagents in polythene bottles results in a loss of water.[7] This fact makes for a nice experiment: a series of plastic bottles are filled to different levels with water (⅓, ½, ⅔ and full), sealed tightly and then stored at room temperature. The bottles are then weighed once a week over a period of up to one year. The rate of water loss is about 2 percent annually for a full bottle of normal thickness and much greater for the partially filled ones where the surface

exposed to water vapour is greater. Conversely an empty bottle can be kept in a beaker of water with a heavy lid. It has to be carefully wiped dry and weighed.

From the properties of polymers studied so far you may be able to make some educated guesses as to reasons for the distribution in Table 6.8 which gives the use of plastic films in Australia for packaging a variety of foods (cost is also a factor).

AUSTRALIAN STANDARD

Australian standards for plastic materials intended for food contact have been prepared, AS 2070 Part 1 1977 polyethylene; Part 2 1977 polyvinylchloride (PVC) compound. The introduction to this standard provides the scope of the problem.

The packaging and processing of food introduces the possibility of migration or transfer of substances from the packaging or wrapping materials to the food. It is essential that the formulation of the packaging material is selected so that the migration of substances from the package is minimised and if migration occurs no toxic hazard exists to the consumer of the food.

This series of specifications is directed to food grade plastics packaging materials but it is intended that these apply to all plastic materials in contact with food, including, for example, food processing equipment and utensils. It is intended that further specifications will be drafted to cover non-plastic packaging materials.

Toxic effects generally can be either 'acute', i.e. more or less immediate from a single experience with a toxic substance as in the case of most forms of accidental poisoning, or 'chronic', i.e. as a result of repeated administration of a number of small doses each in themselves insufficient to cause an immediate 'acute' reaction, but in the long term having a cumulative effect.

The occurrence of 'acute toxicity' due to plastics in contact with food materials is most unlikely since only trace quantities of the potentially toxic materials are likely to migrate. 'Chronic' effects however are possible where small quantities of a biologically active substance transfer from packaging materials and are ingested in small amounts over a long period of time.

With respect to plastics it is necessary to consider the migration of constituents in contact with food from the plastics composition, and the level present in the food. The extent to which migration occurs will depend upon such factors as the contact area, the rate of transfer, the nature of the food, the type of plastics material, the temperature and the contact time. It is therefore necessary to consider the intrinsic toxicity of each ingredient in the plastics composition, its ability to migrate under extreme conditions in an original or altered form and the amounts which may be safely ingested.

The high molecular mass polymer does not itself pose a toxic hazard because it is inert and essentially insoluble in food. Furthermore, if accidentally ingested

it does not have any toxic effects in its passage through the digestive system.

In the preparation of the polymer, numerous additives are added and the nature of these is dependent on the polymer being produced, e.g. polyvinyl chloride or polyethylene. Examples of the additives which may be used are catalysts, suspension and emulsifying agents, stabilisers and polymerisation inhibitors. These additives are bound either chemically or physically into the polymer and may be present in their original or an altered form. In addition, the polymerisation may leave trace quantities of residual monomer or low molecular mass polymer in the product. It is thus necessary to specify the purity of the polymer to be used as a raw material in a plastics composition for a food contact application.

TABLE 6.8 *A variety of plastic films used for packaging food*

Food Item	Cross Linked PE	HDPE	LDPE	Polypropylene	EVA	PVC 10% Plasticiser	PVC 10%–20% Plasticiser	PVC 20% Plasticiser	PVD/PVC copolymer	NC Coated cellulose	PVC Coated cellulose	PVDC Coated cellulose	Polyester	Nylon 6	Nylon 11	Nylon 12
Bread	×		×	×		×	×	×		×	×					
Cakes	×			×		×	×	×	×	×	×					
Crumpets						×	×	×		×						
Biscuits Chocolate												×				
Biscuits Non-Choc.																
Milk		×	×		×											
Powdered Milk			×									×				
Butter		×	×													
Cheese						×	×	×								
Fresh Meat	×	×	×			×	×	×		×						
Frozen Meat	×	×	×			×	×	×								
Chilled Meat						×	×	×	×							
Processed Meat	×	×	×			×	×	×							×	×
Fresh Poultry	×	×	×		×	×	×	×								
Frozen Poultry	×	×	×		×	×	×	×	×							
Cooked Poultry													×	×		
Cereals		×	×													
Chocolate	×	×	×	×		×	×	×		×	×	×				
Non Chocolate Confectionery	×	×	×	×		×	×	×		×	×	×				

	Cross Linked PE	HDPE	LDPE	Polypropylene	EVA	PVC 10% Plasticiser	PVC 10%–20% Plasticiser	PVC 20% Plasticiser	PVD/PVC copolymer	NC Coated cellulose	PVC Coated cellulose	PVDC Coated cellulose	Polyester	Nylon 6	Nylon 11	Nylon 12
Crisps		×	×							×	×	×				
Nuts		×	×							×	×	×				
Crackers		×	×							×	×	×				
Soft Drinks			×													
Squash			×													
Jam						×										
Marmalade						×										
Honey						×										
Prepared Meals		×														
Fresh Fish	×	×	×			×	×	×								
Frozen Fish	×	×	×			×	×	×	×							
Fresh Fruit	×	×	×			×	×	×								
Frozen Fruit	×	×	×													
Fresh Vegetables	×	×	×			×	×	×								
Frozen Vegetables		×	×			×	×	×								
Flour			×													
Sugar			×													
Rice			×							×						
Coconut			×							×						
Noodles, etc.			×													
Salt			×													

List of abbreviations:

HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
NC	Nitrocellulose
EVA	Ethylene Vinyl Acetate (copolymer)
PVDC	Polyvinylidene Chloride
PVC	Polyvinyl Chloride

Source: Plastics Institute of Australia.

The discussion on plastics could continue indefinitely. A suitable topic on which to conclude could be plastic garbage cans. These have traditionally been made from the left-over plastic (off-cuts) of more exacting products and hence

their composition can be very mixed. One result of this is often a relatively high *glass transition temperature* (see Chapter 8 Paints). In a cold (Canberra) winter when the plastic is below its glass transition temperature, it becomes rigid and tends to split under stress. An Australian standard (AS 1535, 1975) has been set which defines two types of plastic bins—one is a cold climate version for which the stress testing is done at −10°C to −14°C. Dibutyl sebacates are particularly effective plasticisers for producing a low glass transition temperature; however they tend to be too volatile for warmer climates (north of Brisbane) and hence there is a second version in the standard for a regular plastic garbage can.

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Chapter 7

THE CHEMISTRY OF HARD- AND SOFT-WARE II: FIBRES, FABRICS & FLAMMABILITY

FIBRES, YARNS, AND FABRICS

When the material in a fabric is given a name it can refer to a number of different things. It may be the name of the *type* of fibre—nylon or acrylic for instance. It may be the *brand* name of that particular fibre—thus Ceylon is Courtauld's nylon and Orlon is DuPont's acrylic. It may be the brand name of the *yarn*, into which the fibres are usually formed before the fabric itself is made—Agilon is the brand name used for a particular stretch nylon yarn. It may be the brand name of a special *treatment*—Koratron is one for a durable press finish. It may be the brand name of the *fabric*—the Moygashel range, for example, can be woven from natural or man-made fibres. Or a more recent development—it may be the brand name used for the fabric in a particular type of *garment*. Thus Tricopress is the brand name used only on approved shirts and pyjamas made from Bri-Nylon, ICI's brand name for its nylon.

In France and the United States fibre brand names can be used only alongside the name of the type of fibre. Different brand versions of the same fibre type vary somewhat, but their similarities are very much greater than their differences. Some characteristics—notably shrinkage—depend very much on the way the fabric is made up. The type of yarn is also important. Yarn can be bulked to make it feel softer and warmer. Crimplene is the yarn made by bulking Terylene (polyester). It is crimped (coiled or crumpled) to give bulk or stretch or given stretch characteristics in other ways, including twisting. Helanca covers a range of crimped or twisted yarns mainly of polyester or nylon.

Fibre definitions[1]

Cotton is a natural cellulose fibre obtained from the boll of the cotton plant. Its quality is dependent on fibre length, fineness, colour and lustre. Cotton is still the world's major textile fibre and is used alone and in blends.

Linen is produced from the fibrous materials in the stem of the flax plant. These fibres in a great variety of thicknessess tend to cling together, giving linen its characteristic 'thick-thin' quality. Linen does not lint. It has poor resistance to flex abrasion, and may crack or show wear along seams and edges where fibres are bent.

Silk is the only natural *continuous* filament fibre and is obtained by unreeling the cocoon of the silkworm. *Raw* silk contains the gum which bound the fibres to the cocoon. *Wild* or *Tussah* silk comes from uncultivated silkworms. *Spun* silk is made from pierced cocoons or *waste* silk, the tangled fibres on the outside of the cocoon. *Weighted* silk contains metallic salts which make it cheaper and more drapeable but less serviceable. Silk is weakened by sunlight and perspiration, and is yellowed by strong soap, age and sunlight.

Acetate is made from cellulose but is considered a man-made fibre because of the significant alteration in properties. It is closely related to rayon. The fabric dissolves in nail polish, paint remover, and some perfumes, e.g. Acete (DuPont).

Triacetate is similar to acetate but has lower strength when wet and has low resistance to abrasion. It is much more heat resistant and hence shows durable crease and pleat retention, dimensional stability, and resistance to glazing during ironing. It can be machine washed, tumble dried and ironed at temperatures up to 230°C (450°F), e.g. Arnel and Tricel (Celanese).

Acrylic is polyacrylonitrile. Brand names include Acrilan, Creslan, Orlon, Zefran (all of which have 10–14 percent of other monomers added to improve dyeing), Verel (which is 40–50 percent vinyl chloride), Dynel (more than 50 percent vinyl chloride), and Belson, Cashmilon, Courtelle, Crylor, Darvan, Dralon, Teklan, Vonnel. The major contributions of acrylic fabrics are their wool-like qualities and their easy care properties. In comparison with wool, acrylic fabrics are stronger, easier to care for, softer, do not felt, and provide more warmth for less weight. Acrylic is not attacked by common solvents, bleaches, dilute acids, or alkalis, and is resistant to weathering.

Spandex (polyurethane) is usually 5–10 percent by weight in blends with other fabrics such as wool, cotton, linen, nylon, or silk, without changing the look and feel of the basic fibre, but it contributes properties of stretch and recovery—in upholstery the fabric can stretch to conform to the contours of furniture.

Modacrylic is a fibre composed of less than 85 percent and more than 35 percent by weight of acrylonitrile units. Dense, fur-like fabrics are produced by combining fibres with different heat shrinkage capacities, so that a surface pile which resembles the hair and undercoat fibres of natural fur can be formed.

Polyamide—various types are: Nylon 66, Nylon 6, Nylon 11 (Rilsan), Antron, Bri-Nylon, Caprolan, Enkalon, Nylon 4.

Nylon is one of the strongest of all man-made fibres in common use. It neither shrinks nor stretches on washing and is abrasion resistant.

Polyolefins—polyethylene with brand names Courlene, Nymplex, Pylen; and polypropylene with brand names Drylene, Herculon, Marvess, Merkalon, Moplen, Polycreast, Pylene, Reevon, Ulstron. Polyethylene and polypropylene are the lightest weight of all fibres and are difficult to dye. Generally used in blankets, carpets, upholstery, and also apparel. They provide better thermal insulation than wool but when used as a filler in quilted pads (and not treated with wash resistant antioxidant) they can catch fire in a tumble drier.

Polyester: Dacron, Diolen, Fortel, Kodel, Tergal, Terlenka, Terylene, Tetoron, Trevira, Vycron. Polyester is generally used in blends with cotton. It does not shrink or stretch appreciably in normal use; heat-set pleats and creases stand up well and water-borne stains may be quickly and simply removed.

Rayon is made from cellulose into two types, (1) cuprammonium, and (2) viscose. In recent years several 'new' rayons called polynosic rayon have been developed with greater wet strength. Rayon is one of the cheapest 'synthetics' and is easily blended.

Chloro-fibres—polyvinylidene chloride and copolymers: Vinyon, Geon, Krekalon, Movel, Pe-Ce, Rhovyl, Saran, Teviron, Tygan, Velon.

Vinal—poly (vinyl alcohol), poly (vinyl acetate) and copolymers: Kuralon, Mewlon, Vinylon.

Mixed fibres

In a blended fabric two or more fibres are blended before spinning them into yarns. In a combination (or union) fabric, individual yarns composed of one fibre are combined during weaving with yarns composed entirely of another fibre.

Cotton and rayon, for example, are combined with other fibres to increase absorbency and comfort, decrease static build-up, improve dyeability, and reduce production costs. Acrylics improve softness and warmth without adding weight. Nylon adds strength. Polyester contributes several properties to blends, including wash and wear qualities of abrasion resistance, wrinkle resistance, and dimensional stability. Acetate improves drapability and texture.

The quantities of blend needed vary considerably: 15 percent nylon improves the utility of wool; 10 percent of elastic fibres give stretch properties to clothes; the addition of 30 percent modacrylic reduces the flammability of acrylic carpets.

FABRICS AND FLAMMABILITY[2,3]

The large sheets of butcher's paper that are often used for children's paintings can be a fire hazard if there are candles or fires around. Paper can be rendered

non-flammable by soaking it in alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. The protection afforded by the alum can be demonstrated by a simple method. If you write on paper with alum solution and allow it to dry, and then heat the paper carefully (over a warm stove) then the dry invisible alum letters become visible as dark carbonised areas. The alum dehydrates the (polyalcohol) cellulose by acting as a proton donor to form H_2O from the —OH groups of the cellulose. Alum is representative of substances which are inert at normal temperatures but become active when heated. However, high retention of flame-retardant properties on washing and dry cleaning is nowadays required of flame-retardant treatments.

The serious nature of clothing fires was aptly summed up in a National Bureau of Standards (1973) report: 'If your house catches fire you will probably escape with your life and your skin. If your pyjamas catch fire you will probably lose your skin and possibly your life.'[2]

A study of burned garments received through the Burns Research Unit at the Royal Children's Hospital, Melbourne, has allowed Tom Pressley of CSIRO Protein Chemistry Division to devise sensible tests for real-life flammability. The most important single property that makes a garment dangerous is ready ignition by momentary exposure to a flame. A special case concerns fabrics with a flammable pile of cotton or rayon (i.e. cellulose). It can be demonstrated that when a dried (in a desiccator) cotton chenille strip is exposed to a flame, the flame rapidly travels over the whole surface, gradually penetrating and eventually lighting the bare fabric over a wide area, even when the bare material is heavy and slow to ignite. The most dangerous garments are those that ignite readily and become a mass of flame in thirty seconds or less; much summer clothing is in this category.

Garment flammability depends on the *fibre*, the *fabric*, and the *fashion*. Most burns are caused by cellulose fabrics, either cotton or rayon, which ignite easily and burn rapidly. Acrylic fibre (e.g. Acrilon, Courtelle, Orlon) is harder to light than cotton, but once alight burns freely. Polyamides (e.g. nylon) and polyesters (e.g. Terylene and Dacron) are rarely involved when worn as outerwear because their ignition temperatures are above their melting points. When exposed to a flame they melt and retreat away without lighting. However, if supported somehow in a blend with another fibre, the melt can burn fiercely. (A nylon/rayon garment is highly flammable.) These materials are less suitable for underwear; if the outer garment burns, the underwear melts and sticks to the skin. Even before melting, the fibres shrink causing close contact with the skin and so can then efficiently conduct heat from the flame to the skin.

Availability of air has a large influence on a fire, so fabric weight and structure have an important effect on burning characteristics. Loosely spun yarn or lightweight or loosely woven fabric ignites more easily and burns more

rapidly than tightly constructed or heavyweight material. A raised or pile surface is an extreme case of loose structure—the cotton chenille dressing gown is one of the most dangerous garments in common use. Conversely heavy weight and tight structure bring safety: cotton jeans of tightly spun and woven drill are relatively safe. It has been found repeatedly in burned garments that the seams remain unburned and act as a sort of 'fire break' to the spread of the burning.

Garment shape also plays a part: a flowing nightdress, loose pyjamas, ski pyjamas, all from cotton, gives a range from dangerous to relatively safe. Data collected by the Burns Research Unit have shown that overseas figures for flame burns to children are not applicable here and also that the local situation is continually changing. A report in 1964 showed a girl:boy ratio of accidents of 3:1. It changed to 1:3 and in 1975 the ratio was 1:2 (see Table 7.1).

TABLE 7.1 *Summary of statistics on clothing fires (based on 271 cases, January 1971–January 1975)*

		percent
SEX	Boys (1½–14 yrs)	66.1
	Girls "	28.4
	Babies (0–1½ yrs)	5.5
Ratio: 2.3 boys : 1 girl		
CLOTHING	Day clothes	68.3
	Nightclothes (including bath robes)	26.2
	Babywear	5.5
Ratio: 2.6 daywear : 1 nightwear		
FABRIC	Cellulose or cellulose blend	81.4
FIRE SOURCE	Solvent, such as petrol or kerosene	45.0
	Matches	15.0
	Domestic fires	8.1

Source: T.A. Pressley, pers. comm.: results from Burns Research Unit, Royal Children's Hospital, Melbourne

Two points to note from Table 7.1 are (1) that the widely held notion that nightclothes are most involved in burning accidents is not valid; and (2) that whereas domestic fires represent a decreasing hazard, the number of accidents involving flammable solvents such as petrol and kerosene is large (adults too are victims of these accidents). Australian standards have been set to deal with the problem and they are now being made mandatory under State laws. The first standard is AS 1176–1976 which defines *methods of test for combustion characteristics of textile materials*. These methods are divided into three parts:

Part 1. Method for the determination of ease of ignition
Part 2. Method for the determination of burning time and heat output
Part 3. Method for the determination of surface burning properties

Parts 1 and 3 in effect measure how easily the fabric can catch fire, while Part 2 indicates the time available to deal with an accident. (These methods can form the basis of some experiments or demonstrations.) Although the individual tests are not very stringent, their combination provides a stiff hurdle for a material to pass.

The next standard, AS 1248–1976, is entitled *Fabrics for Domestic Apparel of the Low Fire Hazard Type*. This standard sets the performance requirement of a material when subjected to the test methods of AS 1176 in order that it might qualify as a low fire hazard material.

Having dealt with the scientific tests and how a safe material should perform, the actual clothes are dealt with by standard AS 1249–1976, *Children's Night Clothes Having Reduced Fire Hazard*. It is divided into three parts:

Part 1. Children's Night Clothes *having* Low Fire Hazard. These are clothes which are made entirely from *material* which has a low fire hazard, that is material which passes the requirements of AS 1248.

Part 2. Children's Night Clothes *designed* to reduce Fire Hazard. This is a complicated part which gives pictures of suitable designs as well as dimensions for sleeve width, etc. It includes an appendix of the burning behaviour of different materials (given here as Appendix 7.1).

Part 3. Garments which do *not* comply with the requirements of Parts 1 and 2.

Having grouped the nightclothes accordingly, there is finally a standard AS 1989–1976 which sets down the *labelling* requirements. These are given in Table 7.2.

In a *Consumer Leaflet*[4] the Standards Association of Australia gives the meanings of the labels to be:

Low Fire Danger	A relatively safe garment made from fabrics which are slow to burn
Designed to reduce Fire Danger	A garment which is close fitting but made from fabrics which are flammable
Warning High Fire Danger	A highly flammable garment

Both the Australian Capital Territory and Victoria already ban children's nightclothes with surface burning properties on the outside of the garment (e.g. cotton chenille and cotton molleton dressing gowns in sizes 0–14). New

TABLE 7.2 *Labelling of children's night clothes for fire hazard*

Classification	Description	Label wording and size
Category 1 (AS 1249, Part 1)	Garments made from domestic apparel fabrics of the low fire hazard type	LOW FIRE DANGER
Category 2 (AS 1249, Part 2)	Garments designed to reduce fire hazard	DESIGNED TO REDUCE FIRE DANGER FLAMMABLE FABRIC
Category 3 (AS 1249, Part 3)	Garments not complying with category 1 or 2 with limitation and requirements as set out in AS 1249, Pt 3.	**WARNING** HIGH FIRE DANGER KEEP AWAY FROM FIRE 

South Wales has announced a similar ban. And because at least one Victorian store evades the spirit of the law by selling molleton by the metre and giving a free dressing gown pattern with it so that mother can make her own garment, New South Wales is legislating to require that such patterns must carry a warning of the danger of certain fabrics.

The Minister of Consumer Affairs in New South Wales has made a press statement to the effect that he will ban *long* winter weight nightdresses of 50 percent (or more) cellulose—i.e. the long flannelette nightdresses. Light weight nightdresses (less than 120 g per square metre) will be permitted as they are summer weight and ignition sources for *nightware* are less common in summer.

For a more detailed discussion see *Choice* April 1977, p. 137—and see also what lawyers can do to an otherwise simple problem! Further information on the burning behaviour of fibres can be found in Appendix 7.1

Natural fibres, such as silk, and skins are low in flammability. Wool only burns in an upward direction and needs plenty of oxygen, so that local depletion causes the flame to be extinguished. In fact, wool is so sensitive to oxygen availability that skiers are safe—it fails to burn above 1000 metres.

CARPETS

The criterion of a hard-wearing carpet is simple—it should stand up to wear without looking shabby. The type of construction does not affect the wear much —it just makes a difference to how the carpet looks and, to some extent, to what it costs. Where you put a carpet and how much use it gets is very important in assessing its life. Underlay also helps a carpet survive. The two most important factors in the carpet itself are *how much pile* and *what it is made of.*

The pile *density*, *height*, and *weight* will tell you how much pile there is. Density is the thing to look for first. Fibres wear more if you tread on the sides rather than the ends, so the more tightly they are packed the more likely they are to stay upright and the carpet to wear better. Provided the pile is equally dense—the higher the better. The type of fibre used is also important, and is discussed in greater detail later in this chapter.

Have a look

1. Bend the carpet samples back on themselves. You can compare samples by seeing how much they gape—the more easily you can see the backing through the pile the less dense is the pile.
2. Tug at a few tufts to see if they are firmly anchored.
3. Look at the backing—a closer weave lasts longer and the threads should be straight and at right angles. A rigid backing will help to keep the carpet in shape.

Underlay

1. Underlay forms a cushion between the carpet and the floor, so that the carpet wears evenly—particularly important if the floor is uneven.
2. It protects the backing from rubbing and rotting.
3. It stops any dirt that comes through the floor boards from soiling or abrading the pile.
4. It provides extra insulation.
5. It makes the carpet feel softer and thicker.

The greater the likely traffic—the heavier the underlay. Do not use foam with underfloor heating as it can disintegrate. Carpets with heavy foam secondary backing (like many tufteds) do not need a separate underlay. This seems to save money, but of course you cannot use the underlay again if you want to change the carpet. There is also the danger that if the underlay disintegrates before the carpet or if it separates from the carpet backing, the carpet will wear unevenly and more quickly.

The Standards Association of Australia has been preparing a standard for

the classification and terminology of textile floor coverings (DR 74062) in which the various terms are also defined pictorially. It will be a valuable document in this area.

The United Kingdom Consumer Association produced a consumer handbook entitled *Carpets* in 1976 for their Advice Centre Servicing Unit. It was edited by G. Clegg and G. Davies, and is 100 pages of superb value at £7.00. Parts of the first two sections and the last part of Section III are reproduced here with permission.

MATERIALS

The properties considered desirable in a carpet—durability, appearance retention, resilience, dirt and stain resistance, ease of cleaning—depend to a large extent on what kind of fibre the carpet is made of. But the characteristics of a fibre are not always constant. They depend on the way the fibre is used. Wool, for example, is generally considered to be a resilient fibre, but if a carpet is constructed from an inadequate amount of loosely-spun woollen yarn, it will flatten relatively quickly. So, although fibre content is an important consideration, there is a danger in making definite assumptions on this basis alone.

Fibres

Fibres are either: *Staple*—short fibres from ½ inch to several inches long; or *Continuous filament*—fibres of indefinite length. All natural fibres, except silk, come in staple form. Man-made fibres are produced in continuous filament form and then chopped into required lengths. Fibres are used either on their own or blended together in various combinations.

Carpet fibres

Natural			*Man-made*	
Animal	*Vegetable*	*Mineral*	*Regenerated*	*Synthetic*
Wool	Cotton	Metal	Rayon (viscose and various modified versions of viscose is the type of rayon normally used in carpet production)	Polyamide (Nylon)
Hair	Jute			Acrylic (e.g. Acrilan)
Silk	Sisal			Polyester (e.g. Terylene)
	Coir			Polypropylene (e.g. Meraklon)
				Polyvinylchloride (PVC) (e.g. Fibravyl)

Natural fibres are derived mainly from animal and vegetable sources.

Man-made fibres are either: *regenerated fibres*—made from natural fibre-forming materials such as cellulose; or: *synthetic fibres*—made from raw materials such as coal and petroleum which are not natural fibre-forming materials. Fibres are produced from these by forcing the liquid base through fine holes in a 'spinneret' which hardens into filaments by chemical action, evaporation or cooling. With the man-made process it is possible, also, to produce a fibre containing more than one fibre type or two different types of the same fibre, called *bi-component fibres*. The two components can be arranged side by side or 'wrapped' around each other. Using bi-component fibres enables a manufacturer to make a carpet directly from fibre without converting into yarn.

Yarns

To produce a continuous thread of adequate strength for carpet manufacture, fibres are generally converted into yarn (apart from exceptions such as bi-component fibres) by spinning and/or twisting. Extra twist may be put into a yarn to give it better resilience or a more textured appearance. *Staple fibre yarns* are produced by a spinning process. The type of staple fibre and the spinning process used determine the texture of the yarn. In a *woollen spun* yarn the fibres lie in random directions and this increases the bulk of the yarn. With a *worsted spun* yarn the fibres are combed before being twisted. This gives a finer, smoother yarn and is used for more expensive, patterned carpets to give clarity to the design. The yarn formed as a result of the spinning process is referred to as a *single* yarn. Two or more of these can be twisted together to form *two-fold, three-fold, four-fold,* and so on.

Continuous filament yarns consist of filaments combined with a small amount of twist to prevent them separating. Variations can be achieved by crimping (processing by heat, steam or pressure) individual filaments to give a fuller texture. Fibres treated in this way are called *bulked continuous filament* (bcf). Sometimes continuous filaments are chopped into staple fibres to give a more 'woolly' appearance. The thickness of continuous filament yarns can be varied according to the size and number of filaments twisted together.

Blends of one or more different fibres in a yarn are produced either for economy or to combine the advantages of different fibres. Generally, at least 20 percent of one fibre is required to affect the carpet's overall characteristics but the amount differs depending on the fibres involved—for example adding as little as 5 percent of nylon to a viscose rayon carpet improves its wearing qualities. A common 'economy' blend is 45 percent wool 45 percent viscose 10 percent nylon. The large proportion of the cheaper fibre, viscose, gives the carpet bulk whilst keeping the price low. Another popular blend is a combination of 80 percent wool and 20 percent nylon. The introduction of nylon gives greater durability than wool alone yet the carpet retains the appearance and feel of wool. Some other commonly used blends are: acrylic/nylon, nylon/viscose, acrylic/viscose, acrylic/viscose nylon.

FIBRE CHARACTERISTICS

Animal fibres

Wool

Although expensive, wool is considered nearest to an ideal fibre for carpets. It retains its appearance well, doesn't soil easily, is soft, warm, resilient and has good resistance to burning and static. Wool is moderately hard wearing if used at a high enough density. *Blends*: Nylon is often combined with wool to improve durability. Wool, nylon and viscose are blended to produce a lower priced carpet.

Hair (from animals other than sheep)

Hair fibre is usually tough, rather coarse and fairly cheap. It is used mainly in the production of cord carpets and felt underlays. *Blends*: It is sometimes combined with viscose rayon and wool to give a softer feel.

Silk

A luxurious and hard wearing fibre, which because of its cost is normally found only in intricately designed Eastern carpets.

Vegetable fibres

Cotton

A hard wearing fibre which is cheap but compresses and loses its appearance quickly. It is most suitable for bathroom rugs which can be washed easily.

Jute

Used mainly as a backing material but sometimes as a cheap fibre in cord carpets. It is hard wearing but loses strength when wet. It is difficult to clean and suffers a rapid loss of appearance. *Blends*: It is frequently blended with viscose rayon for core carpets to combine durability with softness.

Sisal

Used to make cord carpets and matting. It is fairly cheap and very hard wearing but feels harsh.

Coir

A very cheap, harsh but hardwearing fibre used for matting.

Mineral fibres

Stainless Steel

These fibres are sometimes blended in very small quantities with other fibres to counteract static charges. These are used mainly for contract (commercial) carpets because of the high cost.

Man-made fibres regenerated

Viscose Rayon

(e.g. Darelle; Evlan; Evlan M; Fibro). Ordinary viscose is a cheap, low performance fibre which soils and flattens easily. It is easily flammable but a flame-retardant version —Darelle—is available. Modified versions with improved resilience and higher resistance to abrasion and soiling are now being produced for carpeting—Evlan, Evlan M. *Blends*: Both ordinary and modified viscose are used in blends with wool and/or nylon for medium to low price carpets.

Man-made fibres: synthetic

Nylon

(e.g. Antron; Bri-Nylon; DuPont Nylon; Enkalon; Monsanto Nylon; Timbrelle). Basically an expensive fibre but because of its good durability it can be used in low density to produce inexpensive carpet. Nylon is not easily flammable but will melt if exposed to flame. Traditionally, Nylon's main problem has been its retention of static electricity. Consequently it attracts and shows dirt more than most other fibres and needs frequent cleaning. (This is fairly easy, but it can be difficult to remove animal hairs from a nylon carpet). Recently developed nylons are considerably improved. *Blends*: Nylon is often blended with wool and other fibres to add greater durability.

Acrylic

(e.g. Acrilan; Courtelle). The nearest of the synthetic fibres in appearance to wool, with a somewhat similar feel. One of the more expensive synthetics but cheaper than wool and suffers a greater loss of appearance. It has good resistance to abrasion and wears well. Although generally less liable to retain static than nylon, it still has a tendency to attract dirt. However, it has good stain resistance and can be cleaned easily. It is fairly flammable. *Blends*: with nylon and/or wool.

Modacrylic

(e.g. Dynel; Teklan; Verel). Modified acrylics have better flame resistance and, it is claimed, better wear and soil resistance than ordinary acrylics. Consequently they are more expensive.

Polyester

(e.g. Dacron; Terylene). Has similar properties to nylon but is less resilient. However it is not used to the same extent in carpets because it is both more difficult and expensive to produce; but its soft handling qualities make it particularly suitable for shag style carpets (carpets with a pile height over an inch long). *Blends*: Sometimes blended with nylon.

Polypropylene

(e.g. Fibrite; Meraklon). A fairly cheap fibre used mainly as a backing material but sometimes as a pile fibre. As such, it is very hard wearing and has good resistance to soiling and staining. It is particularly suitable for bathrooms and kitchens as it absorbs virtually no moisture and usually has a plastic backing. *Blends*: Occasionally with nylon.

Polyvinylchloride

(e.g. Clevyl; Fibravyl; Movil). Because PVC fibres are non-flammable they are sometimes blended in small quantities with other fibres to improve flame resistance . . .

CARPET BACKING MATERIALS

There are two methods of carpet construction:

a) Where the backing is woven at the same time as the pile (woven and some cord carpets).
b) Where the pile is inserted into or stuck onto an existing backing (tufted and non-woven carpets).

Carpets may have one or two layers of backing: *Primary Backing*—the backing in or to which the pile is anchored. *Secondary Backing*—sometimes added to give a carpet extra stability and resilience.

Primary backing materials

Jute

Woven into hessian is the traditional fibre used for both methods of carpet construction. It gives a carpet a thick, stable and durable backing. It is also strong unless weakened by water. This makes it susceptible to mildew (though it can be proofed against this). The yarn usually has a high oil content which can work its way into the carpet pile and cause soiling, unless controlled during the yarn making process. High density carpets are usually backed with jute to give adequate dimensional stability.

Polypropylene

Was developed as an alternative to jute and is now the material used most frequently. Its advantages over jute are that it is lighter, cleaner, more consistent in quality and resistant to water. A disadvantage of polypropylene is that it does not pick up colour well when the carpet is dyed. With low density pile carpets, this can sometimes cause the backing to show through the pile (referred to as 'grinning'). This can be overcome by adding a thin web of nylon—which will take dye—to the backing. This is called *needleweave*. Polypropylene is available in two forms: *Woven*: Granules of polypropylene are heated and extruded as a film, slit into strips and woven. *Non-Woven*: Usually 'spun-bonded' where filaments are compressed by heat into sheet-form. Non-woven polypropylene will not unravel which prevents the tufts separating, making it particularly suitable for backing carpet tiles and for closely tufted carpets.

Some manufacturers now combine the advantages of both jute and polypropylene in a woven *poly-jute* backing fabric.

Cotton

Is sometimes used as a primary backing material for woven carpets. It is stronger than jute and less affected by water.

Adhesive layer

On almost all tufted and non-woven carpets a coating of latex or PVC is added to the primary backing to strengthen tuft anchorage. Some woven carpets are coated with a starch or modified starch solution, sometimes combined with synthetic resin or latex.

Besides improving tuft anchorage this gives woven carpets additional stiffness and prevents fraying.

Secondary backing materials

Most woven carpets do not structurally need a secondary backing (though some Axminsters are now made with a sheet of foam bonded to the back of the carpet to act as an integral underlay). Most tufted carpets need a secondary backing for added stability and resilience. The most common form of secondary backing is rubber foam or crumb which also acts as an integral underlay. This saves the consumer money in that she doesn't need to buy separate underlay and she will probably be able to fit the carpet herself.

Foam backings were originally used to give support to cheaper, lightweight carpets and were mainly of mediocre quality. Since then much improved and heavier grades of foam have been produced and quite expensive carpets are now foam backed.

Foam

Latex foam is now made mainly from synthetic rubber combined with fillers and additives. The density is controlled by the amount of air introduced into the foam latex mixture. The mixture is then applied to the back of the carpet, 'set' under infra-red heaters and dried to remove excess moisture.

Crumb (or sponge)

This is usually black, often made from reclaimed rubber (e.g. old tyres) which is broken up into granular form then pressed together under heat with a binding agent. It is usually cheaper than foam.

Polyester and PVC

These are also used occasionally for foam backings. They absorb less water and are stronger than latex but more expensive. They are sometimes used for backing carpet tiles where greater dimensional stability is required.

Polypropylene

This is only used as a secondary backing where the primary backing is also polypropylene because of the problems of adhering polypropylene to jute. However, some manufacturers now highlight the fact that their carpets are entirely polypropylene-backed and therefore suitable for potentially wet areas like bathrooms.

Jute

Jute is sometimes used as a secondary backing material but this is increasingly less common. . . .

CONSTRUCTION

The way a carpet is constructed is no longer such an accurate guide by which to assess it. At one time 'woven' was synonymous with 'quality' carpets, and other types with 'cheapness' but this is not particularly true today. The price and performance of a carpet now relate more to the type and amount of fibre used than the method of construction. However, construction still has some bearing on a carpet's durability and appearance retention.

The three main methods of carpet construction are: *woven*, *tufted* and *non-woven*.

Woven carpets

Woven carpets are those where the backing is constructed at the same time as the pile. *Wilton* and *Axminster* are the names given to the two main weaving processes and *not* brand names as is commonly believed. While many high quality carpets are Wiltons or Axminsters, there are others of mediocre quality made by these methods. Although the majority of woven carpets are made from wool, all-synthetic fibre wovens are now available.

A woven carpet is made of warp and weft yarns intertwined. *Warp Yarns* run lengthwise and are of three types:

1) *Chain Warps* which go over and under the weft yarns to bind them. These may be made of cotton or viscose rayon but are now increasingly polypropylene.
2) *Stuffers* which run through the centre of the carpet between the chain warps and the two layers of weft to add bulk and to strengthen the carpet. Stuffers are normally made from jute but sometimes cotton or wool.
3) *Pile Warps* form the carpet surface and are made from all types of fibre used in carpets.

Weft Yarns run from side to side of the fabric. Normally there is both an upper and lower weft. They are usually made from jute or cotton.

Wilton

This process can produce both plain and patterned carpets. They can be *cut pile* (this gives the smooth, level surface most commonly associated with the name Wilton); *loop pile* (Brussels is the name given to loop pile Wiltons); low loop pile (cord carpets) and mixtures of cut and looped pile.

Most Wilton carpets are made on wire looms. The pile warp yarn is carried under the weft and then over a flat wire which raises it above the backing yarns. The width (or height) of the wire determines the depth of the pile. The yarn forms loops which are left uncut for Brussels and cord carpets (a round rather than a flat wire is used for the latter). A small blade, attached to the wire, cuts the loops as the wire is withdrawn to give a cut pile surface.

Figured (patterned) Wilton. These are produced by running several pile yarns of different colours (up to five) through the weave. The carpet design is transferred to a punched card operated mechanism called a *jacquard* which selects the right coloured yarn for each tuft position, lifting it to the surface and leaving the other yarns hidden in the carpet (these yarns are called unused or dead yarn).

The pile yarn is drawn from *bobbins* arranged on *frames*. Each colour comes off a separate frame. A carpet is referred to as a 2, 3, 4, or 5 frame Wilton depending on the number of colours used.

Five colours are normally the maximum but more can be incorporated by *planting* (substituting) one coloured yarn for another in parts of the design. As this is an expensive process it is only used where both the heavier quality of a top grade Wilton and a wide variety of colours are required.

The dead yarn in a patterned Wilton gives it a more solid (and more expensive) construction than a plain Wilton. Occasionally, though, plain Wiltons are made by the jacquard process to produce heavier quality carpet.

Sculptured (sometimes called *embossed* or *carved*) *Pile* Wiltons can also be produced. These combine straight and twisted yarn, cut and loop pile or pile of differing heights (by using varying heights of wire). 'Shag style' Wiltons (carpets with a pile about an inch long) are made by a variation in the kind of wires used.

Face-to-Face Weave is a more economical way of producing a Wilton. Two carpets are woven at the same time by the same pile yarn crossing between two sets of backing yarns. A blade, the width of the carpet, cuts through the pile as it forms, so separating the two carpets. The face to face method is mainly used for lower quality, plain Wilton.

Axminster

This process produces only a cut-pile surface as each tuft is inserted separately. There is no unused yarn running through the carpet which makes it cheaper than the Wilton method. The construction process, also, allows for much greater variety of colour and design, so Axminster carpets are often highly coloured and intricately designed.

Gripper Axminster is the most common method of making Axminsters. The carpet design is transferred to jacquard cards which programme the colour selection and the yarn is mounted on frames behind the loom (as in figured Wilton). Eight is the most common number of frames and although 12 and 16 frame looms are available additional colours are still usually introduced by planting. The different coloured yarns are threaded through carriers which extend across the loom and are controlled by the jacquard mechanism. A row of beak-like pincers (grippers) moves up and takes hold of the free ends of the pre-selected yarns which are then severed at the required length from the carrier. The grippers, carrying the tufts, move down to the weaving position where the tufts are released and bound in place by the backing yarns.

Each colour of yarn used in the pattern in *Spool Axminster* is wound onto 27 inch spools in the order it appears in the design. The required number of spools are placed side by side to make up a complete row of the pattern. As many different rows of spools as are needed to form the pattern repeat are assembled and then mounted between a pair of chains above the loom which carries the rows one after the other to be woven into the carpet. At each stage, the required spools are lowered from their chains and the yarn is drawn down through the backing threads and held there while the spool is withdrawn. The pile yarn is severed from the spool which is returned to the chain. The next row of spools is then lowered to repeat the process.

Spool Axminster is the most flexible weaving method for patterning as, theoretically, each length of yarn wound on to the spool can be a different colour. In practice economic considerations limit the number of colours used, although some floral chintz or Persian designs incorporate over 30 or 40 different shades. Because of the cost of setting up the design, spool Axminster is normally used only for long production runs.

Spool Axminster carpets are less tightly woven than gripper Axminster and need a final coating of modified starch or latex to give them added stiffness. Carpets requiring the colour potential of the spool process and the tighter structure of the gripper process can be produced on a *Spool/Gripper* Loom. The yarn is wound on spools and inserted into the carpet by a gripper mechanism.

If it isn't obvious from the colours in the design, the backing will show which process has been used. With spool Axminster, the backing is smooth and the pattern shows through; with a gripper Axminster the backing is heavily ridged and the pattern does not emerge.

Tuft density

The quality of a carpet is largely determined by the amount of pile it contains (pile density) and its weight. The higher the density the better. In *Axminster* carpets the density can be calculated by multiplying the *pitch*—the number of pile tufts measured across the width of the carpet (fixed at 6 or 7 tufts per inch) by the *number of rows per inch* (which varies between 4 and 10). Therefore, with six pitch Axminster the tuft density ranges from 24–60 tufts per square inch and with seven pitch from 28–70 tufts per square inch.

The *weight* is calculated from the tuft density (number of tufts per square inch), the pile height and the count of the pile yarn.

With *Wilton* carpets, the tuft density and weight of pile are calculated in a similar way but the pitch is not fixed as in an Axminster construction. The number of *frames* used in making the carpet is also important in determining quality as the dead yarn contributes to the strength and resilience of the product.

Identification

Wiltons and Axminsters differ mainly in the colours and designs which can be produced. As an aid to identification, Wiltons have a more closely woven backing and, when patterned, dead yarn shows among the backing material. Only one weft thread normally shows in the backing of a Wilton. In an Axminster double weft threads are visible.

Kara-loc weave

Consumers may see Kara-loc given as a method of construction on some carpet labels. It is another (but rather different) type of weaving process which is used solely by one manufacturer (Crossleys). Kara-loc, it is claimed, allows for a greater variety of patterning, particularly in achieving sculptured and textured effects.

Tufted carpets

Tufted carpets weren't introduced until the mid 1950's and early production problems gave them a reputation of cheapness and inferior quality. They are quicker and more economical to produce than woven carpets and therefore predominate in the lower price ranges. However, expensive, high performance tufted carpets are also now available.

Tufted carpets are produced by inserting the pile yarn into a prepared backing material. The yarns are threaded through a row of needles across the machine. A downward movement of the needles forces the yarn through the backing. Loopers (hooks) hold back the length of yarn required to make the loop while the needles are withdrawn. The loopers then release the loop to pick up the next insertion of yarn. Where a cut pile carpet is being produced, blades sever the loops as they are formed.

When the stitching process is complete, the carpet backing is coated with adhesive to secure the tufts or loops in position. Usually a secondary backing material is also applied.

Colour and design

A major drawback in tufted carpet production has been the limitations in colour variation and design. However, recent developments with differential-dyeing yarns and

colour printing techniques have increased their patterning potential. Sculptured pile effects can be achieved by adding patterning attachments to the tufting machine. Moving the position of the needles creates zig-zag designs. Coloured patterns can be produced by threading the needles with different coloured yarns and programming them to tuft at varying heights.

Tuft density

Slightly different terms are used to express the tuft density of a tufted carpet. Instead of pitch (as in woven carpets), the distance between the tufts widthways is referred to as *gauge* (the smaller the gauge, the better). The most commonly used gauges are $\frac{3}{16}$ in., $\frac{5}{32}$ in., $\frac{1}{8}$ in., though carpets are also produced in gauges of $\frac{1}{10}$ in., $\frac{1}{12}$ in., or $\frac{5}{64}$ in. The number of rows per inch down the length of the carpet is referred to as *stitches per inch* and varies between 4 and 12.

Non-woven carpets

This term refers to the miscellaneous collection of carpets which do not involve *weaving* (woven carpets), *stitching* (tufted carpets), *knotting* (the method used for making carpets by hand) or *knitting* (a popular method of carpet construction in the US and Europe but mainly used only for rugs in the UK).

The two main manufacturing processes for non-woven carpets are *needlepunch* and *bonding*. Neither of these is used to the same extent as weaving or stitching. However, because of their relative cheapness, they are becoming increasingly popular.

Needlepunch (also referred to as needlefelt or needleloom)

'Endura' (Gilt Edge) is a well known carpet made by this method. Needlepunch carpet is cheap because it uses loose fibre rather than yarn. This means there is no pile but a fibrous surface which is punched into the backing by a series of barbed needles. The needles move up and down very rapidly, entangling the fibres with the backing material. The backing is coated with an adhesive to secure the fibres.

The fibre used can be of one type or a mixture. Some needlepunch carpets have a top layer (wear surface) of hardwearing fibres—like nylon—and a substrate of jute or polypropylene.

Bonded

Bonding is the technique of using adhesive to stick pile fibres onto a pre-manufactured backing or support fabric. Some of the more common uses of this process are:

Non-Woven Cord carpets (e.g. Criterion Cord). Loose fibre is pressed into a ridged fibrous web, coated with adhesive and bonded to a similarly coated backing material.

Vernier Method (e.g. Stoddard's Telsax). The pile yarn is folded between, and bonded to, two parallel surfaces of backing material and then cut through the centre to form two cut pile carpets. This is a cheap method of producing a carpet which is similar in appearance to a plain Wilton but lacking a Wilton's high degree of tuft anchorage.

Flocked Carpet. The surface pile is composed of short lengths of fibre (usually nylon) which are implanted vertically into an adhesive coated backing fabric by means of an electrostatic attraction between the fibres and the backing. At present, this type of carpet is used mainly in the contract field and for carpets in cars.

Carpet fibres compared

Pile Fibre	*Basic Cost*	*Durability*	*Resistance to Flattening*	*Soil and Stain Resistance*	*Ease of Cleaning*	*Handle*	*Flame Resistance*	*Resistance to Static*
Acrylic	Expensive	Good	Very Good	Shows dirt easily. Good stain resistance.	Easy; needs to be done frequently. Doesn't soak up liquids.	Resembles wool in appearance and handle.	Is ignited fairly easily but modified versions (modacrylics) are available which have a high level of flame resistance.	Good
Cotton	Cheap	Good	Poor	Fair for stains, poor for dirt.	Easy; needs to be done frequently, colours may run.	Soft, smooth pile.	Fairly flammable	Good
Nylon	Fairly expensive	Very good	Good	Shows dirt easily (although there are some nylons —like *Antron*— which conceal dirt more effectively). Good stain resistance.	Easy; needs to be done frequently.	Rather harsh but nylon for carpets is now being developed with a more wool-like feel.	Moderate. Will melt and may continue to burn slowly.	Poor
Polyester	Expensive	Good	Fairly Good	Shows dirt easily. Good stain resistance, except to oil.	Easy; needs to be done frequently. Doesn't soak up liquids.	Fairly soft texture.	Moderate. Will melt and may continue to burn.	Poor
Polypropylene[1]	Fairly cheap	Very good	Fair	Good resistance to dirt and stains.	Very easy. Doesn't soak up liquids.	Fairly harsh	Moderate. Melts and may continue to burn slowly.	Fairly Good

Sisal	Cheap	Good	Good	Fair—dirt builds up underneath.	Fair—difficult to vacuum clean. Dirt can lodge in or under the pile.	Harsh	Fairly flammable	Good
Viscose[2]	Cheap	Fair	Poor	Shows dirt easily. Fair stain resistance.	Easy, but should not be saturated with shampoo.	Fairly soft and warm.	Burns readily	Good
Modified Viscose[3]	Cheap	Fairly good	Fair	Shows dirt easily. Fair stain resistance.	Easy, but should not be saturated with shampoo.	Fairly soft and warm.	Burns readily but *Darelle* is flame-resistant.	Good
Wool[4]	Expensive	Good	Very good	Good	Easy, but may felt or shrink if made too wet.	Soft, warm.	Good. Does not burn easily, largely self-extinguishing.	Good

[1]Good for kitchens and bathrooms.
[2]Used on its own, only suitable for light traffic areas.
[3]Has better wear resilience and soil resistance than ordinary viscose.
[4]Susceptible to insect attack but usually moth proofed. Can felt under damp conditions.

APPENDIX 7.1

Appendix B from AS 1249, Parts I and 2—1976

Burning behaviour of different classes of fibres

(The list of trade names is not intended to be all-inclusive but covers most fibres that are available in Australia.)

Class of fibre	Generic name	Trade name	Notes
Natural cellulosic	Cotton Linen		All burn readily unless given adequate fire-retardant treatments
Protein (animal)	Wool Silk Mohair Hair and fur		Usually difficult to ignite, burn slowly and in heavier weight cloths tend to extinguish. Very light weight cloths may burn strongly
Man-made			These fibres exhibit a variety of flammability properties. Some burn, some melt and drip away yet others do not support combustion.
	Rayon (including viscose, cupra-ammonium, polynosic)		Rayons burn readily unless given an adequate fire-retardant treatment
	Acetate rayon (including triacetate)	Arnel, Dicel, Tricel	Acetate fibres burn before melting. They ignite and burn readily and generally drip molten polymer
	Fire-retardant rayons and polynosics		The fibre is made with fire-retardant compounds incorporated in the resin. It burns slowly and is more difficult to ignite than natural rayons

Class of fibre	Generic name	Trade name	Notes
	Acrylic	Acrilan, Beslon, Cashmilon, Courtelle, Cresian, Crylor, Dolan Dralon, Orlon, Zefran	Acrylic fibres generally burn before melting, although some ignite only with difficulty. Once ignited acrylic fibres burn strongly and may drip molten polymer
	Chloro-fibres (polyvinyl chloride, polyvinylidene chloride and copolymers)	Clevyl Geon, Movil, Pe-Ce, Teviron, Thermovyl, Tygan, Valren, Vinyon, Leavil Rhovyl	These fibres generally do not burn under normal conditions. On application of a flame they shrink away. If ignition does occur, burning ceases on removal of the flame
	Modacyrlic	Kanekalon, Teklan, Verel Vonnel	Fibres are difficult to ignite. Flammability properties very similar to those of chloro-fibres
	Polychlal	Cordelan	These fibres are difficult to ignite. Flammability properties very similar to those of chloro-fibres and modacrylics
	Polyamide	Antron, Brinylon, Caprolan, Celon, Enkalon, Nylon 6, Nylon 11 (Rilsan), Nylon 66, Nylon 610, Perlon	These fibres melt when heat is applied and generally drip away from the flame. Because of this they may not burn. When blended with some fibres (e.g. cotton, rayon or wool) they are unable to drip away from the flame and will burn, often quite fiercely. Polyamide fabric may also burn when sewn into garments with cotton thread; the threads may act as a support to prevent the burning fibre from dripping away

Class of fibre	Generic name	Trade name	Notes
	Polyester	Dacron, Diolen, Fortrel, Kodel, Tergal, Terlenka, Terylene, Teteron, Trevira, Vycron	Very similar flammability characteristics to polyamide fibres
	Fire-retardant polyester		The fibre is made with fire-retardant compounds incorporated in the resin. They have reduced burning characteristics in blends
	Polyolefin (polyethylene and polypropylene)	Courlene, Drylene, Herculon, Marvess, Meraklon, Nymplex, Polycrest, Pylen or Pylene, Reevon, Spunstron, Ulstron	These fibres melt when ignited and drip molten drops while continuing to burn
	Vinal (polyvinyl alcohol and acetate and copolymers)	Kuralos, Mewlon, Vinylon	Similar flammability characteristics to polyolefin fibres but burn somewhat less readily
	Other fibres of various types	Durette, Kynol, Nomex, PBI	These fibres do not burn under normal conditions, but decompose.

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Chapter 8

THE CHEMISTRY OF HARD- AND SOFT-WARE III: POPULAR PRODUCTS

PAINTS

Historical

Before World War I, practically all pigments, linseed oil, turpentine, and varnishes were imported for bulk sale to tradesmen who mixed their own paints as required. The mid-1920s saw the development of ready-to-use hard gloss paints and nitrocellulose lacquers, and the whole marketing pattern changed —the decorator carried 'colour cards' to arrange colour schemes with his customers and ordered ready-to-use paints from the manufacturers for immediate delivery. The mass media advertising of the 1950s and 1960s and the development of paints and techniques which are easier to apply has led to the situation today where 75 percent of homes are painted by their owners.

Until the early 1950s the *vehicles* used in paints were principally natural 'oils'—tung, fish, linseed—which are to a greater or lesser degree polyunsaturated. The linseed oil was thinned with turpentine and pigmented with white lead (basic lead carbonate, $Pb(OH)_2PbCO_3$) and tinted with one of a small range of colouring agents.

Alkyd resins were introduced into the industry in the 1940s and have since become the basis of nearly all 'oil'-based paints, e.g. house paints, alkyd enamels, undercoats, and primers. Water-based paints, known as latex paints, plastic paints, etc., based on polyvinyl acetate or acrylic resins were introduced in the 1950s and have become increasingly popular. At first these water-based paints were recommended only for interior use but in recent years water-based paints have become available for exterior use. The introduction of easily dispersible pigments ('universal stainers') in the 1960s meant that the retailer need only keep white paint bases and add small quantities of universal stainers to obtain a wide range of colours.

Function

The basic function of a paint, that of protecting a surface from the action of light, water, and air, is achieved by the application of a thin, resistant, impervious, flexible film to the surface. The film usually contains pigments to hide and decorate the surface. Thus paints have two basic components—

1. the vehicle—the liquid part of the paint which polymerises in some way to provide the bonding and protective film, and
2. the pigment—a solid suspended in the vehicle which is opaque, scatters light, and colours the film.

Consumer aspects

Most paint sold to the general public is used indoors and it is generally required to be used over previously painted surfaces. Generally white or pastel colours are chosen. A general order of interest would be:

1. Interior decoration of homes
2. Exterior protection of homes
3. Painting or staining furniture
4. Painting boats or caravans
5. Painting roofs or paving.

The sources of paint can be classified as follows:

1. Large paint firms—products expensive but satisfactory
2. Medium sized paint firms which are well established—their cheaper paints are generally just as good
3. Small firms—cheaper still but may be unsatisfactory
4. Retail store 'house' brands—paint made up by an outside manufacturer, who can be changed from time to time, as can the retailer's specifications.

It should be noted that the surface preparation, application, and film thickness can be more important than the quality of the paint!

Basic terminology[1]

Chalking: Loose pigment powder on the surface of a weathered film left by erosion of the outer layer of binder under action of ultraviolet light. Some chalking is desirable to give a self-cleaning surface.

Checking: Slight fine breaks in the surface of a film visible to the eye or under $\times 10$ magnification.

Cracking: Breaks in the paint film that extend from the surface to the underlying material.

Extender pigment: Pigment which in itself has little hiding power but which enhances the properties of the paint by filling voids in the film, spreading the main pigment, improving brushing quality, etc. Usually natural carbonates and silicates (clay, talc, gypsum, silica).

Flooding: Also known as floating. A defect sometimes occurring in paint films involving the separation of individual pigment particles, thus giving a non-uniform colour.

Flow: The ability of an applied paint film to level out evenly and produce a smooth coat.

Hiding power: The ability of a pigment to hide a surface depends on its refractive index and on the particle size. The measure of hiding power is the area of a black-and-white check design obscured completely by a pound of pigment.

Mineral spirits (Turpentine): A petroleum fraction boiling between 150°C and 200°C, containing aliphatic hydrocarbons. Evaporates from paint as it dries.

Pigment: Provides colour and opacity to dried film. Properties depend on chemical composition, refractive index, and size of particles.

Primer: Paint intended as the first coat on a surface.

Refractive index: Ability of a material to bend a ray of light. The larger the value the greater the refraction, e.g. water $n = 1.33$, crown glass $n = 1.5$, diamond $n = 2.42$. It is related to the density of the material.

Thinner: Usually a volatile solvent added to facilitate application of the paint.

Thixotropy: The property of a liquid or gel to lose viscosity under stress and regain the gel state when the stress is removed. Thixotropic paints flow when the brush is moving but should not drip from the brush.

Varnish: A solution of a natural or synthetic resin in a solvent, sometimes with the addition of a drying oil.

The protective film

There are two ways of establishing the flexible film on the surface to be protected:

1. Apply the monomer and allow it to polymerise *in situ*. The old oil-drying (the oil is the drying agent) paints operated on this principle but curing times tended to be long.
2. Apply a suspension of a high molecular weight polymer in a solvent and allow the solvent to evaporate. This method, which is faster, is utilised in the modern plastic paints. Both oils and alkyds cure (convert from liquid to solid form) by the same mechanism.

Oil-drying paint

The monomer is linseed oil or some other unsaturated oil (tung, soya, castor, menhaden, etc.). These oils are mixtures of long-chain unsaturated fatty acids such as linoleic acid (see Chapter 3):

$$CH_3—(CH_2)_4—CH=CH—CH_2—CH=CH—(CH_2)_7—COOH.$$

The double bonds can react with oxygen on exposure of the oil to air, leading to the formation of peroxides and eventually to polymerisation by cross-linking at the active oxygen sites. The cross-linking can continue until there are two links for every double bond in the original oil, which is far beyond the point required for good film properties. In addition such materials tend to degrade under the influence of the ultraviolet component of sunlight. Yellowing and a tendency to become brittle are two principal ageing deficiencies. The natural oxidation is slow but the rate is enhanced by the use of blown linseed oil (air is blown through the oil heated to 130°C) or of boiled linseed oil (oil is heated to 260°C in the presence of lithage, PbO, giving a lead soap which acts as a drier). Paints which contain lead soaps (at less than 1 percent) but no other lead compounds, such as pigments, are legally non-lead paints. (Lead and other metal soaps—e.g. cobalt and manganese: all metals with variable valency—catalyse the uptake of oxygen and, with the exception of lead, the decomposition to free radicals.)

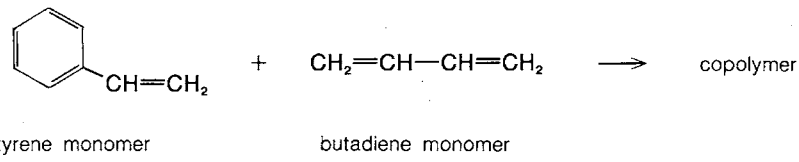
The old oil-based paints had the advantage of being cheap and adhering well to the surface. They are slow drying (several days between coats) and tend to weather because the surface continues to react, which leads to checking and gives a surface unsatisfactory for repainting.

Plastic or latex paints

As mentioned, these paints contain highly polymerised resins. Solutions of such polymers are too viscous to be readily applied and so the paints are formulated as emulsions of the resin solution in water: these emulsions are known in the industry as *latexes*, after the natural milky emulsified juices of certain plants, e.g. rubber. Latex paints have several advantages including speed of drying (several coats can be applied in rapid succession without the necessity of removing the scaffolding), lack of persistent odour, ease of clean up (spills, brushes can be washed with water), non-flammable, non-toxic (at least the vehicle) and they can be painted on damp surfaces. On the other hand, they tend to be low in gloss and rather soft; hardness is achieved by increasing the amount of pigment or of other additives. Their composition varies with the intended use (exterior or interior, nature of surface) and the degree of gloss required. Exterior paints may contain polyvinyl acetate (PVA) based on the monomer vinyl acetate (Figure 8.1) or acrylic polymers based on the monomer methyl methacrylate (also Figure 8.1).

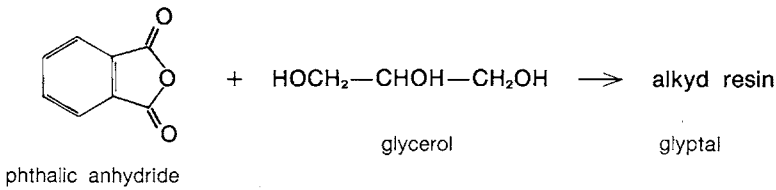
8.1 Vinyl acetate and methyl methacrylate

The latex paints generally contain a high proportion of resin to provide a film that is stable to weathering; gloss paints also have higher resin pigment ratios. Interior paints may also contain PVA or styrene-butadiene resins



8.2 Styrene and butadiene monomers

(Figure 8.2) and they have high proportions of pigment; to improve washability and adhesion up to 15 percent of drying oil or alkyd resin is added. One of the alkyd resins used for this is Glyptal (trade name of a glue), which is formed by the reaction:



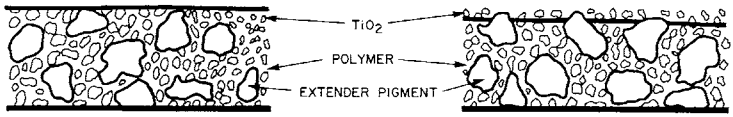
Plastic paints contain a number of additives to stabilise and thicken the emulsion (sodium methacrylates, carboxymethyl cellulose, clays, gum arabic), to assist in dispersion of the pigment (tetrasodium pyrophosphate, lecithin), to reduce foaming, and to preserve the paint. In more humid areas (north of Grafton) anti-mould agents become essential. (This is true also for products such as fibro cement.)

Polymerisation of alkyd resins with polyamides gives *thixotropic* (non-drip) paints which have a jelly-like consistency when standing but which flow under stress when applied by a brush. The degree of thixotropy must be modified so that the brush marks can level out before the paint re-gels.

Chalking

Under the influence of sunlight, oxygen, and water, paints tend to degrade by the long chain of the polymeric binder breaking down into shorter chains. This process continues until pigments at the surface of the paint film become liberated as 'chalky' residue (Figure 8.3). This erosion continues until the entire paint film has weathered away, a process requiring anywhere from one to twenty years. While this erosion is advantageous in white paints by providing

a self-cleaning attribute, it is most undesirable in coloured paints as it gives the impression of fading (coloured pigments are lost from the chalky layer more rapidly than white ones, resulting in a gradual fading).[2] Resistance to chalking can be improved by changing the monomer used to produce the polymer.



Schematic representation of a dried paint film

Paint films degrade during exterior exposure, liberating pigment particles at the surface, that appear as a 'chalky' residue

8.3 Schematic representation of a dried paint film—from Floyd,[2] with permission

Flexibility

Polymeric substances are glass-like in their mechanical behaviour as a function of temperature. Like glass (an inorganic polymer with silica, SiO_2, repeat units), polymers do not 'melt' in the sense that crystalline materials do. Rather they exhibit a characteristic 'glass transition' region in which they pass from a hard, brittle substance to a soft, rubbery, elastic substance (see Chapter 6). Hardness is at a maximum below the glass region and flexibility at its greatest above. These two properties must be balanced.[2]

Hiding power

The hiding power is associated with the difference in refractive index of pigment and polymer, and the reflectivity F is an approximation for the hiding power:

$$F = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}$$

where n_1 is the index of refraction of pigment and n_2 is the index of refraction of polymer. Rutile, TiO_2, is the most commonly used white pigment because of its high index of refraction (2.73). Hiding is therefore maximised by

minimising the refractive index of the polymer. This is accomplished using branching side chains in the monomer so that the polymer density is decreased through poorer packing. A polymer of refractive index $n = 1.0$ would provide a 40 percent increase in opacity over an acrylic polymer/TiO_2 system (acrylic, $n = 1.48$). In other words the expensive TiO_2 can be correspondingly reduced to equal hiding power generating an enticing increase in profits. One major brand of paint has been using small polymer spheres as the 'pigment' to give a white paint. This saves on the use of titanium dioxide. However, the lower density polymer may have other undesirable properties.

The traditional white pigments were white lead, $PbCO_3$, $Pb(OH)_2$, and lithopone, 30 percent ZnS + 70 percent $BaSO_4$. Today the major white pigment is titanium dioxide, TiO_2, which exists in two forms: *rutile* (having the higher refractive index and hence the higher obliterating power but reflecting a light that is slightly yellow) and *anastase*; besides its other advantages, TiO_2 also promotes the self-cleaning of the paint by chalking. Paints sometimes contain mixtures of the two forms in varying proportions to achieve a compromise of their best features.[2]

Particle size

Levelling (disappearance of brush marks after paint application) improves with increasing particle size. As the particles become larger they are encapsulated by polymer rather than being stuck together which reduces the flow properties of the film. Gloss, on the other hand, declines with increasing particle size.[2]

Paint removers

These must act to remove the paint film, or to swell and soften it so that it can be easily removed by scraping or flushing with water. Methylene chloride is the most common organic type of paint remover. It is a small polar molecule and can penetrate the coatings rapidly. Cosolvents are sometimes used to extend the range of usefulness on coatings which are little effected by methylene chloride alone. For example ethanol-methylene chloride enables shellac coatings to be removed. To inhibit the decomposition of chlorinated hydrocarbon solvents various additives are used (amines, epoxides, and aliphatic alcohols).

Methylene chloride and many other solvents are volatile. A wax (usually stearin or ceresin) is added at a maximum concentration in the range of 1–3 percent. The rapid evaporation of the solvent, and consequent cooling, causes the wax to be thrown out of solution to form a continuous surface film which keeps the solvent in the paint. Thickeners are added so that the remover can be used on vertical surfaces, and to provide a solvent reservoir above the paint

film (metal and amine soaps, proteins, starch, clay, etc.). Wetting agents are used in flush-off strippers. For low resistance coatings cheaper solvents can be used—e.g. for lacquers, methylethyl ketone (which incidentally will dissolve epoxy resins such as Araldite). Caustic soda can be used as a paint remover but is not recommended. Suitable additives can increase its effectiveness. Additives which increase stripping rates in caustic alkali solutions are sequestering agents such as gluconates. They speed the removal of the paint film by helping to dissolve oxide pigments, thus creating holes in the coating. Once the coating has been breached the sequesterant helps to remove the coating of oxide, phosphate, etc. from a metal surface, thus loosening the film from beneath. Surfactants are also added. Paint removers of this type are restricted to use on steel substrates but removers based on sodium metasilicate can be used on aluminium and other non-ferrous alloys. The alkali helps to hydrolyse ester linkages present in many polymers.[1]

The composition of various *frypan and oven cleaners* is very similar to the paint strippers described here as they carry out the same sort of job. Paint strippers should *not* be used on frypans because some of the residues may be toxic.

TABLE 8.1 *Examples of coloured pigments*

Colour	Inorganic	Organic
Black	carbon black copper chromate/MnO_2	
Yellow	Pb, Zn, Ba chromates cadmium sulphide iron oxides (ferrite yellow)	azo (arylamide) yellows nickel azo yellow
Blue/Violet	ultramarine Prussian blue cobalt blue	phthalocyanin blue indanthrone blue carbazole violet
Green	chromium oxide mixtures of yellow and blue	phthalocyanin green
Red	red iron oxides cadmium selenide red lead chrome red	azo pigment dyestuffs and toners (e.g. toluidine red—fades badly in tints) quinacridones, perylenes

Source: based on Morgans[3]

Toxicity

Toxic effects depend on two factors:

1. The chemical composition—e.g. compounds of some metals such as lead, cadmium, antimony, barium, are generally poisonous.

2. Solubility—a substance which is *insoluble* in the body fluids, even though it is a compound of a metal whose soluble salts are toxic, will pass through without injury. For example, barium sulphate is used for providing contrast in internal X-ray pictures, and is taken as a barium meal. White lead is soluble in the body fluids rendering it highly toxic. Legislation was passed after World War II to prohibit the use of 'soluble' lead in paints.

Red lead and zinc chromate are used in primer coats; they protect metal surfaces against corrosion. Primers contain fillers such as clay, talc and barytes to give a smooth surface.

Solvents

In Los Angeles County the largest single source of air pollution is the automobile. However in 1966 solvents released from surface coating operations (i.e. all kinds of painting) constituted the largest single *stationary* source of air pollution. Photochemical smog is formed by a sequence of reactions wherein sunlight, oxides of nitrogen, oxygen, and reactive organic chemicals are the chief ingredients (see Chapter 11). A regulation (of Los Angeles County) classifies organic solvents as to their degree of photochemical activity and the emissions are controlled.

Special purpose paints and coatings

Heat-resistant paints

Ordinary paints blister, then char and disintegrate at relatively low temperatures. Coatings for ovens, heaters, stills, engines, turbines, etc. must withstand much greater heat. Paints with silicone vehicles, metallic powders (Al, Zn, Sn to reflect and conduct heat away), and heat-resistant pigments (Cr_2O_3, Ti_2O_3, C, TiO_2, CdSe) are widely used for specialist applications. Polymers of alkyds with saturated fatty acids give non-drying paints which can be baked on as in oven or baked enamels. These must be contrasted with vitreous or porcelain enamel (see later in this chapter).

Fire retardant paints

The addition of a variety of compounds to paint renders it less flammable. These compounds (phosphates, tungstates, borates and carbonates) decompose on heating to give gases which do not support combustion and hence tend to extinguish the flames.

An alternative approach is to add a substance that fuses on heating to give a glass-like layer on the surface.

A third approach is to use non-flammable constituents—silicones, chlorinated resins, mineral powders. Water-based paints are usually non-flammable before they are applied.

Antifouling, fungicidal, insecticidal paints

Antifouling paints have much application in marine construction. They usually contain inorganic poisons (mainly Cu and Hg salts) or organic molecules (such as pentachlorophenol). More recently organo-tin groups have been directly incorporated into the polymer. These have been found to be very effective against marine organisms while at the same time rapidly decomposing to non-toxic inorganic tin on release into the sea water. DDT and other insecticides have been added to paints to control insects.

Luminous paints

These paints fall into two groups:

1. *Fluorescent* paints absorb ultraviolet radiation and re-emit it as visible light only while being irradiated; they contain zinc and cadmium sulphides, together with organic dyes.
2. *Phosphorescent* paints continue to glow for some hours after the irradiation has ceased; phosphors include again ZnS (green, yellow, orange) or CuS and SrS (bluish) while certain salts can be used to change the colour.

ADHESIVE BONDING[4,5]

Adhesive bonding can mean a variety of operations—sealing envelopes, applying bandages, repairing torn paper with cellophane tape are some common meanings. Adhesion involves the fastening together of solid materials by a thin, generally continuous, intermediate layer.

Today's hardware shops provide a bewildering assortment of packages and types of adhesive bonding and, for a start, it is as well to warn that adhesive bonding does not meet all fastening applications. More elaborate surface preparation is required than for mechanical fasteners which function quite well with dirty surfaces. The mechanical strength of most adhesives takes time to develop and pressure is generally required to ensure the necessary close contact. Adhesive bonding can be 'irreversible' in the sense that the structure can be disfigured or destroyed if pulled apart. Adhesive bond failures can be classified into adhesive and cohesive. *Adhesive failure* occurs when the adhesive does not adhere properly to either of the materials, while if both faces of the

ruptured connection have the same (adhesive) material you have *cohesive failure.*

Adhesive failure occurs when the surfaces have not been prepared properly or when there is a large difference in surface energy between the substrate and the adhesive. Liquids only wet surfaces with higher surface energies (the solid equivalent of liquid surface tension). Polar adhesives with molecules which attract each other strongly and are thus liquids of high surface energy do not adhere well to Teflon or polyethylene. Cohesive failure often occurs along weaknesses caused by gas bubbles from volatile by-products of the solidification process—a thinner glueline by using less adhesive can be the answer here.

The process of bonding can be described as falling into two types—physical and chemical. Cooling and solvent evaporation are two physical reaction cures. The sizes of the adhesive polymer remains the same as when the bond was applied and the physical adhesion can be readily destroyed. Starch and animal and polyvinylacetate emulsions (white glues) all solidify by the evaporation of water and so may not be used where exposure to water is likely to occur. The chemical bonding results from a reaction which changes the nature of the adhesive. The cyanoacrylate systems cure rapidly with traces of moisture as catalyst.

TABLE 8.2 *Adhesives*

Adhesive / Substrate	Animal	Casein	Vegetable	Urea-formaldehyde	Phenol-formaldehyde	Resorcinol-formaldehyde	PVA	PVA water-resistant	Natural rubber	Synthetic rubber	Plastic	Epoxy	Hot melt
Cardboard	×*	×	×				×	×					×
Ceramics							×	×		×		×	
Glass										×		×	
Leather	×						×	×	×	×		×	×
Metal					×					×		×	×
Paper	×		×				×	×	×	×	×		×
Plastics							×	×	×	×	×	×	×
Rubber									×	×		×	
Textiles	×						×	×	×	×	×		
Tiles										×		×	
Vinyl											×		
Wood (exterior)					×	×		×				×	
Wood (interior)	×	×		×	×	×	×	×				×	×

*Look for a cross against *both* substances you intend to join

Source: New Zealand Consumer Council[4]

It can be seen from Table 8.2 that some adhesives can be multipurpose.

Polyvinylacetate glues are white milky liquids generally sold in squeeze bottles. They consist of a latex of polymer, fillers, and plasticisers in water and are analogues of rubber latexes. They keep very well in a sealed container. Their setting time is short for porous substrates such as paper and cardboard (two–three minutes) but longer for non-porous ones such as woodwork, ceramics (twelve hours). Surplus glue can be wiped off with a wet rag before it has set. The glue line is transparent and the set glue is resistant to hydrocarbon solvents (oil, grease, etc.). Formulations with an acid hardener have better water-resistance. The joint softens with heat and normally has poor creep resistance.

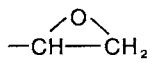
Plastic glues are glues made to join plastics and are generally clear solutions. They set by loss of solvent and the joint is not very strong. They are suitable for light-weight applications such as models, books, display ceramics, leather, etc.

Some plastics require special treatment. Vinyl plastics (inflatable toys, swimming pool liners, some upholstery, etc.) can be joined with the vinyl kits. Polystyrene cements are available for polystyrene toys. Polyethylene is very non-polar and so some polarity has to be introduced by heating it in air with a torch (but not so as to melt it). The surface has become suitably polar if water will spread on the plastic. It can then be bonded with most flexible adhesives except water-based ones (e.g. not PVA).

Synthetic rubber glues include the elastomeric (contact, pressure sensitive) adhesives and silicone rubber cements. They are stronger than natural rubber. While neoprene rubber adhesives lose solvents in the setting process, the others absorb moisture to set.

Epoxy resins

Epoxy resins were introduced commercially just over twenty years ago. The term is applied to a whole family of resins and combination of resins and curing agents whose properties can vary very widely. An epoxy resin is defined as a molecule that contains more than one epoxy group (Figure 8.4) and is capable of being converted into a thermosetting plastic by the use of curing agents or catalysts.



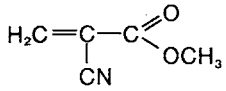
8.4 The epoxy group

Epoxy resins have good adhesion to a wide range of materials including metals, wood, concrete, glass, ceramics, and many of the plastics. This is due to the presence of polar groups in the cured resin. Since no water or other

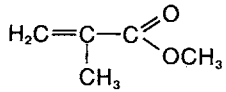
by-products are liberated during the curing of epoxy resins, they exhibit very low shrinkage. They can be formulated to withstand very high temperatures. They are chemically very resistant. The most commonly used curing agents are polyfunctional amines in the form of an amine adduct (to reduce the volatility of the objectionable amines).

Ultrafast setting adhesive

An interesting new cement sold for home use at the present time was first introduced by Kodak for industrial purposes (Eastman 910). It is a one-component system and depends on the polymerisation reaction of a monomer *methyl 2-cyano-acrylate* (Permabond, miracle adhesive, etc.), shown in Figure 8.5.



methyl 2-cyano-acrylate



methyl 2-methacrylate
(forms perspex)

8.5 Acrylates

It is an exceedingly strong adhesive, very fast setting (ten seconds to two minutes) and bonds a wide variety of materials. Doubts have been expressed as to its safety as a consumer product because of the toxic vapour (tolerance 2 ppm in air) and fast setting time. The glue adheres very strongly to the skin and is difficult to remove—in the United States a boy's eye was glued shut by a squirt of the liquid.

Formaldehyde resins

The group of formaldehyde resins are related to bakelite—the original plastic. They have a number of specialist applications. Urea-formaldehyde is used in low-stress veneer applications such as joining formica to wood, while resorcinol and phenol-formaldehyde have use in marine applications and exterior furniture.[6]

VITREOUS ENAMEL

Vitreous enamels (called porcelain enamels in North America) are alkali borosilicate glasses formulated to have temperature expansion coefficients (the amount by which the material becomes larger when it is heated) slightly lower than the metal base to which they are applied. Thus they are in compression up to the normal enamel service temperatures, a feature taking advantage of

the high compressive strengths which glasses possess. Normally the base metal is covered with two layers—a dark 'ground coat' next to the metal, covered with a decorative coating. (Lately, though, with special grades of steel now available, the ground coat can be eliminated.) A ceramic glaze is similar to a vitreous enamel, except that the substrate for the ceramic glaze is non-metallic (e.g. clay), generally has a low expansion coefficient and is weak under tension, and brittle.

The basic operations in the two processes are in principle identical.

1. Manufacture of the glass
2. Melting of the glass to a slip (frit or flake)
3. Application of the slip to the substrate
4. Drying
5. Firing at around 830°C (1500°F).

Contrary to what one might expect, vitreous enamel is not a thermal insulator but is a relatively good heat conductor when applied in thin coats and so is useful in ovens.[7]

The *pyrolytic self-clean* ovens literally burn off foods at temperatures of 430°C (800°F) to 540°C (1000°F). They are put through the cleaning cycle periodically and the higher temperature is held for about 1½ hours.

The *continuously cleaning* ovens work on an entirely different principle. The enamels inside the oven have a porous structure (like pumice) which has the effect of increasing the surface area of the material by a factor of forty to eighty times the apparent surface coating area. The surface catalyses the burning of fats and oils and so removes them at cooking temperatures. They are less effective with other soils such as sugar.[8]

(*Paint enamel* is a completely different material: it is basically a normal paint that is dried by baking at a relatively low temperature to remove traces of solvent.)

PORTLAND CEMENT AND CONCRETE

Portland cement derives its name from the similarity of the set cement to the stone from the famous quarries of Portland, England. Cement clinker is the product obtained by heating a ground mixture of limestone and clay to approximately 1450°C at which temperature a portion of the raw mix is fused. Four chief 'clinker minerals' are formed. Untreated Portland cement clinker, owing to its low surface area, does not react with water. Increasing the fineness by grinding produces the reactive material. When mixed with water Portland cement hardens after setting, even under water; its strength development does not depend on drying or on reaction with atmospheric CO_2 (which occurs over a period of years). To regulate the fast setting, which starts within minutes, gypsum, $CaSO_4.2H_2O$, is interground with the clinker (tricalcium aluminate and

calcium sulphate react with water almost immediately to form crystalline hydrates. If enough sulphate is available, hydrated calcium aluminate sulphates are formed on the surface of the unhydrated particles, thus preventing their fast hydration.) The first theories of cement hardening were put forward by Le Chatelier (1893) and Michaelis (1893), both famous for other contributions to physical chemistry.[9]

The system containing cement, water, sand, aggregate (gravel), and air is called *concrete*. Concrete's most important engineering property is its *compressive* strength, i.e. strength against compression. Its *tensile* strength, i.e. strength against stretching, is only about one-tenth of its compressive strength. Both the aggregate and the cement paste have higher tensile strengths than the concrete they form—suggesting that the weakest part of a hardened concrete is in the interface between cement paste and aggregate and sand. It is because of these properties that reinforcement with steel mesh is used with concrete and why some structures are *prestressed* to ensure that the concrete is compressed rather than stretched.

Why does concrete crack?

Concrete changes its volume for a number of reasons. Expansion can be caused by the presence of undesirable compounds (e.g. MgO and CaO). Alkalis can dissolve some of the aggregate containing amorphous silica or carbonate minerals. Shrinkage can be caused by carbonation (reaction with carbon dioxide in the air).

The problem of volume changes caused by freezing of water (ice has a 9 percent greater volume than water) is overcome by the use of surfactants to entrap air in the concrete, thus making room for expansion.

Concrete mixtures

The proportioning of the ingredients is usually in the order of cement, sand and gravel by volume e.g. 1:3:6 lean mixture; 1:2:4 for stronger structures, reinforced cement, or when concrete is used under water; 1:1:2 when exposed to sea water (free of lime and alumina). The amount of water required to combine chemically with cement is about 16 percent by weight but, for efficient mixing, a greater amount than this must be used.

An effective waterproof concrete developed by the United States Geological survey admixes a heavy residual mineral oil (density 0.93—engine oil, new or old, seems to work well) with the Portland cement and sand in the ratio of 1:3, and oil not more than 10 percent by weight of the cement. In fact 50 percent water to oil works well. This concrete takes half as long again to set but its compressive strength is only slightly reduced. The grip on steel

is greatly decreased but on barred bars, wire mesh, or expanded metal it is satisfactory.[10]

Sugar inhibits the setting of concrete and also weakens it. A tanker of sugar syrup is often kept on hand for dealing with large scale spillage of concrete. The exact mechanism of this process is unknown although some sugars, e.g. sucrose and glucose, are particularly effective. The interaction of sucrose and cement is probably related to the effect that sucrose has on teeth enamel—a mineral related to cement.

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Chapter 9

CHEMISTRY IN THE MEDICINE CABINET I—HISTORY AND SOCIOLOGY

HISTORICAL[1]

One of the earliest records of human medication is to be found in an Egyptian papyrus dating from 1550 B.C.. During the nineteenth century the isolation and examination of the active principles of plant drugs were developed, while the twentieth century has heralded the manufacture and distribution of potent synthetic drugs. Early medicaments were mainly alkaloids (complex plant chemicals containing nitrogen); the toxic properties of the mandrake, the opium poppy, and the nux vomica bean are due in each case to alkaloids—atropine, morphine, and strychnine respectively.

The first synthetic drugs were aspirin and procaine (used as a minor anaesthetic in dentistry). This development stimulated interest in synthetic drug production—an interest strongly reinforced by the discovery of the organic arsenicals as a treatment for venereal disease and of the antibacterial action of certain dyestuffs; this second discovery led in turn to the development of the sulphonamides, which encouraged firms already engaged in the dyestuff industry (the main chemical industry at the time) to move into pharmaceutical preparations. Table 9.1 shows this development. The first pharmacopoeia, designed to regulate standards for drug purity, was promulgated in 1846, and in 1960 the first international edition was prepared by the World Health Organization (WHO).

Drugs were traditionally taken by mouth, but in 1853 the hypodermic syringe was invented. It allowed drugs to be put directly into the bloodstream and so given rapid action, e.g. morphine. Later the hypodermic syringe was used to administer drugs which are destroyed in the gut, such as insulin. Anaesthesia became possible by injection, removing the limitation of having to use gases. Preparations for injection had to be sterile and preferably made

up in single-dose containers, and fabrication moved out of the hands of the pharmacists to the drug manufacturer. The packaging became, to a large extent, the product; the cost of the drug itself a minor component. Another important development was the development of the compressed *tablet* (or 'tabloid' as it was first known).

TABLE 9.1 *The rise of potent drugs*

1846	Ether first used as an anaesthetic in surgery
1876	Salicylates found to be pain killers
1884	Cocaine found to be a local anaesthetic
1899	Aspirin synthesised
1902	Adrenaline isolated from the adrenal gland
1903	Veronal (barbitone—the first barbiturate)
1905	Organic arsenic compounds used for the treatment of venereal disease
1907	Ergot alkaloids found to counteract adrenaline
1911	Vitamin studies started
1912	Phenobarbitone used as an anti-epileptic
1916	Heparin used as an anticoagulant
1929	Penicillin discovered—no chemical studies because of crudeness of product
1935	Activity of the sulphonamides discovered and used on man
1936	Pethidine, the first synthetic narcotic, synthesised
1937	Curare introduced as a muscular relaxant
1941	Penicillin first used (on a London policeman suffering severe blood poisoning from a shaving cut)
1943	Diphenylhydramine—the first practical antihistamine
1950s	Development of tranquillisers Synthetic anti-inflammatory steroids
1960	Oral antidiabetic drugs

The international pharmaceutical industry started after World War I and grew quickly to multi-national proportions. By the 1950s painstaking research was giving way to a new era of commercialism—aimed at achieving the greatest possible consumption of pills and medicines.

By the end of the fifties difficulties were becoming apparent. Really new drugs were becoming harder to find. The areas of therapeutics which remained to be countered were becoming fewer, but the disorders were less easily treated. Some afflicted only a comparatively small number of people, frequently those in hospital and not likely to prove a source of great income and prosperity to the manufacturer even if better curative agents were to be found.

SOCIOLOGY

Dr Donald Gould (medical contributor to *New Scientist* and *New Statesman*) discussed on the ABC Insight program (488—June 1974) the topic 'Can we handle modern drugs?' In his view

> . . . by far the most important failing in the way we use medicines at the moment lies in an almost total lack of understanding by the medical profession and the public (but the medical profession is the responsible part of the scene) of what modern drugs are, how they should be used and indeed, what effect they have when they are used.

A strong statement but worth examining.

The following discussion is taken from Dr Gould's Insight talk[2], and an article he published in the *New Scientist*.[3] As we saw in the historical introduction, up to thirty or forty years ago there were hardly any effective drugs which a physician could use—there were really only a handful of effective remedies. The result was that the tradition of medicine (on the medical as opposed to the surgical side) has been to concentrate on diagnosis and prognosis, upon putting a very precise label on the disease and predicting the patient's future. This skill represented the physician's mystique. Medical textbooks give pages and pages on a disease like smallpox—on the signs and symptoms, history and so forth and a little bit at the end about treatment and if really *avant garde* a footnote on the side-effects or contra-indications of the treatment.

This state of affairs has come about because the pharmaceutical industry has developed independently of the medical profession. The new drugs have seldom come from the medical profession. The pharmaceutical industry supports research in universities and in their own laboratories, tests new compounds that have been discovered and finally develops a product which will do something to a disease in a patient, with of course the idea of being able to sell it and make a profit. They offer it to doctors, who gratefully accept these weapons because not long ago they hardly had any effective weapons at all. Doctors spend some of their formal education in medical school learning pharmacology and therapeutics but what they learn may be out of date in a couple of years and their training in this area of medicine is not very extensive. Doctors obtain nearly all the information on modern drugs from the pharmaceutical industry, which is not a healthy situation. When the United Kingdom Committee for Safety on Drugs went into their task of surveying all drugs prescribed or sold directly they had about 55,000 medicinal substances to cope with. There is considerable duplication of drugs of similar nature in areas where no really new developments are occurring, particularly for high sales complaints such as anxiety (see Appendix 9.3)

Drug advertising directed at the doctors represents a very large fraction of company expenditure. It includes lush advertisements, sending around

representatives to doctors' surgeries and hospitals, film shows, etc. In fairness, there is no point in developing a new drug if doctors are not made aware of its existence. The objective of true education is to cultivate the mind for the purpose of forming independent judgments, whereas promotion eschews the very concept of independent assessment and depends on reiteration of statements which may become believed by association or by sheer repetition. It is a characteristic of many business executives that they absorb the ideas and claims of their company so completely that they begin to lose the capability for rational judgment.

In *Prescription Medicine Industry in Australia—Fact Book 1973,* published by the Australian Pharmaceutical Manufacturers Association, it is stated that 'The source of the most complete information on any new agent is its manufacturer . . .). There was a recent Ph.D. thesis by L.W. Afterman on a comparative study of Australian and American regulation of the pharmaceutical industry. This thesis pointed to the lack of control over drug advertising aimed directly at doctors. Even with media advertising, controls over the advertising of pharmaceutical preparations are complex, fragmentary, and vary with the availability and origin of the product. The Australian Government exercises control over the labelling of imported drugs and of drugs sold to, or paid for by, the Government. (The States all have various laws relating to labelling.)

Advertising can do very much more than just make doctors aware of a product. Antibiotics are extremely valuable drugs which kill germs and yet have low toxicity for the patient. But as soon as you use an antibiotic, you begin to get germs which become resistant to it. Through natural selection and the transfer of immunity a whole new breed of resistant germs develop. If doctors give antibiotics routinely for children with a sore throat and a cough, which are almost always caused by viruses for which antibiotics are absolutely useless, you encourage the growth of these resistant strains. The antibiotic is given 'just in case' there is a further infection by bacteria such as tonsillitis which would respond to antibiotics. A swab and pathology test for any bacterial infection should precede the use of an antibiotic unless there is obviously need for urgent treatment. Pharmaceutical advertising tends to encourage the overuse of drugs. It raises the hopes of the patient as well as the doctor. Patients (or worried parents) often feel that they are getting less than adequate service if a chest or throat infection is not treated with an antibiotic.

Limited studies have been carried out in hospitals in the United Kingdom on groups of, say, 500 patients who have been put on an antibiotic. They are closely examined and pathology tests are carried out. The results have shown that perhaps up to half of the patients had no infection at all, and that of the other half, the drug used was inappropriate. Perhaps only 25 percent of them were given the right drug in the right dosage. The 'right' in the case

of drugs comes from clinical trials which are published in learned journals, the information is abstracted and put into common language and used in advertisements, promotional literature, and in the sales talk of the medical representatives. For the clinical trials, specialists in the hospitals take the new drug and decide how to use it and report on the results obtained. The clinical trial gives essential information on the efficacy of the drug, dosage, undesirable or intolerable side-effects, etc. But the clinical trial is conducted by a group of eager beaver doctors, who are particularly keen on studying in as much detail as they can the effect of giving that particular medicine. They are going to write a paper on it which makes them particularly keen. The exercise is carried out on a carefully selected group of patients who all have, say, arthritis and they don't have all sorts of other things as well, such as bronchitis or kidney disease, because that might invalidate the results. The results of the clinical trial are used as the basis for the use of that drug in actual practice. In actual practice, however, things are very different. The patient, particularly if old, has several diseases and you don't know what the interactions will be. Second, you don't know how the patient will take the drug. In hospital the nurse ensures the right amount is taken at the correct time (unless you are particularly recalcitrant). In practice the patient gets the prescription filled at a pharmacy and you have no idea whether the patient is taking half the correct dosage or twice or none at all. In the case of psychiatric patients taking psychotropic drugs, about 50 percent don't take them at all. With other medicines under-usage is very prevalent indeed. In a study done in the United Kingdom in the north country town of Hartleypool, 500 families were chosen at random and were asked to turn out their medicine cabinets; 43,000 tablets were recovered. Referring back to antibiotics, it is very important to complete a course, because if you don't, the surviving germs can cause the disease to flare up again and the survivors become more resistant to the antibiotic because they are the tough ones which will give rise to this new nasty breed. How many patients who have been prescribed a course of antibiotic treatment feel better in a couple of days time and stop the treatment? Less frequently other patients think that if they take double the dosage prescribed, they will get better twice as fast.

While doctors make occasional mistakes in prescribing, the greater concern is the general overprescribing tendency. The source of drug information is basically the drug manufacturer and their job is to sell drugs.

The doctors themselves are very concerned with this problem. The facts presented in the paper 'Selling Drugs by "Educating" Physicians' written over ten years ago by a United States medical practitioner are much more worrying today than they were even then.[4] The paper describes the methods used by drug companies in promoting their products to physicians. Even by 1960 there were about 400 new products introduced by the drug companies annually, of

which no more than forty were new chemical entities, most being slight modifications or different preparations and mixtures of established agents. Really new drugs, requiring advancement in the knowledge of the physician for their use, probably accounted for less than six compounds a year (1960).

That is the sort of situation we have currently, of course, with detergents and toothpaste, but drugs are too dangerous to allow them to be played with in such a manner. The drug companies are not interested in the equally important business of teaching doctors when not to use drugs. Although the pharmaceutical industry is attacked for over-promotion and profit orientation, the problem can really only be resolved by the training of doctors and patients, and the provision of an independent source of information—the Drug Evaluation Committee of the Australian Department of Health could fill that role. In the United States a group of physicians under the aegis of Consumers Union publishes on a non-profit basis a bi-weekly *Medical Letter*. It consists of only a few pages but has very pertinent comments in which manufacturers' claims are often contradicted in very plain terms in contrast to the quarterly issues of its Australian equivalent.

Pharmacists are well-qualified people whose speciality is drugs, but their skills are being largely wasted. There is a case for patients selecting a pharmacist in the same way as they select a doctor; the pharmacist would then become responsible for maintaining a watch on a person's drug history and act as adviser on technical matters to the doctors of the customers on his list. There is a critical need for monitoring of drug intake because of drug interactions. The New South Wales Pharmaceutical Society held a Continuing Education Series of lectures on drug interactions in 1974 outlining the specialised and difficult problems involved and the widespread nature of the problems (see chapter 10). Increasing the importance of the pharmacist's role would make it desirable to move the shampoos and lipsticks back into the supermarkets—not to speak of the toys. The distinction between such real pharmacies and 'drug stores' exists in many European countries.

Terminology—What's *in* a name?

The unnecessary multiplicity of commercial names for drugs of the same kind can lead to confusion and wastage.

Drugs have three sorts of names. In order to have an unambiguous precise name for a chemical substance an internationally agreed system has been devised to provide a *systematic* name. Because this is unwieldy, subject to typographical error, and highly forgettable there is a simple uniform 'official' or 'non-proprietary' name, often called the *generic* name, approved on an

international basis for a chemical likely to prove worthwhile as a drug. The third name, the *trade* name is a creation of the manufacturer of the product. When a trade name is specified in a medical prescription (89.7 percent of the time according to the industry), only that particular brand may be dispensed.

Mims No. 1

The first Australian edition of this pharmaceutical handbook appeared in January 1977. Beautifully produced and bound, quarto size, with full colour reproduction, the annual is 4.5 cm thick (including advertisements). It starts off with a product identification section which illustrates in colour the majority of solid identifiable dosage forms (tablets, capsules, etc.) available for prescription (white unmarked tablets are not shown). This is followed by a section on drugs in pregnancy and lactation; a guide to clinically significant drug interactions; the GP's library; a guide to poisoning by therapeutic substances; a directory of manufacturers; a guide to adjustment of dosages in renal failure; and tables of Normal Values. Then there is a large section on prescription by therapeutic class giving composition actions, indications, contra-indications, precautions or warnings, adverse reactions, dosage and administration, and presentation. Finally there is a series of indices. Subsidiary booklets come out every second month. The series is available free to the medical profession and at cost to pharmacists.

It is a shame that it is produced by industry rather than the Australian Department of Health, as consumers are paying for it anyway. It narrows the gap between the information available to medical practitioners and such of their patients as are sufficiently motivated to obtain a copy (municipal library?). It could have interesting repercussions—both good and bad.

The arguments for generic labelling are basically that it provides a simple, unambiguous international label for drugs and a doctor is more likely to know

exactly what substance he is dealing with. A trade name effectively disguises the constituents of a combined preparation, thus increasing the chances of a patient receiving something with ingredients which, to him, are potentially hazardous.

Many preparations are marketed under different names in different countries (for trade mark reasons). The same name may refer to different drugs in different countries—which can have unfortunate results for travellers. Some examples are Anotox, Avlon, Benol, Bilagen, Bilitrast, Cedrox (which can be vitamin C or aspirin!) and we are only up to C in the alphabet.[5]

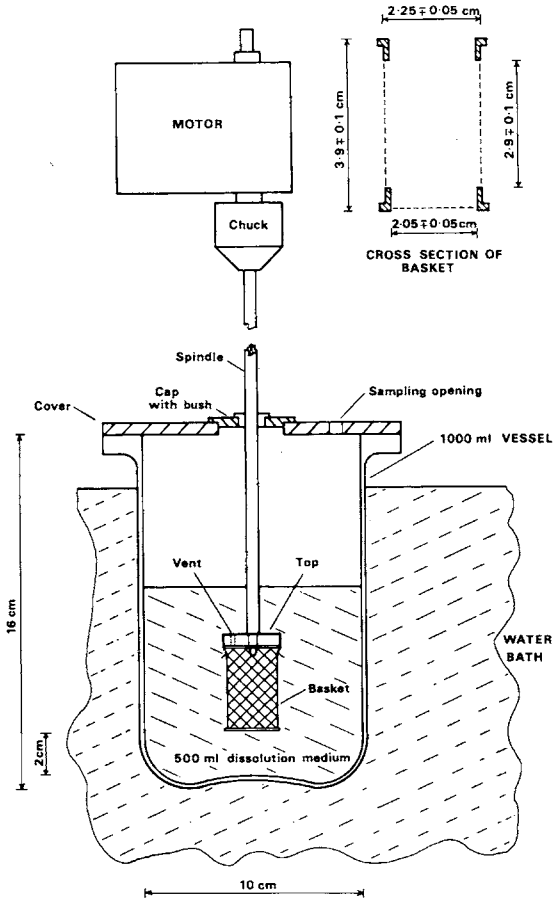
The pharmaceutical industry's reply to this is that preparations may differ in their bio-availability (this word sounds similar to biodegradability but it means something else, although the motives for using it may not be so very different—competition of image rather than of product).

It is true that the manufacture of the pill in which the drug is contained plays a critical role in the stability of the drug and the rate of its release. In Australia, poor quality control in this aspect led to the development of standard testing methods by the National Biological Standards Laboratory (initially for digoxin, 1966), using an automated pill dissolver illustrated in Figure 9.1.

The introduction of paracetamol to replace phenacetin in APC mixtures led initially to some unstable preparations. An interesting aspect is that of *polymorphism* (different solid state structures for the same chemical). Chloramphenicol palmitate exists in two forms only one of which is biologically active. In the other the long hydrocarbon chain is possibly 'wrapped around' the outside of the crystal preventing it from dissolving. There are other cases as well, but not published.

The industry is deliberately confusing science with commerce. In 1971 there were about 40,000 trade names used internationally for 5000 distinct pharmaceuticals. Aspirin has 198 international synonyms and, as well, there are its salts: ammonium (one name), lithium (three), solium (four), calcium or soluble (thirty-six), magnesium (twenty) and aluminium (twenty). All the trade names are different—a triumph in marketing linguistics. Some perspective can be obtained when we examine for example the number of drugs approved by the United States Food and Drug Administration. For the fiscal year 1969–1970 there were fifty-one (about one a week). Of these about twenty could be considered 'new entities'—i.e. new chemicals not previously marketed in the United States. However, many of these new drugs although technically new entities, represented merely variations on familiar themes and in some cases nothing more than molecular manipulation; the number of really new contributions was small indeed.

Generic labelling ensures that molecular manipulations are obvious because the names will be related. Compare the list of generic and trade names for some tricyclic antidepressants in Table 9.3. A set of similar sounding trade names may be coincidental and does not necessarily mean that there is a relationship between the drugs.



9.1 An automated pill dissolver. Apparatus for measuring rate of dissolution of tablets in simulated intestine fluids (National Biological Standards, Dept of Health, Canberra)

TABLE 9.2 *New drugs marketed in the United States 1950–1971 (No.)*

	1950	'51	'52	'53	'54	'55	'56	'57	'58	'59	'60	'61	'62	'63	'64	'65	'66	'67	'68	'69	'70	'71	TOTAL
Total new products	326	321	314	353	380	403	401	400	370	315	311	275	255	213	162	119	82	83	101	71	110	83	5438
New single chemicals	28	35	35	48	38	31	42	51	44	63	45	41	28	18	17	23	13	25	41	11	16	14	680
Important therapeutic advances[1]	6	6	14	10	8	14	10	13	12	21	15	15	16	10	10	12	8	12	9	4	8		233
Duplicate single products[2]	100	74	77	79	87	90	79	88	73	49	64	33	47	43	34	23	16	26	36	26	52	40	1236
Combination products[3]	198	212	202	226	255	282	280	261	253	203	202	191	180	152	111	73	53	32	51	34	42	29	3522
New dosage forms[4]	118	120	170	97	108	96	77	96	109	104	98	106	84	52	41	22	26	14	21	12	23	30	1613[5]

Source: Basic Data, Paul deHaen Inc., New York, N.Y.

1. New single chemicals that have been classified as therapeutic advances by Dr Marvin Seife, Office of Scientific Evaluation, Bureau of Drugs, FDA.
2. Duplicate single products: products such as ampicillin which are put out by various manufacturers.
3. Combination products: any product having more than one active ingredient.
4. New dosage forms: a product which has originally been marketed in tablets is now offered in ampoules, suppositories, etc.
5. Not included in Total New Products.

TABLE 9.3 *Generic and trade names for tricyclic antidepressants*

GENERIC NAME	TRADE NAMES
imipramine 10 mg	*Imiprin, Iramil, Prodepress, Tofranil plus 20 other trade names**
imipramine 25 mg	*Imiprin, Iramil, Prodepress, Tofranil, Somipra Melipramine*
desipramine	*Pertofran plus 7 other trade names**
trimipramine	*Surmontil plus 2 other trade names**
chlorimipramine	*Anafranil**
amitriptyline	*Laroxyl, Saroten, Tryptanol, plus 22 other trade names**
nortriptyline	*Allegron, Nortab, Aventyl (capsule), plus 14 other trade names**
protriptyline	*Concordin, Triptil, plus 3 other trade names.**

* Not available under Pharmaceutical Benefits Scheme

An interesting illustration of the confusion resulting from industry practices has been devised by a former Professor of Pharmacology at Albany (New York) Medical College, Dr Solomon Garb. Dr Garb describes what would happen if drug manufacturers were responsible for the manufacture and marketing of baked beans:

> They would all stop using the word 'beans' and each would give the product a new, coined name . . . Picture the confusion in the grocery store if beans were no longer named 'beans' but if each maker gave a completely new name to his product. Further, try to imagine what would happen if there were 300–500 additional new names of this type in the grocery store each year. This is approximately what is happening in medicine, and it is becoming exceedingly difficult for physicians to keep things clear.[6]

As far as prescription drugs are concerned in Australia, the Department of Health acts as the consumer in paying the bill (on our behalf of course), and the prices of drugs are negotiated with the manufacturers.

The full story of the thalidomide tragedy has been revealed in *Thalidomide and the Power of the Drug Companies* by H. Sjostrom and R. Nilsson (see Appendix 9.1). It is hard to believe that the facts revealed in this book relating to the suppression of evidence on the dangers of thalidomide are true. The large number of trade names under which thalidomide was sold meant that Contergen (the German trade mark), the birth-deforming effects of which were reported in a Stockholm newspaper, was not recognised by Swedish doctors as Neurosedyn—the Swedish brand name. In Australia the effects of thalidomide led to the formation of the Australian Drug Evaluation Committee whose main role is to see that a thalidomide situation does not happen again.

Non-prescription drugs

Traditionally there has always been a distinction between proprietary, or patent medicines that the consumer may buy over the pharmacy counter, and drugs that have to be prescribed by a physician. In modern terminology the former are referred to as *proprietary* medicines and the latter as *ethical* drugs, where the word *ethical* refers to the classification of the drug and not to any other connotation of the word. Some companies are engaged in over-the-counter ethical preparations which are products sold to the public without a prescription, but normally not advertised in the consumer press. The whole subject is a semantic smog.

THE SCHEDULES

The NHMRC Uniform Poisons Standards has eight schedules for drugs and chemicals, which the States have adopted into their Poisons Acts.

Schedule 1—Substances which are extremely dangerous to human life.

Schedule 2—Substances which are dangerous to human life if misused or carelessly handled.

Schedule 3—Substances for therapeutic use which are of a sufficiently dangerous nature as to warrant their distribution to be restricted to pharmacists or pharmacy trainees and medical, dental and veterinary practitioners. These substances should be stored in a separate part of the premises to which customers do not have access.

Schedule 4—Substances or preparations, the supply of which, in the public interest, should be restricted to medical, dental or veterinary prescription, together with potentially harmful substances or preparations pending the evaluation of their toxic or deleterious nature.

Schedule 5—Substances or preparations of a hazardous nature which must be readily available to the public but which require caution in handling, use and storage.

Schedule 6—Substances or preparations of a poisonous nature which must be readily available to the public for domestic, agricultural, pastoral, horticultural, veterinary, photographic or industrial purposes or for the destruction of pests.

Schedule 7—Substances or preparations of exceptional danger which require special precautions in manufacture and use and for which special individual labelling and distribution regulations may be required.

Schedule 8—Substances or preparations which are addiction producing or potentially addiction producing including those so classified by the United Nations Organization or its agencies.

A scheduled substance has specified labelling requirements, including warnings, statements of contents, strengths, etc. and must include the manufacturer's name and address. It is important to realise that the schedules do not form a numerical hierarchy. S1 is not more dangerous or less dangerous

than S8 or *vice versa*. In a way this is unfortunate as a hierarchical classification might be quite useful.

S1 These are very dangerous substances *not* normally required for any usual purpose and so do not occur in medicine or commerce (except where exempted) e.g. bromine.

S2 These are dangerous substances which *are* usual—sold only by pharmacists e.g. silver nitrate, mercury (except in scientific instruments).

For drugs labelled S3 you have to know what you want and ask specifically for it. The NHMRC (May 1973) list of S3 substances includes antihistamines, e.g. Polaramine (except meclozine, cyclizine, and chlorocyclizine), chloral hydrate (for calming children), Enterovioform (a now discredited but once common treatment for traveller's diarrhoea—which in 1975 was scheduled as S4—insulin, various synthetic adrenalins, etc. An interesting conflict in decisions is shown in the market place in the case of Benadryl, which requires prescription in the Australian Capital Territory where it is S4, but a few miles away in New South Wales is available over the counter as S3.

S3 All S3 drugs are basically those which are quite potent and are needed so regularly by sufferers of specific ailments that requiring a prescription each time is considered unwarranted.

S4 The S4 classification is the one generally seen on prescription-only drugs and it contains one of the largest lists of chemicals. The distinction between the three pharmaceutical schedules is sometimes very fine.

Plain aspirin without any codeine may be sold by any supermarket, self-service store, or any other shop. If it contains codeine up to 1 percent it is classified as S2 and can only be sold in a pharmacy. If it contains 1–2.5 percent codeine it becomes S4 and subject to a doctor's prescription; more than 2.5 percent it becomes S8. A mixture of any two or more of aspirin, caffeine, paracetamol,

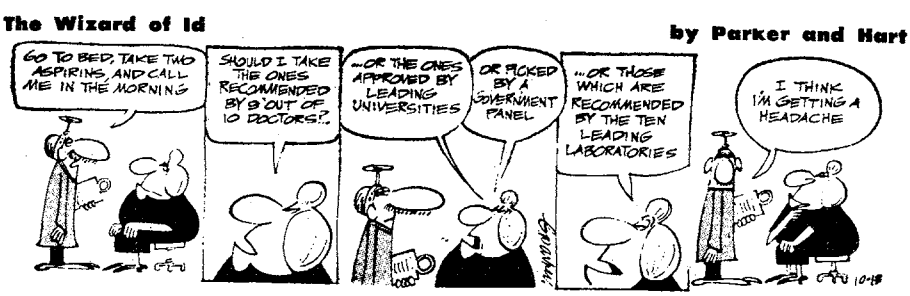


PLATE 9.I *Id has a headache*

Wallpaper pastes are sometimes protected with fungicide and are then unsuitable for preschool children to use in pasting. A selection is illustrated in the photograph.

Products 1 and 3 are examples of old and new packaging of the same product appearing together. Product 1 is labelled as required for S6 scheduled products* while Product 3 is labelled in accordance with Schedule S5 which means it does not contain organo-tin fungicide (neither product is any longer produced or sold by the manufacturer —17 June 1977). They both do contain a 'bittering' agent (sucrose octo-acetate) which is meant to make the taste of this material unpleasant. The products are a blend of cellulose ethers and starch. They are being replaced by a new product, Polylap FP—a starch-based tributyl tin oxide protected adhesive (not illustrated.)

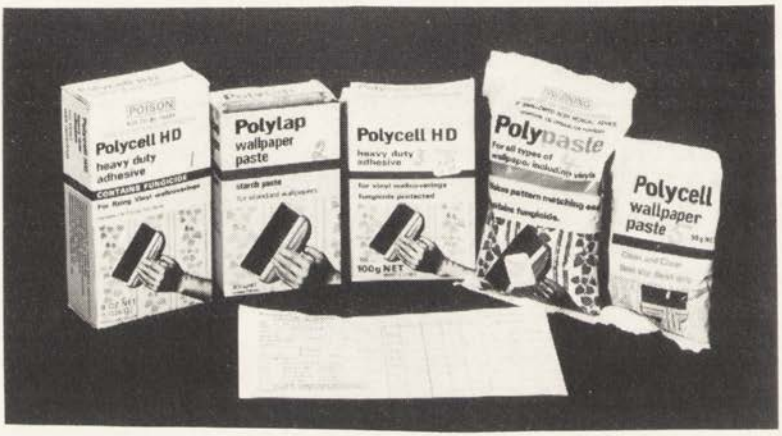


PLATE 9.II *Polycell products*

Product 4, a blend of starch-ether and starch, contains a proprietary organo-tin compound which is allegedly less toxic, less irritant, and more effective than tributyl tin oxide. Product 3 uses a different type of fungicide called Captan—ICI trade mark, and also the generic name in Australia for (*N*-trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide. This compound is not covered by the Poisons Schedules. Product 2 is a blend of starches and Product 5 is a neutral blend of cellulose ethers; these do not contain fungicide. Product 5 is recommended for pasting purposes by pre-school children.

*Product 1 did not however, contain any tin and could have been an old packet filled with a more recent product.

salicylamide, and their derivatives should be scheduled S4. Some of these preparations are listed in Table 9.4.

Table 9.4. lists branded preparations which may be prescribed—all contain aspirin. Those in the first column are available for general sale, those in the second column are 'chemist-only' lines, and those in the third column are schedule 4 'prescription-only' lines. The list does not claim to be exhaustive and a similar range exists without aspirin but with paracetamol—often considered more desirable—instead.

TABLE 9.4 *Brand preparations containing aspirin*

Not scheduled: open sale	Schedule 2: chemists only		Schedule 4: prescription only
Aspirin alone and mixtures	Aspirin and mixtures with 1% or less of codeine		Aspirin and mixtures with 1–2½% of codeine
Acytosal	Angesil	Codral	Codiphen Forte
Alka-Seltzer	Asco-tin	Codral— yellow label	Codral Forte
Asopax	Aspalgin	Codral soluble	
Aspichinina	Burco	Decrin	
Aspro	Burcosol	Ethidyne	
Bi-prin	Calasco	Hycodin	
Disprin	Co-com	Onadox	
Infatabs	Codacet	Para-pavrin	
Novosprin	Codacet soluble	Pirophen	
Prodol	Code-Co	Solcode	
Provoprin	Codiphen	Solgesil	
Rasprin Junior	Codis	Solusal Co	
Solprin		Veganin	
Solusal			

Source: Thorp.[1]

The contention put by pharmacy guilds that restricting the sale of all drugs to pharmacies on the grounds of long-term toxicity of even drugs like aspirin is weakened by the advertisements which appear in their trade journals offering inducements 'to boost your analgesic sales'. As a result of discussion in the first edition of this book, the Australian Consumers Association carried out a survey on the behaviour of pharmacists when approached with a request for analgesics in large quantities. The results, published in *Choice* February

1976, were alarming. The industry was disturbed, as is shown by the following extract from the *Australian Journal of Pharmacy*, March 1976, p.121:

> The Pharmaceutical Society of Australia believes 'strong intra-professional action' needs to be taken to ensure that pharmacist exercise personal supervision over sales of minor analgesics.
>
> '. . . in 97 randomly chosen pharmacies in all capital cities *Choice* buying panel members purchased unusually large quantities (12 packs of large sizes) of five common analgesic products. On 73 occasions sales were made by a pharmacy assistant, and buyers were refused the dozen packs asked for at only three pharmacies. . . . (pharmacies), far from taking action to question the unusual size of the request, encouraged and hoped to increase the size of the sale.

Advertising drugs

Prescription drugs cannot be advertised on radio or television. As of 1 June 1977 a new voluntary code for the advertising of proprietary medicines and appliances came into being through a joint committee of newspapers, radio and television broadcasters, advertisers, pharmaceutical manufacturers, and pharmacists, under the guidance of the Commonwealth Department of Health. Prohibited are claims for relief from complaints that should be dealt with by a medical or dental practitioner. These form an interesting list—including development of the bust, baldness, potency, and raising the height. Menstrual pain is included, except for relief thereof!

The code includes a long-overdue section on analgesics. Analgesics advertisements must include the approved name of the drugs contained in the preparation and a warning against prolonged use. The warnings on radio and television are to be spoken as part of the advertising message using the same vocal expressions as for the main message. An advertisement for analgesics shall not contain:

1. Any claim that analgesic consumption is safe
2. Any claim that a preparation will relax, relieve tension, sedate or stimulate
3. Unsubstantiated claims that one preparation is appreciably less irritant to the stomach, more rapidly absorbed, faster in action, or more effective or less harmful than another

Advertisements relating to vitamins are also spelled out:

1. No suggestions of food lacking nutriments through soil depletion
2. Vitamin therapy can only help if there is a 'deficiency' (undefined)
3. No claims or dramatisation of benefits for irritability, sexual activity, nervousness, or of stimulation of appetite or growth, or providing nutritional insurance
4. No claims for good looks, good health, and long life can necessarily be attributed to the use of vitamins

The acceptance of this code will have to be seen to be believed

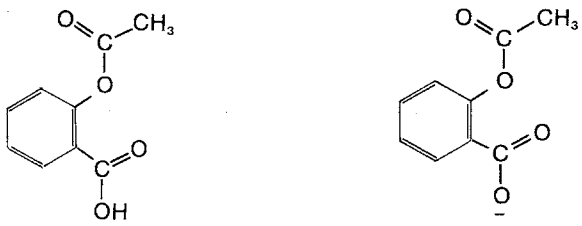
There are further sections on claims, treatment, professional recommendation, and testimonials. A very interesting clause is the one on disparagements:

An advertisement relating to goods for therapeutic use shall not contain claims intended to disparage other medication *or the medical or allied professions.* [my italics]

Copies of the code are available from the Australian Department of Health. Breaches are best reported to the Minister for Health (Parliament House Canberra) for an assured reply. For media other than radio and TV the State Acts or the *Trade Practices Act* 1974 apply (Section 52 Part V Consumer Requirements). It says *inter alia:* 'A corporation shall not, in trade or commerce, engage in conduct that is misleading or deceptive' (see Chapter 14—Sources of Consumer Information—for information circulars of the Trade Practices Commission who dealt with breaches of this Act.)

Back to analgesics and some chemistry . . .

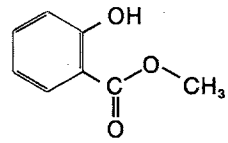
Recent experiments have shown that both salicylic acid and acetylsalicylic acid (aspirin) can breach the protective barrier in the stomach and cause stomach bleeding. For most people the bleeding produced is trivial—from half to two millilitres after two tablets—however for some people it can be hundreds of millilitres requiring emergency hospitalisation. In acid solution aspirin is un-ionised (Figure 9.2(a)) and is fat-soluble and can diffuse through the stomach protective barrier. Once through it is in a neutral environment—it ionises and then cannot pass back again. The rate of diffusion is enhanced by alcohol even when the contents of the stomach have a low acidity. The cocktail story of aspirin and alcohol being potent is seen to be well founded. Such co-operative action is often called *synergism* (see Chapter 5.)



(a) acid solution (b) neutral solution

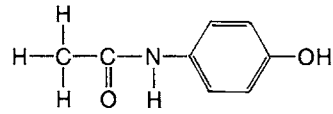
9.2 Aspirin in acid and neutral solutions

The related methyl salicylate (Figure 9.3), which has the common name oil of wintergreen, is used externally to ease the pain from rheumatism and strained muscles. Aspirin that is kept too long begins to hydrolyse to salicylic acid which is not tolerated too well by the human body.



9.3 Methyl salicylate

Soluble aspirin is either the sodium or the calcium salt of normal aspirin —they immediately form aspirin in the acid stomach in the form of *fine* crystals which possibly cause less gastric distress. Some analgesics such as Panadol contain *p*-acetylaminophenol (4-hydroxyacetanilide, paracetamol)—see Figure 9.4—which is comparable to aspirin as a pain-reliever but costs about ten times as much.



9.4 Paracetamol

Well—back on schedule(s).

S5 Schedule 5 can be regarded as the 'hardware' schedule. It contains a variety of chemicals used around the home—from epoxy resins, turpentine, and kerosene to moth balls, antifungal agents in wallpaper paste, and some pesticides.

S6 For the consumer this represents the pesticide and OTC (over the counter) veterinary products.

S7 Awkward chemicals needing special rules, e.g. vinyl chloride monomer (Chapter 6), *o*-tolidine (Chapter 5).

S8 Addictive drugs—morphine, pethidine, etc. which are legal.

Prohibited substance list

Odd bedfellows here: cannabis and heroin, thalidomide and 1,1,1-trichloroethane in aerosols for therapeutic use. In spite of its horrific history as a sedative, thalidomide is harmless as a chemical, provided it is not swallowed regularly. Its scheduling here represents political rather than scientific thinking.

There is also a list of *exemptions* to which the Uniform Poisons Schedules do not apply: timber and wallboard; ceramics; electrical components and electric lamps; vitreous enamels; explosives, glazed pottery, matches, motor fuels, lubricants, paper, photographic paper and film, inorganic pigments unless S6, paints as defined in the paint standard, blankets moth-proofed with dieldrin in the mill during finishing as directed by CSIRO.

Poison scheduling has not really come to grips with chemical substances outside the immediate medical, veterinary, and agricultural area.

APPENDIX 9.1

Thalidomide—a tragedy of malpractice and deception*

Thalidomide and the Power of the Drug Companies by Henning Sjostrom and Robert Nilsson. Published by Penguin, price $1.35.

In October 1960 two German doctors, members of the staff of the Institute of Human Genetics in Munster, exhibited two grossly deformed infants at the annual meeting of paediatricians in Kassel.

The babies' arms were so short that the hands seems to project almost directly from the shoulders. The legs, less affected, showed similar distortions. An abnormality of the blood vessels disfigured the faces of both children and one of them also suffered from a constriction of the small intestine. The two physicians had never before seen such a combination of malformations; not surprisingly, since this type of congenital malformation, on the research evidence then available, occurred no more frequently than one in four million births.

The German paediatricians concluded that the gross malformation picture represented a new clinical syndrome. Its cause has subsequently and tragically become a household word—thalidomide.

The tragedy of thalidomide seen as a story of an innocent case of a tranquilliser drug turning out to have monstrous side effects on the unborn, is hard enough for the mind to comprehend and accept.

It is almost impossible to adjust the mind to take in the possibility that the whole tragedy has far more sinister overtones; that thalidomide was marketed with an eye to profit first and tragic side effects a long way second; and that it was recognised as being a dangerous drug, for the damage it could do to the nervous system when it was put on the market; and even that the threat to the foetus was recognised for some time before it was withdrawn.

Yet this is how the authors of *Thalidomide and the Power of the Drug Companies* see the disaster. Far from the tragedy which occurred despite the best efforts of doctors and scientists to ensure the safety of the drug, [it is] a tragedy which should never have occurred if regulations had been tight enough. If clinical testing had been thorough

* Book review reprinted from the *Financial Review* with permission.

enough, if repeated warnings from physicians had been heeded and if, and this above all, the greed for profit had not so easily taken precedence over almost every other consideration in the marketing of thalidomide-containing drugs, notably on the part of the German company which first produced it.

Chemie Grunenthal was formed as a subsidiary of a German soap, detergent and cosmetics firm, in 1946, and began to produce antibiotics, which had a ready sale in epidemic-fearful postwar Germany.

Henning Sjostrom, a Swedish lawyer who advised the prosecution in several international thalidomide law suits, and Robert Nilsson, a Swedish research chemist, the authors of this shocking indictment of the company, argue that it frequently revealed itself to be a less than ethical operation, both in its marketing tactics and its lack of concern for the side effects of its products, long before thalidomide shot it into the unwelcome headlines.

In the mid-fifties Chemie Grunenthal entered a new area of pharmaceutical preparations, moving from antibiotics to the highly profitable field of sedatives and hypnotics.

In 1958 Grunenthal opened a massive publicity campaign for Contergan, the brand name for its thalidomide-containing tranquilliser. Soon it was launched on the international market, sold by licensees in 11 European, seven African, 17 Asiatic and 11 countries in the Western hemisphere, under 37 different brand names.

By 1961, the year when Contergan was finally withdrawn from the German market, total sales of thalidomide had reached a value of DM12.4 million which, added to export income of at least 25 per cent of that total, amounted to a highly profitable market for Grunenthal.

The drug was sold without prescription in Germany. The special publicity for thalidomide, masterminded for all countries by the manufacturers themselves, made great play of the product as 'completely innocuous', 'atoxic'. A British advertisement emphasised the safety of the drug with a picture of a small child taking a bottle from a medicine shelf.

By 1959, with the sales explosively increasing with the growing exploitation of markets—a liquid form of Contergan for children became West Germany's babysitter —adverse reports of severe side effects began to appear. Doctors and pharmacists commented on severe constipation, dizziness, decrease in blood pressure.

As early as September, 1959, the use of Contergan was dropped in a German hospital because of severe cases of purpura, or local haemorrhage of the skin. Grunenthal's Swiss affiliate relayed to the home company that Swiss doctors had reported tremor of the hands following the use of Softenon—the Swiss brand name.

'Once and never again. This is a horrible drug', announced a Swiss physician—in 1959!

Soon reports of irreversible side effects began to filter through to Grunenthal. A case of polyneuritis, a permanent impairment of the nervous system, was reported. Grunenthal commented that this had never been observed before, though later evidence showed that the company's own clinical trials of thalidomide in 1956 had revealed the possibility of polyneuritis.

Worse followed—reports of disturbances of the gait and of sensibility in fingers and toes, involuntary twitching of the facial muscles, double vision, even epileptic seizures.

None of this mounting body of evidence inspired any reaction in Grunenthal, beyond concern for their sales, which continued to rocket. Dr Heinrich Muckter, who developed thalidomide and directed its sales campaigns, wrote in April, 1960, 'Everything must be done to avoid prescription enforcement, since already a substantial amount of our turnover comes from over-the-counter sales.'

In the first four months of 1960, again despite the mounting body of adverse evidence against thalidomide, a quarter of a million leaflets were distributed extolling the drug as 'completely harmless, even for infants', 'non toxic' and 'harmless even over long periods of use'.

And in the background the company went to enormous lengths to suppress critical articles; it hired private detectives to report on the lives of physicians who displayed a hostile attitude to Contergan; it continued its policy of minimising the risks associated with the drug by advertising the rarity of adverse effects and the drug's therapeutic effectiveness; and it persuaded co-operative physicians to report favourably on the drug —one of whom testified at the later prosecution of Chemie Grunenthal that he had observed a case of Contergan polyneuritis the day after his article praising the drug's virtues had been published, but could not prevent the company from continuing to use his article for promotion purposes.

This story of intrigue, deception, callousness and greed is enough on its own. It is merely the curtain-raiser to the nightmare which was to come. Read further and, accepting the accuracy of these two Swedes' laboriously and magnificently researched account, you cannot but feel sick in the stomach.

It would surely not have been too much to have hoped that a mere hint of possible foetal damage of the magnitude of that which began to be revealed at the end of 1960 would have prompted a major reaction from the manufacturers.

But no. International requests for information about the passage of the drug from mother to embryo were treated non-committally—as they had to be in the light of Grunenthal's failure to include any trials on pregnant animals prior to launching their drug in a fanfare of publicity and recommendations for use by pregnant women.

Cases of extremely rare phocomelia [Gk: a monster having limbs so short as to suggest the flappers of a seal] appeared more and more frequently.

But leaflets to the effect that 'Contergan is a safe drug' continued to pour out and even when the mounting pressure of public opinion finally forced the withdrawal of the drug from the German market, the company was active in promoting the idea of resuming production as soon as possible.

The book goes much further than a straight indictment of what its authors clearly see as a company without a shred of integrity. Its record of the slowly grinding, badly oiled wheels of drug control agencies in Japan, Sweden, America, Canada, as well as Germany, show clearly that the machinery for drug control was inadequate and that there were major deficiencies in provisions for the development of new drugs. Even now pre-clinical animal tests are recommended only indirectly in Germany and this in a country with possibly 6,700 cases of phocomelia.

The book names names; quotes damning evidence from the pens of scientists and doctors; and quotes extensively from the profit-oriented comments of Grunenthal from the company's own documents—most of which had to be seized in police raids.

The book spares nobody. It comments that Dr William McBride notified the Australian representatives of Distillers, the British distributors of Distaval, of his suspicions of thalidomide malformations, but his observations never reached head office.

The Swedish Medical Board did not finally advise the Swedish distributors, Astra, to include a warning for polyneuritis in their thalidomide brochures until two weeks after Chemie Grunenthal had actually been forced to withdraw the drug completely from the German market.

Richardson Merrell, United States licensees for thalidomide, distributed 2,528,412 thalidomide tablets for 'experimental purposes' before Kevadon, the U.S. thalidomide brand, was released and approved by the FDA [Food and Drug Administration], but the FDA itself was unable, in the event, to track them all down.

They had been given to 20,000 patients in containers bearing no more than the directions for use.

The totally inadequate material available before the introduction of thalidomide in various countries, the faults of which must have been quite obvious to Chemie Grunenthal and its licensees, shows, say the book, that 'thalidomide was introduced according to the method of Russian roulette'.

The large number of trade names under which thalidomide was sold meant that a teratogenic action as the result of Contergan reported in a Stockholm newspaper was not recognised by Swedish doctors as Neurosedyn—the Swedish brand name for thalidomide.

And to round the whole horrifying episode off is the story of the extensive prosecution of the German company at Aachen, a case which was ultimately abandoned, but in which bitter wrangling and accusation, character assassination and high-powered drug company public relations activity went on, while outside the courtroom three thalidomide victims played while their mothers followed the case, and were daily reminders to the protagonists of what had been achieved in the name of profit.

The book raises a thousand different questions. It strongly suggests that the mysteries of science may be placing too much power in the hands of those who are out for profits.

It questions the role of commercial interests in drug production; the expenditure of enormous sums on drug publicity; the use of marketing brand names rather than generic terms; the emphasis of much pharmaceutical research, inevitably in a competitive market, on producing minor variations of a competitor's product rather than concentrating on new and beneficial drug developments.

It argues a case for some form of State-owned drug industry, if only as a means to break up an unsound non-competitive situation.

It pursues the increasingly pressing question of the need to evaluate much more carefully the therapeutic advantages of each new drug against the side effects that the drug may impose.

The tragedy of thalidomide is that its function, simply as a tranquilliser and sleeping agent, was by no means of the life saving nature which might have justified even the early revealed and relatively minor side effects let alone the ultimate and monstrous side effects.

It argues that pharmaceutical companies still shy away from accepting strict liability on the grounds that the drug industry is working uniquely for the benefit of mankind and is therefore not comparable to other industries—a spurious argument since this, like any other type of industry in the West, exists for profit.

It argues above all, and most tragically of all, that the industry and medical authorities cannot legitimately argue of thalidomide that 'nobody ever thought of such a possibility' and 'this catastrophe was unavoidable'.

The shocking evidence of this book is that the 'possibility was always there; that the catastrophe was not inevitable'.

The knowledge of large scale screening of drugs for teratogenic activity was available within the field of experimental embryology but, with some exceptions in the USA, no use was made of these methods within the pharmaceutical industry.

It was well known, even before the tragedy of multiple malformations woke the world to the problem, that drugs which may be innocuous to adults may cause severe damage to the young underdeveloped child, and most particularly to the unborn child.

Medical science, like nuclear science, can work miracles or wreak havoc.

'Sometimes man does not seem to learn even from disaster.'

—Yvonne Preston

APPENDIX 9.2: CHILD POISONING

The problem of accidental poisoning in children is a serious one. The figures from the Adelaide Children's Hospital for the last eight years are as follows:

Categories and modes of child poisoning, South Australia, 1969–76

	1969	1970	1971	1972	1973	1974	1975	1976
Categories								
1. Animal hazards	43	36	47	34	39	36	36	30
2. Cosmetics	27	33	42	38	43	36	23	15
3. External and topical medicinals	77	43	43	63	61	36	41	28
4. Internal and parenteral medicinals	534	528	598	592	545	499	462	373
5. Gases, vapours and fumes	14	6	12	2	3	34	1	2
6. Household products	148	121	138	128	140	117	115	92
7. Noxious foodstuffs	28	15	23	5	25	10	45	6
8. Plants	52	33	25	40	31	21	38	33
9. Solvents (non-petroleum)	7	9	7	5	5	5	7	8
10. Pesticides, agricultural and veterinary	96	106	95	78	86	84	56	57
11. Petroleum distillates	198	167	176	162	153	106	89	75
12. Miscellaneous (dyes, adhesives, etc.)	50	78	80	93	99	47	56	58
TOTALS:	1274	1175	1286	1240	1230	1031	969	777
Mode of poisoning								
A — Homicidal	5	1		1	2	4	1	
B — Suicidal	13	3	11	17	5	7	10	7
C — Therapeutic misadventure	32	30	25	28	21	21	14	11
D — Other accidental causes	1118	1050	1142	1112	1128	965	883	716
E — Allergy and idiosyncrasy	104	90	100	71	66	31	54	30
F — Mode undetermined	2	1	8	11	8	3	7	13
TOTALS:	1274	1175	1286	1240	1230	1031	969	777

Source: Child and Home Safety Advisory Committee, National Safety Council, Bowden, S.A. 5007. Reprinted with permission.

The following age breakdown indicates that poisoning is largely a problem of the 1–4 age group.

Break-down, by age groups, for child poisoning, South Australia, 1976

Age 1976	Male Total	Male Hospitalised*	Female Total	Female Hospitalised*
1	15	1	21	3
1–2	130	38	110	36
2–3	125	25	105	24
3–4	67	19	43	11
4–5	32	6	25	10
5–9	34	11	33	10
9–14	26	12	11	4
	429	112	348	98

*The 210 hospital admissions in 1976 occupied an average three bed days and there was one death.

A breakdown of individual product groups under some major headings follows:

Child poisoning, by individual product and major groups, 1971–6

Internal and Parenteral Medicines	*Cases Treated* 1971	1972	1973	1974	1975	1976
Various forms of alcohol	6	12	10	8	9	14
Analgesics (top cause: a brand of infant aspirin*)	75	91	68	67	49	37
Anorectics, stimulants	4	7	9	6	6	8
Antibiotics, anti-infectives	12	17	16	10	6	16
Anti-depressants	32	33	32	26	16	16
Anti-diarrhoea agents	4	1	2	3	5	1
Anti-emetics	17	14	8	12	4	15
Anti-epileptics	11	6	20	9	10	4
Anti-histamines	55	62	44	55	44	39
Anti-inflammatory agents	5	7	9	9	12	8
Anti-spasmodics	8	5	3	6	3	5
Barbiturates	25	22	20	16	13	6
Bronchodilators	11	15	13	22	10	18
Cardiovascular drugs	12	13	11	11	15	19
Contraceptives, oral	12	14	11	6	7	4
Cough and cold mixtures	46	41	45	36	22	30
Laxatives	18	21	27	22	16	15
Penicillins	48	27	29	20	31	13
Tranquillisers	72	81	53	61	71	40
Vaccines, injections	24	17	22	15	14	6
Vitamins, tonics, food supplements	5	6	6	2	7	1

*The original statistics list individual brand names which have not been reproduced here because incidence is a function also of market share. An examination of the actual products indicates that attractive flavours and colours are a prime cause.

External and Topical Medicines	*Cases Treated*					
	1971	1972	1973	1974	1975	1976
Nasal products	4	13	11	7	9	1
Oils (particularly camphorated)	14	24	28	18	14	10
Cosmetics						
Deodorants	2	—	2	—	—	—
Hair products	3	—	3	2	2	—
Nail products	7	12	12	6	3	3
Perfumes	10	10	15	10	6	6
Shampoos	13	7	2	7	7	4
Toiletries	7	9	9	11	5	2
Household products						
Bleaching agents	17	19	20	16	19	9
Caustic cleaners (for toilets, drains, floor strippers, frypan cleaners, oven cleaners)	11	18	16	12	13	24
Deodorising agents (air)	29	18	18	28	22	9
Detergents (non-laundry)	12	4	12	15	12	17
Disinfectants	35	32	40	22	23	18
Liquid cleaners	7	11	9	7	8	2
Polishes, waxes	18	22	15	10	14	9
Powder cleaners	6	2	5	3	2	1
Washing powders	3	2	5	4	2	3
Solvents (particularly methylated spirits)	7	5	5	5	7	8
Petroleum distillates (particularly kerosene, turpentine [turps], petroleum)	176	162	153	106	89	75
Agricultural products (particularly lime)	17	13	20	11	7	11
Pesticides (particularly mothballs)	78	85	62	67	48	42
Noxious foodstuffs	24	5	25	10	45	6
Plants (a fascinating variety—mushrooms stand out)	25	40	31	21	38	33
Miscellaneous (adhesives, catalysts and construction acids, particularly methyl-ethylketone peroxide)	19	25	25	12	12	22
Chemicals	21	22	25	13	19	17
Animal hazards (mainly spiders)	47	34	39	36	36	30

Complete statistics are available from the source.

APPENDIX 9.3
MOST FREQUENTLY PRESCRIBED DRUGS, 1971 AND 1974

The most frequently prescribed drugs in Australia in the years ending 30 June 1971 and 1974 were:

Proprietary name	Prescriptions (No.)	Type	Manufacturer
1971			
Indocid	2,161,716	anti-rheumatic	Merck Sharp and Dohme
Aldomet	1,385,808	anti-hypertension	M. S. & D.
Mysteclin	1,249,566	antibiotic	Squibb
Valium	1,215,203	minor tranquilliser	Roche
Amytal	1,184,136	barbiturate sedative	Lilly
Mylanta	934,732	anti-acid mixture	Parke-Davis
Tryptanol	884,473	antidepressant	M. S. & D.
Erythrocin	760,190	antibiotic	Abbott
Unbranded	608,005	semi-synthetic penicillin	—
Penbritin	568,923	semi-synthetic penicillin	Beecham
1974			
Valium (5 mg)	2,932,061	minor tranquilliser	Roche
Indocid	2,139,684	anti-rheumatic	M. S. & D.
Mysteclin-V	1,773,266	antibiotic	Squibb
Valium (2 mg)	1,686,411	minor tranquilliser	Roche
Aldomet	1,570,018	anti-hypertension	M. S. & D.
Mogadon	1,498,087	sleeping tablet	Roche
Tryptanol	1,149,611	antidepressant	M. S. & D.
Neogynon or Nordiol 21	not available	contraceptive pill	Schering AG/YF Pharmaceuticals
Chlotride	1,133,948	diuretic	Charles E. Frost
Slow-K	1,131,279	fluid replacement	Zyma

All companies are United States except Roche, which is Swiss. Valium was included in the Pharmaceutical Benefits Scheme in December 1972

Prescription Order on Pharmaceutical Benefits Top 20 Generic Items, Year Ended June 1976*

Generic code	Items	Example of proprietary name	Prescriptions (No.)	Cost† ($)
783	Diazepam	Valium	3,791,047	9,026,995
339	Norgestrel with ethinyloestradiol	Nordiol	2,657,901	7,181,441
940	Trimethoprim with sulphamethoxazole	Trib	2,621,407	8,933,822
698	Indomethacin	Indocid	2,442,620	8,841,753
416	Phenoxymethyl penicillin	Peni-Vee, Falcopen, Allaphen, Abbocillin-V.	2,299,462	6,054,626
123	Ampicillin	Penbritin	2,277,825	8,100,150
565	Tetracycline buffered with nystatin	Mysteclin	2,078,654	6,890,031
859	Nitrazepam	Mogadon	1,919,134	3,453,191
255	Erythromycin	Erythrocin	1,890,485	6,804,125
361	Ibuprofen	Brufen	1,842,254	5,271,505
363	Methyldopa	Aldomet	1,819,188	11,987,128
692	Amitriptyline	Tryptanol	1,671,998	4,092,045
538	Amoxycillin	Amoxil, Moxacin	1,573,631	6,210,499
465	Potassium chloride	Slow K	1,559,698	3,714,739
175	Chlorothiazide	Chlotride	1,551,806	4,896,113
680	Frusemide	Lasix	1,521,229	7,622,212
488	Dextropropoxyphene hydrochloride and paracetamol	Di-Gesic	1,327,291	2,007,124
112	Aluminium hydroxide gel with magnesium hydroxide	Aludrox Mylanta	1,315,835	2,747,888
162	Salbutamol	Ventolin	1,270,863	4,119,735
962	Betamethasone valerate	Betnovate ½	1,259,077	2,798,170
	GRAND TOTAL		101,649,715	315,026,451

*Part of a table of the top 50 from the Information Section, Pharmaceutical Benefits Branch, Department of Health.

†Cost includes patient contribution but excludes retrospective adjustments of dispensing fees. Tables of prescribed items, e.g. Valium 5 mg, Valium 2 mg, as well as individual manufacturer's share, are also available.

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This is a standard reference work on pharmaceutical nomenclature. It lists *40,000* synonyms for *5000* distinct pharmaceuticals. (Compare the 3rd edition 1966, *26,000* synonyms for *4000* substances.) Volume I contains the *structural* formula of the 4000 drugs and a running index number. The systematic chemical name of the compound (IUPAC rules); proposed and recommended WHO *non-proprietary* or generic names (in italics); and all the trade names are listed. Brief reference to therapeutic uses are also given. Volume II contains a group index to facilitate the finding of drugs related to each other chemically or pharmacologically with 1500 keywords. It also contains the 40,000 synonyms with index numbers corresponding to the structural formulae of Volume I.

Many preparations are marketed under different names in different countries (for trade mark reasons). The *same name* may refer to *different drugs* in different countries. It is hard to see that, for example, the antibiotics *chloramphenicol* and *tetracycline* need 203 and 190 synonyms respectively.

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Chapter 10

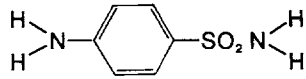
CHEMISTRY IN THE MEDICINE CABINET II—PILLS, POTIONS, AND PALLIATIVES

A discussion of the chemistry of drugs could easily fill a course on its own. It has a fascinating history for a start. The modern research on the mode of action of drugs is exciting and potentially very useful in paving the way for a more scientific selection of effective substances. It is perhaps not realised how much we still rely on naturally occurring substances—either directly or with some modification—for our pharmaceuticals. Even where it is possible to synthesise a drug such as morphine, it is often more economical to produce it from a plant and then perhaps add a few trimmings. A substance as complex as insulin is only synthesised once! This is done because synthesis is the ultimate proof of the correctness of the structure of the compound. However, as new and better chemistry is developed, the synthetic route to a drug can again become interesting and competitive.

I have selected only a section of this huge subject, and will concentrate particularly on the drugs that affect behaviour. These have become a consumer item in the sense that their use is spread widely across the population and some of the preparations are available without a medico's script. They also have the greatest potential for abuse.

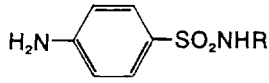
Drugs can be classified under headings of what they do, e.g. *analgesics* (pain deadening), *sedatives*, tranquillisers (reduce anxiety), *stimulants*, anti-depressants, hallucinogens, etc. But from the point of view of understanding, the relation between structure and activity is more useful. Let us consider the very first of the antibacterial drugs—the *sulphonamides*, which were found effective against the 'cocci infections' caused by the bacteria streptococci, gonococci, and pneumococci.

The basic compound is called sulphanilamide, which is illustrated in Figure 10.1

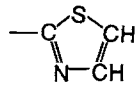


10.1 p-aminobenzenesulphonamide

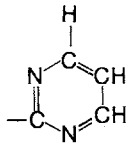
A whole *family* of derivatives can be built up on this compound by modifying the molecule in a manner which either changes its potency or reduces side-effects or toxicity. Thus if we write a general formula for a sulphonamide as



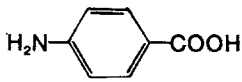
then in sulphathiazole, R =



and in sulphadiazine, R =



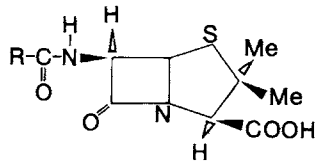
These are then members of the sulphonamide family or generic group. It appears that the effectiveness of these drugs depends on maintaining the basic structure and shape of the molecule, and you might wonder why. One of the essential growth compounds for most bacteria which are susceptible to the sulphonamides is *p-aminobenzoic acid*:



The theory is that bacteria absorb a sulphonamide 'by mistake' because its shape and charge distribution are similar to *p*-aminobenzoic acid, and then they cannot metabolise it. It fits into the cell machinery but then doesn't come out, i.e. it *blocks* the active sites. The sulphonamides as chemicals have been known for a long time but their medical value was discovered in 1934 by Domagk only by accident while looking at a series of azo-dyes used for counting bacteria. Why are the sulphonamides active against bacteria and not against people? Well, *p*-aminobenzoic acid is used by bacteria to produce folic acid

which they need, just as we do. By blocking the enzyme which carries out the first step the bacteria get no folic acid. Humans do not synthesise folic acid but obtain it from their food, and so the sulphonamides cannot deprive them of it.

A similar situation exists with *antibiotics*. These are substances produced by micro-organisms within themselves which, when excreted, interfere with the growth or metabolism of other micro-organisms—a sort of chemical warfare on a microbe scale. In 1929, Fleming discovered a mould of the *Penicillium* genus which inhibited the growth of certain bacteria. The active compound was called *penicillin* (Figure 10.2).



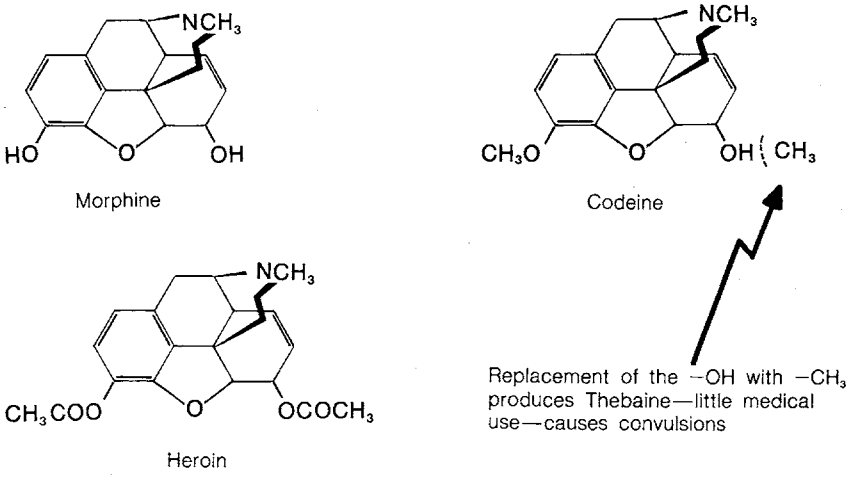
10.2 Penicillin

In the original penicillin, the R-group was a mixture. The R-group is varied often by adding molecules to the nutrient solution in which the mould is growing to produce many different penicillins. The mode of action of penicillin has only recently been determined. Penicillin interferes with the building up of the cell wall (which is continuously being digested and rebuilt) and the cells of certain bacteria are very much more sensitive to this interference. Penicillin is effective against a series of bacteria called Gram-positive (which take up and hold a certain stain or dye) but not against Gram-negative bacteria (in which the stain is washed out). In addition many bacteria have developed or can develop the *enzyme* or biological catalyst *penicillinase* (*-ase* always means the enzyme which is related to the compound or chemical reaction immediately preceding it), which can destroy *penicillin*.

In order to balance the argument on safety testing of drugs it should be pointed out that penicillin is quite toxic to guinea pigs. During the war there was no time to carry through an adequate testing program on animals. Just as well?

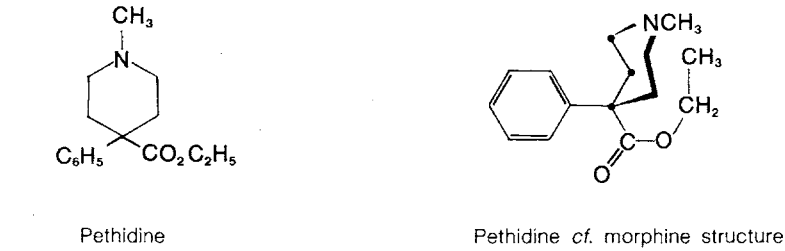
Now we will go on to discuss the behavioural drugs. In order to see how sensitive structure is in relation to pharmaceutical activity, consider the alkaloids associated with opium.[1] The alkaloid morphine was first isolated from the latex of the opium poppy (*Papaver somniferum*) by the German pharmacist Sertürner in 1805, although the ancient Babylonians probably used crude opium to relieve pain as long ago as 3000 B.C. Its addictive properties were

known from early times. In 1832 another alkaloid, codeine, was isolated from opium. Although codeine had only about one-tenth of the potency of morphine its prolonged use does not lead to physical dependence. In 1898 morphine was acetylated to produce diacetyl morphine or *heroin*, which was quickly realised to be even more addictive than morphine. Figure 10.3 illustrates the structure of morphine and some of its derivatives.



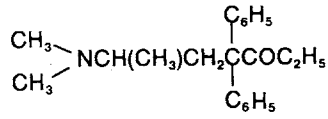
10.3 Morphine and its derivatives

The first potent analgesic to be prepared which did not depend upon opium for its prime source was discovered quite by chance in 1939 by Eisleb and Schaumann during a search for atropine-like activity. The substance *pethidine* seems only vaguely related to morphine but if the molecule is drawn to show a particular *conformation* the relationship becomes apparent (Figure 10.4).

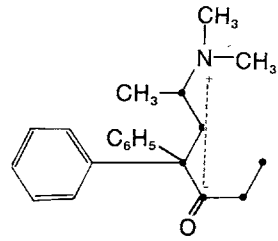


10.4 Pethidine

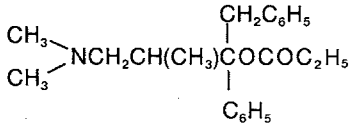
In 1946 the first member of an important new group of synthetic analgesics (based on 3,3-diphenylpropylamine) was introduced under the name *methadone*. Again the structural relation to morphine can be detected when the flexible methadone molecule is rearranged (Figure 10.5).



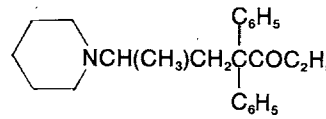
methadone
only the laevo form is active



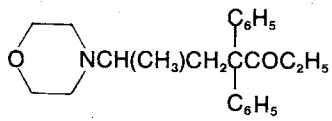
methadone *cf.* morphine structure



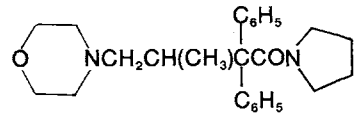
propoxyphene



dipipanone



phenadoxone

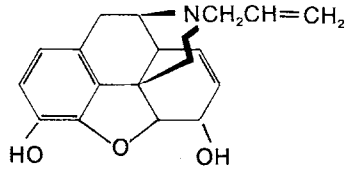


dextromoramide

10.5 Methadone and structurally related compounds

As long ago as 1915 a simple derivative of codeine was prepared in which the methyl group attached to the nitrogen ring was replaced by another alkyl group. Although this compound seemed itself devoid of any analgesic properties it was noted that it *antagonised* the properties of codeine. In 1941 a corresponding transformation was affected on morphine to give a substance which was named *nalorphine* (Figure 10.6). The first and obvious use of nalorphine was therefore to treat cases of poisoning by morphine and its derivatives. However, it has also proved very useful for diagnosing cases of addiction. When nalorphine is given to a person addicted to morphine or any of its derivatives it brings about a rapid and conspicuous onset of withdrawal symptoms. Also if a new drug is given over a period of some weeks, followed by an injection of nalorphine and this leads to the onset of withdrawal

symptoms, this can be taken to indicate that the particular drug is liable to cause dependence.



10.6 Nalorphine

In spite of reports of the discovery of strong analgesics which are non-addictive, it appears that addiction and analgesia go together. The time of onset of physical addiction of the opiates used to be characterised as follows:

1. Heroin—4–5 days
2. Morphine—1 week
3. Pethidine—10 days–2 weeks
4. Methadone—1 month

This can be compared with the barbiturates, where addiction takes about six months. Comparison of potency is done in two ways. Chemists consider a mole-for-mole effect between drugs. Physicians compare them on a dose for dose basis—where in fact the amount of material in a dose will be different for different drugs. In order to maintain a steady level of the drug in the body, the dosing must take into account the half-life of the drug in the body —see Table 10.1. Both these approaches have validity in their particular usage but the distinction must be kept in mind. For more on morphine substitutes see *Scientific American*, November 1966, p 131.

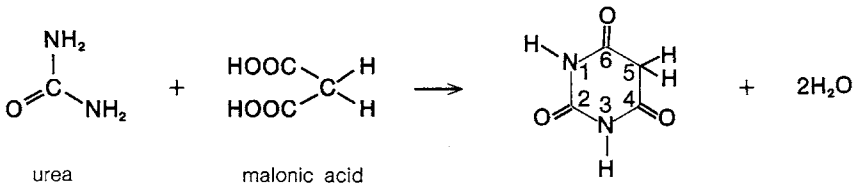
TABLE 10.1 *Half-lives of various drugs in the human body*

	hours
Penicillin	0.5
Erythromycin	1.6
p-aminosalicylic acid	1.9
Streptomycin	2.3
Chlorotetracycline	3.5
Imipramine	3.5
Aspirin	5.8
Pentobarbitone	42.0
Phenylbutazone	45.0
Bromide anion	180.0

Source: Albert[22]

Barbiturates

Barbiturates were the major ingredients which used to be used in sleeping pills and provided valuable adjuncts to anaesthetics.[3] Phenobarbitone, one of the earliest barbiturates to be synthesised, has distinctive anticonvulsant properties useful in the treatment of epilepsy. Barbiturates are derivatives of barbituric acid, first synthesised more than 100 years ago by the German chemist von Bäyer (of aspirin fame), by the reaction:



urea malonic acid barbituric acid

Barbituric acid is not pharmacologically active. Replacement of the hydrogen atoms at the fifth carbon position with alkyl or aryl substituents yields drugs with sedative or hypnotic properties.

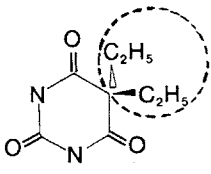
Since 1900, well over 2000 barbiturates have been synthesised; some are illustrated in Figure 10.7. A mere half dozen became widely adopted in medicine but now they are no longer considered suitable to induce sleep and have fallen into disuse. The chain length of the substituents at the C-5 position plays an important role in establishing the action of a particular barbiturate. Phenobarbitone, with phenyl group at C-5, was more valued for its selective anticonvulsant activity than for its sedative properties. Alkyl groups at C-5 also provide anticonvulsant activity. However, if the chain is too long or if alkyl groups are placed on the two nitrogen atoms at positions one and three, *convulsants* are produced.

If thiourea, $S{=}C(NH_2)_2$, is used in place of urea in the synthesising reaction, thiobarbiturates are obtained; an example is thiopentone, illustrated in Figure 10.7.

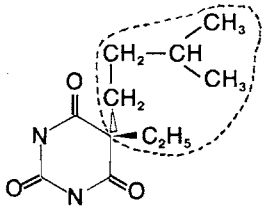
Generally, the more fat-soluble a barbiturate is made, by having non-polar groups, the more rapid is the onset of the action. Hypnotic properties may often be increased by increasing fat solubility and may be abolished by introducing polar groups on the side chains. Barbiturates and alcohol are both metabolised in the liver and even when both are taken at non-toxic dosages the combination can be toxic because the alcohol retards the excretion of the barbiturate. This is one example of a drug interaction.

The problem with all *chemically* effective hypnotics is that first time up they reduce dreaming. As a certain amount of dreaming is essential to the brain, the amount of dreaming experienced on coming off the barbiturate is

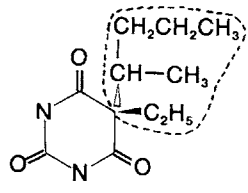
believed to increase to make up the loss. This can have the effect of apparently interrupting sleep (although it is often an illusion) so that the haggard patient will feel like taking more drugs. It may take many days or several weeks to re-establish a normal sleep pattern. (Some rats treated with barbiturates were found to suddenly respond less to a given dose than previously. The cause was exposure to DDT which activates the same liver detoxification enzymes that destroy barbiturates.) The word *chemically* is emphasised because in many cases sleep is induced indirectly, e.g. by relieving anxiety with a tranquilliser or a placebo (used because of the major interaction between expectation and effect).



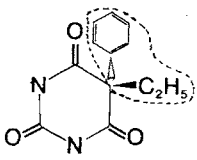
barbitone



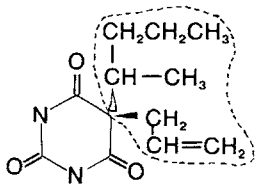
amobarbitone



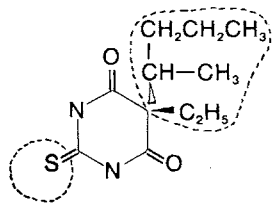
pentobarbitone



phenobarbitone



secobarbitone



thiopentone

10.7 Barbiturates

Barbiturates are sometimes classified according to length of action although this method is discounted by some authorities.

TABLE 10.2 *Classification of barbiturates according to action time*

A	*long acting* barbitone (Veronal); phenobarbitone*; mephobarbitone (Mebaral); diallybarbituric acid (Dial)
B	*intermediate duration* amobarbitone (Amytal); aprobaritone (Alurate); butobarbitone (Sonabarb;* butethal (neonal); hexethal (Oral); vinbarbitone (Delvinal)
C	*short acting* cyclobarbitone (Amnosed)*; pentobarbitone (Nembutal, Petab, Sommital, Penbon, Sodepent, Pentone, Pentobeta);* secobarbitone (Seconal)
D	*ultrashort acting* hexobarbitone sodium (Evipal); thiamylal sodium (Surital)†; thiopentonesodium (Pentothal)†

Names in parentheses are trade names
*Available under the Pharmaceutical Benefits Scheme
†The thiobarbiturates (Pentothal and Surital) are inactive by mouth and can be administered only by intravenous or rectal routes—they belong to the group of infamous truth drugs

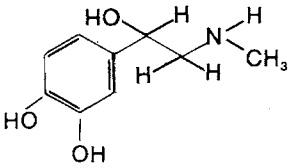
Both *tolerance* (increasing quantities needed for an effect) and physical dependence occur with high doses. The barbiturates stimulate enzymes in the liver that break down the drug thus reducing its effect. Although tolerance develops to the sedative effects of the drugs, the lethal dose remains essentially constant. As tolerance increases, therefore, the margin of safety decreases, and accidental poisoning may occur at doses that no longer provide sedation. The *therapeutic index* is the ratio of the toxic dose to the effective dose. The larger this factor the greater is the safety in the use of the drug. The therapeutic index is dependent on two types of drug tolerance:

pharmokinetic tolerance	*pharmodynamic tolerance*
a tolerance due to changes in the concentration of drug in the body caused by changes in liver activity	a tolerance caused by the receptor (where the drug acts) requiring more drug while the concentration for receptor poisoning may not change

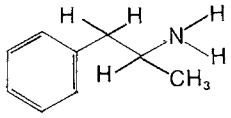
Amphetamines

Amphetamines were used to treat obesity, mild depression, narcolepsy (a tendency to fall asleep at any time), and certain behavioural disorders in children. The latter is the only current use. They cannot be prescribed without

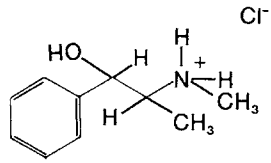
the consent of the Director-General of Health. Amphetamines are pep pills. Ordinary therapeutic doses of 10–30 mg per day provide a feeling of wellbeing and increased alertness. Amphetamines are structurally similar to the naturally occurring *biogenic amines* such as *ephedrine* which act as stimulants of the central nervous system, in similar manner to adrenaline.



adrenaline
(epinephrine)



'amphetamine'



ephedrine hydrochloride

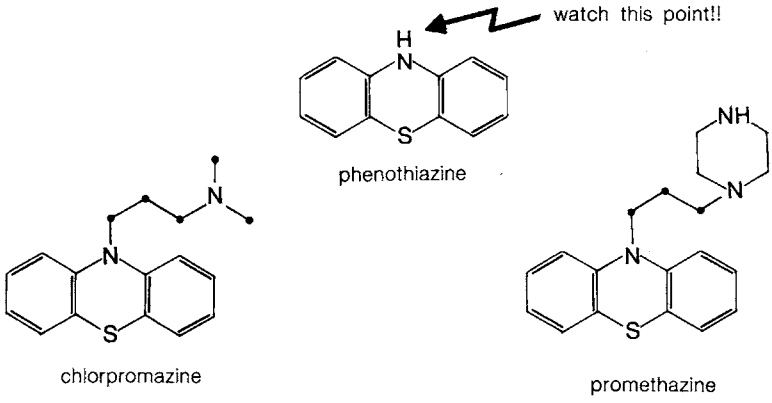
10.8 Biogenic amines

Amphetamine (as well as the other two compounds illustrated in Figure 10.8) is *optically active*. This means there are two compounds with *exactly the same formula* but whose structures are mirror images of each other and cannot be superimposed. (If you look at your two hands they are pretty much the same shape—I hope!—but you can't place one hand in an identical position on top of the other; however if you hold them parallel one acts as the image of the other in an imaginary mirror placed in between. In fact the two pairs of chemicals related in this way are called left and right handed(!)—or using the Greek, *laevo* and *dextro* or just *l*- and *d*- for short. It is actually a bit more complicated than this . . . but then, isn't it all?) Strange as it may seem, compounds differing only in this way can be biologically very different in their activity. *Benzedrine* is a 50–50 mixture (racemic) of the *d*- and *l*-amphetamine but as the *l*- is less active on the central nervous system, pure *d*- or *dexedrine* is obviously nearly twice as potent.

Amphetamines and barbiturates were often used in conjunction. Thus amphetamines may be consumed in the morning to alleviate the symptoms of a barbiturate hangover, whilst the barbiturates may be necessary to counteract the stimulant properties of amphetamine and allow the user to sleep. (In case of overdose they were also used as mutual antidotes—the deeply held belief by the public in antidotes is somewhat dangerous, because although two substances may be antidote in *one* aspect, they can reinforce each other (*synergism*) in other side effects—the death rate can be very high.) The amphetamines also form a family of drugs although the pattern is somewhat difficult to see and tends to overlap other categories of drugs.

Tranquillisers

These are drugs which sedate without inducing sleep. The *major* tranquillisers are used in the treatment of psychotic disorders and many of them are based on a compound called *phenothiazine* (Figure 10.9).



10.9 Phenothiazine and two of its derivatives

TABLE 10.3 *Series of phenothiazine tranquillisers with different types of substituent*

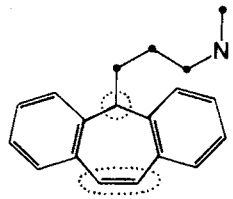
Generic name	Trade name (Pharmaceutical Benefits Scheme)
Aliphatic series	
chlorpromazine	Largactil, Plegomazine, Promacid, Protran, Serazone
(laevo-promazine)	
promethazine HCl	Phenergan
Piperidine series	
thioridazine	Melleril
pericyazine	Neulactil
Piperazine series	
prochlorperazine	Stemetil, Compazine, Anti-Naus
thiopropazate	Dartalan
fluphenazine	Anatensol
fluphenazine enanthate	Anatensol Enanthate
fluphenazine decanoate	Modecate
trifluoperazine	Stelazine, Calmazine, Terfluzin

Derivatives of *phenothiazine* which retain the sulphur atom but not the nitrogen are the thioxanthine tranquillisers, which are listed on Table 10.4.

TABLE 10.4 *Thioxanthine tranquillisers*

Generic name	Trade name
chlorprothizene	Taractan
clopenthixol	Sordinol
flupenthixol	Fluanxol
thiothixene	Narvane

If the sulphur and the nitrogen atoms of phenothiazine are replaced by —CH=CH— and —CH— respectively, one of the derivatives is protriptyline —Figure 10.10; compare it with the tricyclic antidepressants in Figure 10.12.

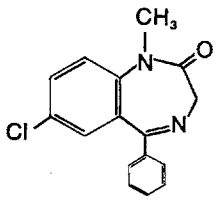


10.10 Protriptyline

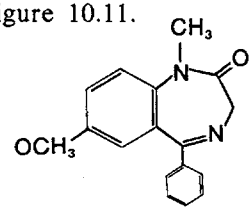
All these compounds are used to relieve anxiety, over-excitement, and restlessness, and they affect the brain stem rather than the cortex. Their use has profoundly modified the problems of the mental hospital but they do carry a high incidence of adverse reactions.

Minor tranquillisers

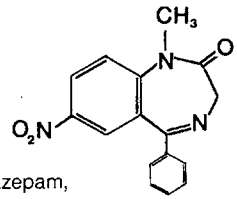
The most common of the minor tranquillisers are built up on a benzodiazepine nucleus; four are illustrated in Figure 10.11.



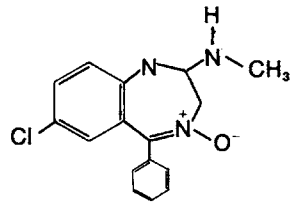
1. diazepam, trade name: Valium



2. oxazepam, trade name: Serenid



3. nitrazepam, trade name: Mogadon (sleeping pill)



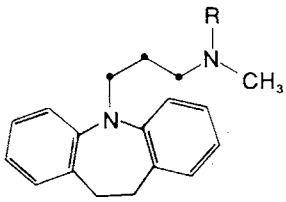
4. chlordiazepoxide, trade name: Librium

10.11 Minor tranquillisers

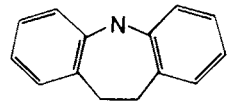
Librium was used in the treatment of neuroses, behaviour disturbances, alcoholism, and as premedication for anaesthesia. Valium is used in treating musculo-skeletal disorders, relieving spasms, and improving sleep pattern. All these substances can lead to drug dependence and withdrawal symptoms. At the present time Valium is used for virtually everything—it is the drug with the fastest increase in prescription—and Mogadon is the preferred drug for sleeplessness.

Tricyclic antidepressants

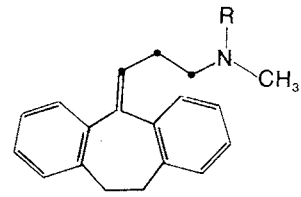
Depression is a problem which faces many people and the 'tricyclics', usually derived from *dibenzazepine*, form a popular family of antidepressants. These drugs have as many side effects as the tranquillisers. They present a particular problem of overdose abuse, and they are not *all* on the Pharmaceutical Benefits Scheme list.



imipramine, where R = $-CH_3$
desipramine, where R = $-H$



dibenzazepine



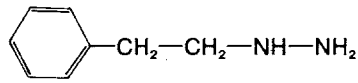
amitriptyline, where R = $-CH_3$
nortriptyline, where R = $-H$

10.12 Tricyclic antidepressants

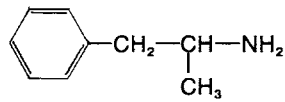
TABLE 10.5 *Tricyclic antidepressants*

Generic name	Trade name (Pharmaceutical Benefits Scheme)
imipramine	Tofranil, Imiprin, Iramil, Prodepress
desipramine	Pertofran
amitriptyline	Tryptanol, Laroxyl, Saroten
nortriptyline	Aventyl, Allegran, Nortab
protriptyline	Concordin, Triptil
dibenzepin	Noveril
trimipramine	Surmontil
doxepin	Sinequan, Quitaxon

An interesting series of drugs that was once used for depression are the so-called *monoamine oxidase inhibitors* (or MAO inhibitors); the name means that they have the capacity to inhibit an enzyme which is normally responsible for removing certain substances (those *biogenic amines* again!) such as noradrenaline and serotonin from the body. Currently there is considerable evidence that depressive illnesses are associated with a *decrease* in the level of these amines in certain parts of the central nervous system, so that by inhibiting their destruction, their level is increased! An example of a biogenic amine is phenelzine, illustrated in Figure 10.13; notice its close similarity to amphetamine, which is illustrated in Figure 10.14.



10.13 Phenelzine



10.14 Amphetamine

Other MAO inhibitors are listed in Table 10.6.

TABLE 10.6 *MAO inhibitors*

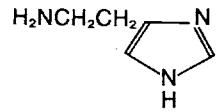
Generic name	Trade name (none on Pharmaceutical Benefits Scheme)	
iproniazid	Marsilid	—5% rate of liver damage
phenelzine	Nardil	
nialamide	Niamid	—less effective than a placebo
isocarboxazid	Marplan	
tranylcypromine	Parnate	—strong 'cheese' effect (see below)
mebanazine	Actomol	

Patients treated with these drugs have to be warned to avoid eating cheese, certain wines such as red Chianti, certain beers, foodstuffs such as marmite

and bovril, and must not take any other medication without consulting their doctor. The reason for this is that these foodstuffs contain *tyramine* which is normally broken down in the alimentary canal. When MAO inhibiting drugs are used the enzymes which carry out the breakdown are inhibited, allowing tyramine into the bloodstream. This causes a massive release of noradrenalin which in turn causes a sudden fluctuation in blood pressure producing intense headache—or worse.

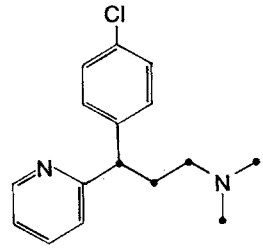
Antihistamines

Many people are allergic to pollen, stings, dust, etc. An *allergen* is a substance that initiates the allergic response—it is usually a protein but sometimes a polysaccharide. For a person with pollen allergy, a pollen grain enters the nose and clings to the mucous membrane. The nasal secretions acting on the pollen grain release the grain's allergens and other soluble components, which penetrate the outer layer of the mucous membrane. By a series of events that are not well understood the allergen forms a complex with an antibody of a type which is present in unusually high concentrations in allergic persons. The complex is responsible for the release of the allergy mediators of which one of the most potent is histamine (Figure 10.15). Histamine is formed by the breakdown of the amino acid histidine; it accounts for many of the symptoms of hayfever, bronchial asthma, and other allergies.



10.15 Histamine

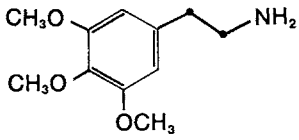
Antihistamines are most widely used for treating allergies and there are more than fifty types available. Many of these contain, as does histamine, an ethylamine group, $-CH_2CH_2N=$. These drugs compete with histamine for the receptor sites normally occupied by histamine on cells where it causes the effects of allergic reactions. An example of a well-known antihistamine is Polaramine (Figure 10.16). Note that some of the tricyclic antidepressants have antihistamine effects as well, because they also contain the ethylamine group.



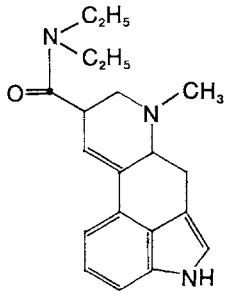
10.16 Dexchlorpheniramine (Polaramine)

Hallucinogenic drugs

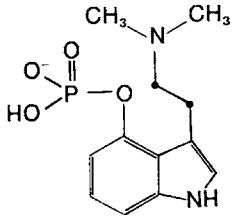
Hallucinogenic (or psychotomimetic) drugs derived from various plants have been used from time immemorial. They were used for religious purposes and for festivals and orgies. The use of the poisonous toadstool *Amanita muscaria* extends over thousands of years. The Aztec and Mayan cultures used the peyote cactus from which *mescaline* (Figure 10.17) is derived. They also used the psilocybe mushroom (or sacred mushroom Teonanacotl) the active principle of which is *psilocybin* (Figure 10.18) and is about thirty times as potent as mescaline. This mushroom is also found in Australia, in northern Queensland and Darwin, and in Canberra! From a plant called ipomoea the Mexican Indians obtained a substance similar to lysergic acid (Figure 10.18), and from the plant *Datura stramonum* (thorn apple) they imbibed *scopalamine* and



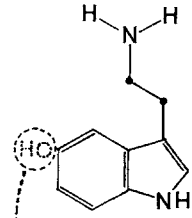
10.17 Mescaline



lysergide (LSD_{25})

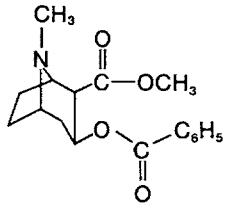


psilocin
(psilocybin)



tryptamine
(5-OH tryptamine is
also important)

10.18 Some hallucinogens



10.19 Cocaine (blocks nerve transmissions)

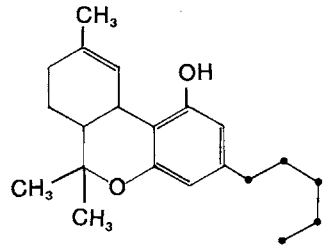
atropine. Other plants used in Central and South America contained *cocaine* (Figure 10.19) and there is at least one hallucinogenic animal, a caterpillar found in bamboo stems. An interesting fact is that tannin in tea contains gallic acid which can be converted to mescaline by complex chemistry. Mescaline was made famous by Aldous Huxley. It is classed as a *catecholamine* along with amphetamines to which it is structurally related (compare the structures).

Lysergic acid diethylamide (LSD)

LSD is classed as an *indoleamine*. It is one of the most potent known drugs and doses as low as 20–25 μg (1 μg = 10^{-6} g, 1 millionth of a gram), are capable of causing marked effects in susceptible individuals. It was at one stage believed to cause chromosome damage when taken in large doses but this is now disputed. Lysergide (Figure 10.18) was discovered, in a chemical sense, by the Swiss chemist Albert Hofmann in 1938, when he accidentally ingested some of the compound while investigating a modified ergotamine as an improved drug for childbirth. Clandestine manufacture is usually from ergot alkaloids to yield lysergic acid to which the diethyl groups are easily added. Ergot itself is found on many plants—particularly rye. An ergot alkaloid is used to induce uterine contractions. In ergotamine, the diethylamino group is replaced by a peptide (a mini-protein).

Cannabis

Cannabis, extracted from marihuana, hashish, Indian hemp, has a long history. The most active ingredient in the extract is *tetrahydrocannabinol*, THC (Figure 10.20). THC can be obtained from the fruiting or flowering tops of the cannabis plant whose cultivation in Australia is banned. There are many other ingredients in cannabis other than THC and their long-term effects are unknown. It is believed to be less harmful than tobacco.



10.20 Tetrahydrocannabinol (THC)

Drug Interactions

This is an extremely important area of study—especially in the days where the family doctor concept is under threat of extinction. One drug can change the pharmacological effect of another—using the term *drug* in the evident sense to include alcohol, some foods, and food additives, etc. Some even precipitate in the bottle, e.g. tetracycline and calcium ion.

For a start, drugs which are taken orally have to be absorbed through the gut and this can be influenced by other material present. By using suitable coatings a drug can be absorbed either in the acid stomach or the alkaline duodenum. Once the drug is in the plasma it can become bound to protein and only a small percentage remains free and active. This percentage can be drastically altered by another drug which kicks the first one off its protein site. Often use is made of this method to boost the efficiency of a drug. Also a drug can affect the efficiency of an enzyme and hence influence the rate at which a second drug is broken down by that enzyme. The MAO inhibitor 'cheese' effect is a classic example.

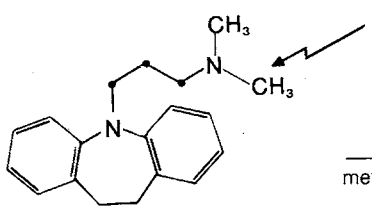
The way and speed with which drugs are metabolised by the body can also depend on *genetic factors*, so that comparisons between animals and man and between individuals can be misleading. They also depend on *physiological factors*—such as age, diet, hormones including the effects of pregnancy, and disease states—especially if the liver is involved. The old are particularly liable to be treated with several drugs simultaneously and they in particular will have impaired metabolism which will affect the drugs' effect on them.

Very often a drug is changed in the body to another compound. Sometimes the new compounds are inactive, sometimes more active than the original. The original may even be completely inactive and it is the new compound (metabolite) that is the 'real' drug. Some examples of this are shown in Figure 10.21.

In fact the body can be used as a chemical factory! Note the tremendous importance of the liver in the metabolism of drugs. You may begin to realise what immense problems this opens up. Not only do we have to have information about the effect of a new drug we may want to introduce—but also about the effect it has on other drugs and they on it. We have to know what other compounds it forms in the body and what their properties are. The rat is still one of the most popular animals used in toxicity testing but it has active micro-organisms present in its stomach so that orally administered drugs may be extensively metabolised by bacteria even before absorption, giving a markedly different metabolic pattern from that obtained in humans. On the other hand many drugs used in treatment of illness are of high molecular weight (greater than 400) and as a consequence are excreted in the bile as well as the urine, so that they are frequently subject to bacterial metabolism in the intestines.

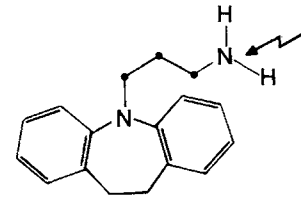
Drug

Product

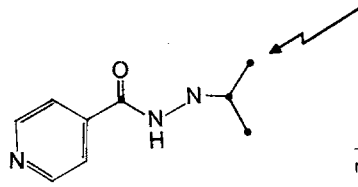


imipramine
probably inactive

body
metabolism

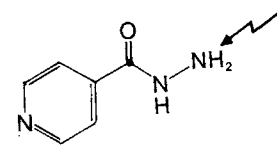


desmethylimipramine
antidepressant

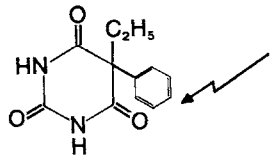


iproniazid
antidepressant

body
metabolism

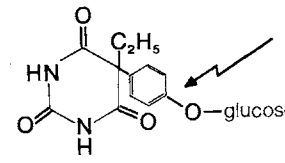


isoniazid
antitubercular

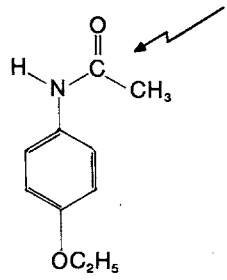


phenobarbitone
hypnotic

body
metabolism

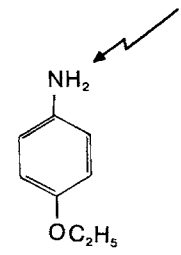


p-hydroxyphenobarbitone glucuronide
inactive, readily excreted



phenacetin
(acetophenetidine)
analgesic, antipyretic

body
metabolism



p-phenetidin
methaemoglobin-former
reduces red blood cell efficiency

10.21 Effects of metabolism on the pharmacological activity of drugs

These products can be reabsorbed and further metabolised by the liver—a cycle of absorption, metabolism by the body, excretion, bacterial metabolism, reabsorption and metabolism by the body.

To top it all there is also the time factor to be considered—which we will deal with more fully under another heading. The chemical β-naphthylamine was a very important intermediate in the dyestuff industry. It was found, however, that it is a very potent carcinogen—it causes cancer of the bladder. It took a long time to realise this because there is a time lag of about thirty years between contact and cancer. It was only because a large number of ex-employees of a German chemical firm all died of the same disease at about the same time that the link with the past could be established. The same story has repeated itself more recently with the chemical vinyl chloride used in the manufacture of the plastic polyvinyl chloride.

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Chapter 11

CHEMISTRY OF THE CAR AND OTHER ENERGY USERS

ENERGY

In this chapter we will deal with energy and other topics not necessarily directly related to the car. Energy comes in many different forms. It comes as chemical energy in the form of fuel and food, as potential energy in the form, for example, of water stored in high dams for hydro power, as electricity, as tidal energy, as nuclear energy. Except for nuclear energy, all the other forms come indirectly from sunlight which grew the plants that became the fossil fuels, or raised the water (by evaporation and then rain) into the dams, either of which can be converted into electricity. Tidal energy is generated by the gravitational action of the moon (which is consequently moving away from us, slowly). Nuclear energy is released by the fission (breaking up) of large atoms such as uranium and plutonium, or the fusion of small ones such as heavy hydrogen. The earth receives energy directly from the sun—about 200,000 million megajoules every second. About 30 percent of the incident radiation is reflected directly back out into space, nearly 50 percent is converted into heat, another 20 percent evaporates water from land and sea to power the water cycle. A tiny but important fraction is used in photosynthesis by plants which convert carbon dioxide and water into glucose and cellulose and other materials.

The joule is the metric unit of energy. A joule is about one quarter of a calorie, the 'old' unit of energy. The word Calorie when used with food is actually a kilocalorie or 1000 calories. The units used for energy include kilojoule (kJ, a thousand joules) and megajoule (MJ, a million joules).

Chemical energy is one of the most efficient ways of storing energy. A litre of petrol weighs about 800 g and can yield 35 MJ of energy by oxidation.

It is interesting to compare various forms and costs of energy to the consumer. See Table 11.1, figures are for 1977.

TABLE 11.1 *The costs of energy to the consumer*

Type of energy storage	Inherent energy value (MJ)	Cost per kilo ($)	Cost other ($)	Cost per hundred MJ($)
1 kg of petrol (1.2 litres)	42*	0.20		0.46
1 kg of heating oil	42*	0.13		0.31
1 kg of butter (1 litre of fat, 200 ml of water)	31*	1.60		5.20
1 kg of sugar	17*	0.31		1.82
12 volt 50 amp-hour car battery	2.16		2.00 (charging fee)	93
1 kW radiator	3.6 per hour		0.023–0.055 per hour	0.64–1.53 per hour

Recommended daily allowance of usable energy for people:

9MJ

12MJ

An average woman weighing 60 kg, 160 cm tall uses energy as follows

Basal metabolism	6 MJ/day
normal activities	3MJ/day

so increasing *activity* by 10 percent uses up 0.3 MJ, supplied to her by one slice of bread (dieting is the only answer!)

Rowing	4 MJ/hour for a 15 minute race	1 MJ
Gardening	0.8 MJ/hour for 3 hours	2.4 MJ

*This is the energy released on burning the material—not its availability to humans on eating.

Comparison of heating costs

Comparisons of heating costs can be obtained from the local electricity authority (some figures are given in Appendix 11.1) and from the oil companies, there seems to be no connection between the two sets of figures. There are two important parameters to the calculation. First, the heat value of the fuel—the amount of heat produced when a quantity of fuel is completely burnt—or when any energy source is completely converted to heat. Different heat values for different fuels are due to the difference in the individual values

for carbon and hydrogen: H = 121 MJ/kg, C = 33.7 MK/kg—and the density of the material when costs are given per litre—and non-burning impurities. The heat value for all hydrocarbons lies between the values for hydrogen and carbon, closer to the C value because C is heavier than H. The second parameter is the efficiency—i.e. the heat delivered to the room as the percentage of the total heat available from the heat source. Just how efficiently the heat delivered to the room actually warms us is discussed in Appendix 11.2. To make the calculation we also need to know the relationships between the various energy units. As well as the Calorie, older units of energy include the British Thermal Unit, BTU, and the Therm; the unit of electrical energy is the kilowatt hour, kWh. The prices used in the calculations are subject to change (upwards) at rapidly decreasing intervals. They should be used only as a basis for comparison, not as a conclusion.

1kJ	= 0.948 BTU	1 MJ	= 948 BTU
Therm	= 100,000 BTU		
	= 105.5 MJ		
1 kWh	= 3412 BTU		
	= 3.6 MJ		
		1 MJ	= 0.28 kWh
1 J	= 0.24 calories	1 calorie	= 4.18 J
1 horsepower hour	= 2.69 MJ	1 MJ	= 0.37 horsepower hour

Electricity

The cost of a unit of electricity varies with usage and location. Using Canberra and Bega rates for 1977 gives a good spread. Taking a rate of 2.3 (6.8) cents/unit, and an efficiency of 100 percent (which means input and output costs are the same), then the cost per energy unit works out at 0.64 (1.9) cents/MJ.

	Average cost per unit	
	Canberra (¢)	Bega (¢)
On a bill of $21*	3.3	11.6
30	2.6	10.5
50	2.3	6.8
70	2.2	5.4

Canberra: first 50 units at 7.7 cents; next 500 at 3.03 cents; rest at 1.95 cents

Bega: first 120 units at 13.13 cents; next 240 at 8.62 cents; rest at 3.58 cents

* Minimum quantity tariff for Bega

Gas

We shall limit the discussion to bottled gas which is all that is available in the Australian Capital Territory. The efficiency of an unflued gas heater is about 90 percent. For flued liquid petroleum gas heating the maximum and minimum efficiencies are given by the British Standard (BS 1250 Part 4) as 78 percent and 50 percent. The United Kingdom Ministry of Housing gives an average of 60 percent. Bottled gas is generally sold by weight (but occasionally also by volume, which of course depends on the temperature—if you buy by volume make sure you only buy on cold days!). The heat value of gas is 49 MJ/kg or 25.5 MJ/litre (Aust. Liquefied Petroleum Gas Association).

TABLE 11.2 *Comparative heating costs March 1977 Canberra*

Fuel	Cost/Unit (cents)	Cost per MJ heat value (cents)	Cost for heat at 60% efficiency (cents)
Gas			
Shellgas	24.47/kg	0.50	0.83
Speed-E-Gas	12.628/l	0.46	0.77
Shellgas	22.27/kg	0.45	0.75
Essogas	21.194/kg	0.43	0.72
Shellgas*	16.292/kg	0.33	0.55
Oils†			
Kerosene	15.40/litre	0.75	1.25
Heating oil	10.94/litre	0.53	0.88
Distillate	10.05/litre	0.49	0.82
Diesel fuel#	9.63/litre	0.47	0.78
Coke§	$3.20/36 kg bag	0.33	0.55
Splitwood§	$28.00/tonne	0.23	0.38
Greenwood§	" "	0.42	0.70
Briquettes§	$3.60/50 kg bag	0.30	0.48
Electricity	Canberra	0.64	0.64
	Bega	1.50	1.50

*Special high usage rate.
†Higher efficiencies are obtained with well maintained heaters on optimal (generally high) settings.
#In 1975 diesel fuel was only *half* the cost of heating oil.
§A slow combustion stove has an average efficiency of 50–65 percent but for an open fire the efficiency is much less, average 20 percent, which boosts the costs to well above other forms of heating.

Oil

The heating value of oil type fuels varies a little (kerosene 36.7 MJ/litre, heating oil 37.7 MJ/l, distillate 38 MJ/litre, diesel fuel 38 MJ/litre. The efficiency of an unflued oil heater is about 95 percent, while flued oil heaters can vary from 50 percent to 75 percent. For comparison we shall use 60 percent as the average efficiency.

Solid fuel

The heating value of coke and coal is 27 MJ/kg; split wood is 12.4 MJ/kg but drops to 6.7 MJ/kg for green wood; briquettes are 24.75 MJ/kg.

Comparative heating costs in the Australian Capital Territory, at March 1977 are given in table 11.2. It does *not* take account of any fixed costs, e.g. supply or hire of gas cylinders, installation of oil tanks, etc.

The householder must consider capital costs and maintenance. All currently available commercial sources of energy produce pollution. Coals, briquettes, and wood are the worst for air pollution followed by diesel oil, heating oil, and then LP gas. Electricity pollutes somewhere else—either in coal burning, in nuclear waste disposal, or the flooding of areas such as Lake Pedder.

Heating costs can also be reduced through use of adequate insulation. The transmission coefficient for heat is given the symbol U and is the rate at which heat is transferred through a building structure in watts per square metre degrees Celsius temperature difference, J.s m^{-2} T^{-1}. Some typical values for winter are given in Table 11.3. The smaller the coefficient the *better* the insulator.

WORK

In the preceding section we discussed the generation of heat—thermal energy —from air acting with common energy sources; fossil fuels (oil, gas coal), wood, and electricity (hydropower, coal-burning, nuclear). In this section we will deal with the other major use for our energy resources—the generation of useful work or *mechanical energy*, and here we will emphasise those aspects relating to transportation, especially the motor car.

Combustion engines

All combustion engines convert heat energy into mechanical energy and the heat is produced from fossil fuels such as petrol, diesel fuel, coal, etc. During the conversion there are losses due to friction in the mechanical parts of the engine and, for cars, frictional losses on the road and against the air. Quite apart from these 'mechanical' losses there is a much more fundamental loss. Let us first consider the paradox in some of our sayings. There is a statement called the first law of thermodynamics which says *Energy can be neither created nor destroyed.* Energy is converted from one form into another, e.g.

TABLE 11.3 *Heat transmission coefficients: winter values*

Part I—Walls

Construction	Thickness cm	Mass per unit area kg/m²	*Interior Finish* None	Gypsum plaster 15mm
Concrete (specified)	10	240	4.6	4.2
	30	720	2.8	2.6
Double clay brick 2 # 9 cm @ 6 cm air gap	24	346	2.1	2.0
Hollow concrete block (Besser)	9	100	2.6	2.4
	19	150	2.0	1.9
			fibrous plaster 9 mm	plaster board 12 mm
Brick veneer 9 cm brick; 15 cm air gap	24	184	2.0	1.9
Weatherboard outside with timber framing	12.5	35	2.1	2.0
As above with 7.5 cm of Rockwool and 2.5 cm air gap	12.5	40	0.5	0.5

Part 2—Suspended floors (heat flow down)

Construction	Thickness cm	Mass per unit area kg/m²	*Interior Finish* None	Vinyl tiles 3 mm	Carpet and underlay
Concrete					
10 cm + 2.5 cm sand and cement topping	12.5	287	2.4	2.35	1.2
30 cm + 2.5 cm sand and cement topping	32.5	767	1.8	1.8	1.0
2.2 cm timber floor	12.2	32	2.1	2.0	1.1
2.5 cm chipboard	12.5	28	2.0	2.0	1.1
2.2 cm timber plus Alfoil with 10 cm air gap	12.2	32	0.8	0.8	0.6
2.5 cm chipboard plus Alfoil with 10 cm air gap	12.5	28	0.8	0.8	0.6

Part 3—Pitched roofs (heat flow up)

Construction	Mass per unit area kg/m²	*Plasterboard 12 mm insulation* None	Mineral fibre 10 cm	Aluminium foil	Polystyrene blocks
Concrete tiles	69	2.8	0.4		
Terracotta tiles	74	2.8	0.4	no data	no data
Concrete tiles and sarking	69	1.6	0.35		

Source: Air Conditioning Systems Design Manual, Australian Department of Housing and Construction, 1974

from sunlight to filled dams, to electricity, to electric motor movement, and finally to heat (as frictional losses). *Whatever* cycle you take, the final result is always heat. On the other hand we read about how we are 'using up energy at too fast a rate'. This statement is technically wrong. The first law of thermodynamics is (as far as we know) correct. Energy is not used up, it is converted into less useful, and finally useless forms. This is not the same thing as being used up. It is the *usefulness* of the energy which we are using up, not the energy itself. A street-full of hot exhaust gases is obviously not as useful as tanks full of petrol. The measure of uselessness is called the *entropy*, a concept which we will not pursue here further.

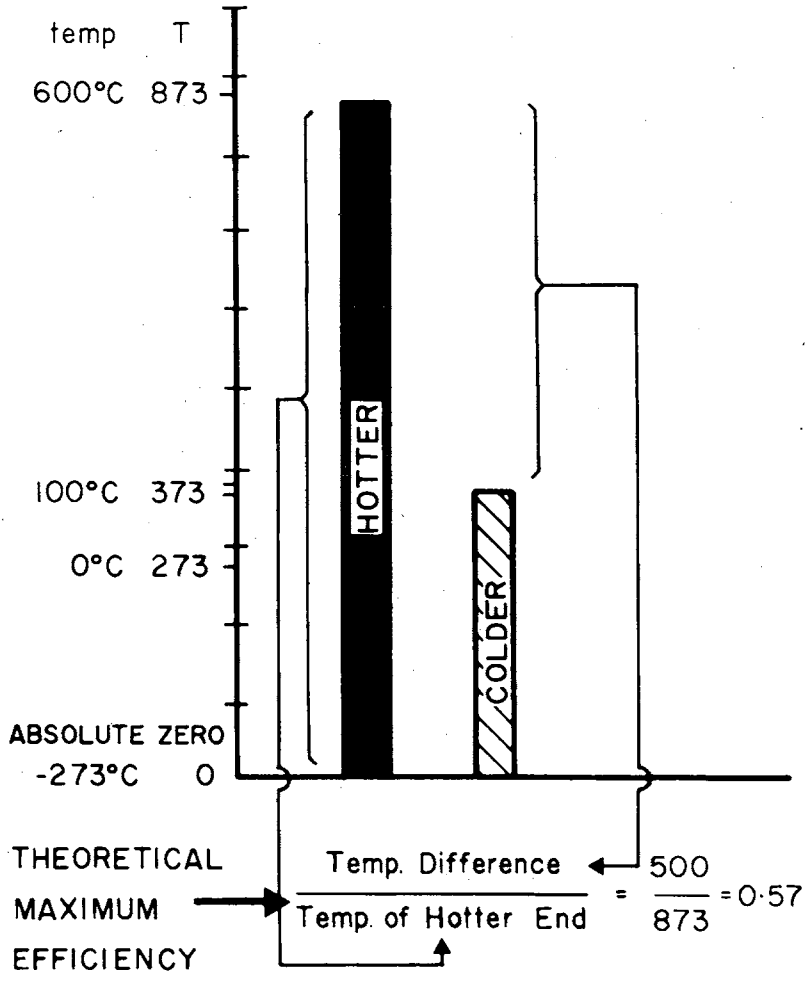
Most of the 'higher' forms of energy such as electrical, mechanical, nuclear, solar, and chemical energy (with reservations) are about equally useful.

Heat is the interesting one. Although it is the least useful form of energy, its usefulness is variable. The 'hotter' heat is, the more useful it is. To be more correct, the greater the difference between the temperature at which heat goes into an engine and that at which it comes out of the engine, the more useful it is. If you think about it, all combustion engines have a hot in, and a colder out (in a car, it is the hot cylinder and colder exhaust; in a steam engine, it is the hot boiler and colder condenser). All such engines are called *heat engines*. The *theoretical* (without any losses) efficiency with which heat can be converted into other forms of energy such as mechanical is given by the following formula:

$$\text{Efficiency} = \frac{(t + 273)_{\text{hot input}} - (t + 273)_{\text{colder exhaust}}}{(t + 273)_{\text{hot input}}}$$

where t is the temperature in degrees Celsius.

The 273 converts Celsius degrees into absolute degrees of temperature—the ultimate in coldness or the absolute zero of temperature is −273°C.



11.1 Thermal efficiency

If the gas in the cylinder of a car engine has an *average* temperature of about 600°C (the peak temperature is much higher—see later in the section on gas turbines) and the exhaust temperature is 100°C, the maximum possible efficiency is (873−373)/873 = 57 percent. Transmission losses cut this back to 20–25 percent in real life. A brief description of some combustion engines follows.

Steam engine

The steam engine is an external combustion engine: the fuel is burnt external to the motor. Hence a wide variety of fuels can be used, and can be burned efficiently without additives! However the power/weight ratio is unfavourable compared with the later internal combustion engines, and acceleration is lower. It also requires a driving fluid (water) which has to be carted around as well as the fuel.

Diesel engine

A diesel engine is an internal combustion engine which explodes its charge by the heating due to compression. Both four-stroke and two-stroke engines are used. The four-stroke diesel cycle is:

1. Down—charge with air
2. Up—compression with heating (compression ratio varies from 16:1 to 23:1)
3. Down—fuel injection: burning and expansion with a smaller rise in cylinder pressure than for petrol engines
4. Up—exhaust

The diesel engine exhausts only about a tenth of the amount of carbon monoxide exhausted by the petrol engine. Hydrocarbon emission is about the same. Blowby is negligible in the diesel engine, since the cylinders contain only air on the compression stroke. Evaporation emissions are also low because the diesel uses a closed injection fuel system and because diesel fuel is less volatile than petrol. Nitrogen oxides levels in the exhaust gases are probably worse than for petrol engines. The major problem is smoke and odour. The smoke can be reduced by about 50 percent by adding about 0.25 percent barium additives (!), which probably work by inhibiting the dehydrogenation of hydrocarbons to carbon particles or/and promoting their oxidation. The sulphur in the fuel helps to convert about 75 percent of the barium to insoluble barium sulphate.

Diesels with their higher compression ratio and higher temperatures are more efficient than petrol engines, running up to about 35 percent thermal efficiency.

Petrol engines

This is the most common internal combustion engine for family cars. Like the diesel, both two- and four-stroke cycles are possible, with the latter being the more common and more efficient (but more complex mechanically). The differences between petrol and diesel engines are: petrol engines work on lower compression (usually 7–10:1) and thus need a spark to ignite the charge; carburation is more common than fuel injection; a more volatile, more highly flammable fuel (petrol) is used and this normally contains a range of additives (see later this chapter) to 'improve' its performance. The basic four-stroke petrol cycle looks like:

1. Down—air *and fuel* intake
2. Up—compression and *spark ignition* near completion of compression
3. Down—power stroke: expansion due to increased volume of gas and rise in temperature
4. Up—exhaust stroke

A major problem with petrol engines is that of atmospheric pollution, due to:

1. Lead compounds from $PbEt_4$—anti-knock additives (see later this chapter)
2. Carbon monoxide, CO, from incomplete combustion.
3. Nitrogen oxides, NO, NO_2, etc. formed from air during the high temperatures of the explosion.
4. Hydrocarbons—unburnt or incompletely burnt fuel: 65 percent in exhaust, 15 percent from evaporation, 20 percent from blowby (gases that escape past the piston rings into the oil sump). The amount of emission here is determined by infra-red photometry.

As increasing the compression ratio increases the thermal efficiency and performance of the motor, this has been a standard 'advance' in automotive design. The increased compression, however, requires higher octane fuel (see later this chapter and Appendix 11.4), necessitating increased lead tetra-alkyl content and hence more pollution. Also more nitrogen oxides are formed at the higher temperatures of the high compression engines. With the current emphasis on pollution problems the compression ratio in modern cars has begun to drop. The decrease in power output is usually made up by a larger capacity (size of cylinders)—lower economy, more carbon monoxide and hydrocarbon pollution. You can't win! See Appendix 11.5.

Some general facts about the energy consumption in petrol cars follow.

The heat value of the fuel is distributed as:

useful work	24 percent
cooling water	33 percent
exhaust	36 percent
friction	7 percent

The temperatures in the engine vary:

near the spark plug	1000–1650°C
central electrode of plug	500–900°C
cylinder wall (water cooled)	80–150°C
cylinder wall (air cooled)	95–220°C
exhaust valve	up to 860°C
piston base	300–500°C

At the point of ignition the piston, plugs, etc., reach temperatures of 2000–2500°C and withstand pressures of 3–6 MPa (1 atm $\approx$ 0.1 MPa).

Methane

Sewage gas is 95 percent methane, 4 percent CO_2. The production from four London sewage works in 1939 amounted to over 1 million cubic feet per day (equivalent to about 5000 litres of petrol). Methane has a high heating value (42 MJ/kg—18,000 BTU per lb = 950–975 BTU per cubic foot) about twice that of coal gas. It does not dilute or destroy the oil film on the cylinder walls.

While on the topic of car engines here are a few handy definitions

Compression ratio

A compression ratio of 10:1 means the mixture of petrol and air is compressed to one-tenth of its volume at normal outside air pressure and then ignited. Methanol, CH_3OH, is often used as a racing fuel. This is not because it has more 'power' (44 MJ/kg for all hydrocarbon fuels such as petrol, diesel oil, kerosene, heating oil, etc. and only 19 MJ/kg for alcohols), but because of its higher octane rating (160) it can be used at higher compression ratios (19:1 or higher).

The internal combustion engine is in fact a gas engine, where gas is the working medium, heated by the ignition of the mixture causing expansion. If we can get a cool and therefore more concentrated charge into the engine we will get a higher power output. For example, alcohol needs more heat to convert it from liquid to vapour (0.5 MJ compared to 0.14 MJ for petrol) allowing it to act as a refrigerant and cool the gas entering the cylinder between cycles. The alcohol fuel is usually ethyl alcohol with 0.5 percent of vile tasting pyridine—it costs about 1½ times the cost of top grade petrol and about double the amount is needed because of the heat value difference.

Air-fuel ratio

A petrol engine has an air to fuel ratio of 14:1 to 15:1. For alcohol as a fuel the ratio is 7:1 to 9:1 which means carburetter jets for alcohol are ($\sqrt{2}$ = 1.4) times in diameter (not twice!). (Carburetter = burette used in cars.)

Nitromethane (CH_3NO_2) is also used in bike racing—it supplies its own oxygen for burning, but it produces nitric acid in the exhaust and requires the driver to use a gas mask. It increases power but *reduces* the allowable compression ratio.

Safety aspects

Flash point

This is the temperature to which a fuel must be heated before vapours will ignite by a free flame in the presence of air.
Flash points:

methanol	+11°C	diethyl ether	−45°C	*n*-hexane	−21°C	nitromethane	+35°C
ethanol	+13°C	1,4-dioxan	+12°C	benzene	−11°C	carbon tetrachloride*	
cyclohexanol	+68°C	cyclohexanone	+44°C	*n*-heptane	−4°C	chloroform*	
ethyleneglycol	+111°C			*n*-octane	+13°C	methylene chloride*	
				n-decane	+46°C		

*non-flammable

Ignition temperature

The temperature at which a combustible mixture with air ignites in the absence of a flame.

H_2	580°C	*n*-pentane vapour	309°C
petrol	550°C	carbon disulphide	100°C
town gas	600–650°C	acetylene	335°C

Flammability range

This is the range in composition of vapour with air in which explosions can occur. In fuel-rich mixtures there is insufficient oxygen to sustain combustion. In air-rich mixtures there is insufficient fuel.

Other engines

Sarich orbital engine

After the initial flurry of interest in this engine, little has been heard about developments. The initial specifications given were that for a 150 kW engine

(200 hp) the power-to-weight ratio was 3.3 kW/kg compared to a conventional V8 piston engine of the same power of 0.41 kW/kg and a Wankel engine of 0.82 kW/kg. It has high torque at low speeds. Compared to a 150 kW V8 engine with some 388 moving parts, the Sarich has only 12.

General Motors Sel-1 steam car

This engine requires 30–45 seconds to build up sufficient steam. Its fuel consumption is approximately 1.3 km/litre and it covers 3.5 kilometres/litre of water. It weighs 200 kg more than the petrol engine it replaces but has only half the power.

Gas turbine

These have large acceleration lags (1.5–7 seconds) and their high continuous operating temperature of 3500°C means a high production of nitrogen oxides (NO_x). NO_x is produced at temperatures above 2900°C which is only intermittently reached in a piston engine.

Electrical motors

The electrical motor is simplicity itself. There is only one major moving part —the rotor—and the modern electrical motors are remarkably efficient in operation. Some 80 percent of the electrical power is commonly converted into mechanical energy, the efficiency depending on the loading—the rest, as usual, is 'degraded' to heat. The theoretical efficiency is 100 percent because the electric motor is not a heat engine—it does not use heat as the driving energy. The problem for transportation purposes is twofold—electrical engines have a much lower (by about five times when batteries are included) power-to-weight ratio than the more usual petrol engine. The standard batteries (see later this chapter) are heavy and have a low power capacity. In an electric car the battery weight constitutes about half the weight of the car, to give a total of about two tonnes (for a converted standard sedan). About 14 kW continuous power can be achieved. The high efficiency and particularly the very low pollution aspects of electrical motors are currently drawing much research in an effort to overcome weight and capacity problems.

All other common portable power sources involve combustion processes—either internal (within a closed system) or external (the burning fuel is open to the air).

Solar powered air engine

In the early nineteenth century Robert and James Stirling devised a method of driving an engine using air in the cylinder and heat supplied by a furnace

through a heating surface. In Stirling's engine, the heating effect was slow and eventually the heater surface burned out, and so the engine was abandoned.

Importantly, Stirling's idea was to use a *regenerator*, which in essence is a heat storage device, so that some of the heat rejected during the engine cycle of operation was stored and re-used in another part of the cycle of operation. When Stirling built his engine his regenerator was a massive construction using sheet iron plates maintained at high temperature at one end by the furnace and at low temperature at the other end by a water cooler. With the inclusion of the regenerator in the engine cycle of operation the engine had a higher thermal efficiency than any other form of engine using heat energy and this is still true today.

PLATE 11.I *The Enfield 8000 — showing its plug-in recharging connection. Electric Commuting Car No. 859 off the production line at the Enfield Works in England. It weighs one tonne with half the weight in its eight 12-volt batteries (the engine is only a tenth of the weight of the batteries and hidden away behind the seats). It recharges overnight from a 240 volt supply and has a range the next day of 50 kilometres.* (Canberra Times, 14 September 1977)

There has been a revival in interest in the Stirling cycle with its process of regeneration recently,[1] and modern research has shown that with improved manufacturing techniques and by using gases other than air, in particular helium and hydrogen, and operating the engine at higher cylinder pressures, engines with thermal efficiencies as high as 40 percent with good power outputs are possible and in fact have been constructed.

The principle followed in this engine has been applied in satellites as a power source using solar energy as the external heat source. Also some large industrial organisations are developing this type of engine. Some of these new forms of the engine are being used in German buses, burning gas or petroleum products to provide the heat energy.

The mechanical engineering department at Swinburne College of Technology in Melbourne has been conducting experiments on the Stirling engine.[2] One object of the experiments is to harness solar energy. A demonstration of this engine is given by the Swinburne Travelling Science Show, and in their course on consumer chemistry.

Refrigerators and air conditioners

A refrigerator is a heat engine running in reverse. In a heat engine, heat is pumped in at a high temperature and exhausted at a lower temperature to produce mechanical work.

In a refrigerator mechanical work put into the compressor (by an electric motor) takes heat from the colder (inside) part and exhausts it at the hotter (outside coils) part. Exactly the opposite operation. The energy efficiency for this process, namely the heat removed from the inside of the cabinet divided by the mechanical energy needed to do this is given theoretically by inverting the equation given earlier for the heat engine

$$\text{Efficiency} = \frac{(t + 273)_{\text{hot}}}{(t + 273)_{\text{hot}} - (t + 273)_{\text{cold}}}$$

where t is the temperature in degrees Celsius.

If the inside of a refrigerator is $-18°C$ (in the freezer) and the outside temperature around the coils is 40°C, then the theoretical efficiency is

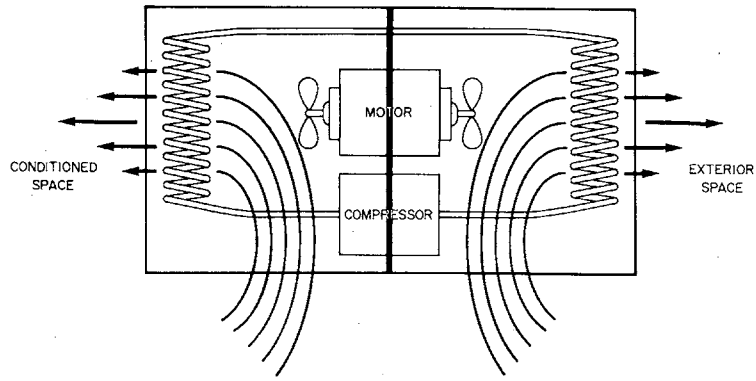
$$313/(313 - 255) = 5.4$$

The ratio is greater than unity—you are *transferring* (not producing) about six times as much heat as the mechanical energy you are putting in. This ignores the heat produced by the electric motor. The larger the difference between inside and outside temperature the lower the efficiency. That means the colder you operate your fridge or the poorer the outside coils are ventilated

the less efficient the operation. (Some modern freezers fully enclose outside coils for aesthetic reasons—this increases your power consumption.)

When electricity is *converted* directly into heat as, say, in a radiator, the efficiency of conversion as we discussed earlier is 100 percent. If we transfer heat from a colder source (say outside a house) to the inside—that is use a refrigerator with the cabinet 'outside', so to speak, and the heat removing coils 'inside'—we would be heating our house with an efficiency of about 540 percent. Why don't we do this? Well this is exactly what happens in a reverse cycle air conditioner[3] (see Figure 11.2).

An air conditioner is a refrigerator. In normal operation it cools the house and heats the air outside. In reverse cycle it heats the house and cools the air outside. The same operation is involved in each case—only the compression and expansion coils are interchanged. The actual efficiency obtained in practice varies from 1.6 to 2.6 whereas in theory to maintain an inside temperature of 20°C and with an outside temperature on the coils of 50°C the theoretical efficiency is about 10.



11.2 Reverse cycle air conditioner

Problem

Assume that the total cost of operating the air conditioner as a heat pump (pumping heat from the cold outside into a house) is four times the theoretical power cost for perfect efficiency, whereas the cost of direct electrical heating is just the power cost. If the room temperature is 27°C, at what outdoor temperature would the two systems yield equal cost?

Before you get carried away—there are other considerations such as capital cost and maintenance which are part of the consumer (and energy) equation! On this topic there is an MIT report: *Consumer Appliances—The Real Cost*.[4] The life cycle cost (i.e. the cost over the whole life of an appliance) of a refrigerator consists of 58 percent electrical power cost, while purchase price, 36 percent, and servicing, 6 percent, are smaller. In contrast, for colour television electrical power contributes only 12 percent, with purchase price 53 percent and servicing 35 percent.

ENERGY DOWN ON THE FARM

In energy terms, our modern food system is expensive. Processing and distribution use up a lot of energy—far more than is actually contained in the food itself. At present much of that energy comes from oil—a resource that is becoming scarce and expensive.[5]

Food and fuel are interchangeable. Farm produce can be chemically converted into fuel, and microbes can convert petroleum into food. However, a point that arose in our introductory comparison of costs of consumer energy must now be clarified. It is important to distinguish the fuel value of food when it is burnt and the nutritional energy value when it is eaten. Only about three-quarters of the fuel energy in our food is absorbed when we eat. The figures to be used here refer to *fuel* energy. The indigestible cellulose of course can be converted to sewer gas.

The arrival of a perfectly cooked meal on the dinner table marks the end of a long chain of energy-devouring processes. These begin not on the farm but in an earlier primary industry: mining. Before we can have mechanised agriculture we must have machines. All of this takes a great deal of energy, as does the production of fertilisers and pesticides, and the provision of irrigation. Even after it passes through the farm gate, most food still requires more energy expenditure for some kind of processing and packaging before it is transported to the supermarket. From there it usually is driven home in the back of a car. Finally in the kitchen it is likely to spend some time in a refrigerator before at last being cooked to become our meal.

Two Canberra scientists at CSIRO (Dr Roger Gifford and Dr Richard Millington) have studied this energy usage.[6] The energy budget is a very broad one, dealing only with the aggregate of all Australian agricultural production over the years 1965–69. Individual products have not been isolated because the web of energy inputs for each product cannot be clearly traced. Plant material harvested by man and his livestock represent a mere 0.01 percent of the sunshine (falling on rural land) that could be usefully absorbed by plants. Nevertheless, this plant matter has a fuel value about 1.5 times greater than all the fuel energy burned by people in Australia. Only about 15 percent of this massive amount of plant tissue is harvested directly—the rest is eaten by livestock and converted into wool and animal products.

The energy inputs to farm products before they leave the farm are as set out in Table 11.4.

TABLE 11.4 *Energy input on the farm*

	$\times 10^{15}$ joules per annum	
Direct farm use		sub-total
fuel	46.2	
electricity	8.4	54.6
Fertiliser		
mining	3.5	
shipping	9.8	
manufacture	5.5	18.8
Farm machinery (mining and manufacture)		6.8
Agricultural chemicals		4.4
Road transport not included elsewhere		1.0
Farm labour		1.2
		86.8

Many of the less tangible inputs to farming have been omitted from the budget such as agricultural research and extension. The energy inputs to farm products after they leave the farm are set out in Table 11.5.

Food processing and distribution use much more energy than food production. Omitted from the table are such indirect items as the energy used for building food factories, refrigerators, and stoves. About 14 percent of the energy in food produce leaving the farm comes from animals, and it costs three joules of grain (at least) to produce one joule of meat. Losses during processing, retailing, kitchen preparation, and digestion are difficult to estimate, but it seems that we absorb into our bodies only about half the fuel value that leaves the farm.

In summary, what the final balance showed was that for each joule of *digestible* food energy eaten in Australia at least 5 joules are expended in making it available of which:

—0.6 joules is in getting it to the farm gate—11 percent
—2 joules in taking it from the farm to the retail store—38 percent
—2.8 joules in getting it from the store to the dinner table—51 percent

TABLE 11.5 *Energy input from farm to dinner table*

	$\times 10^{15}$ joules per annum	
Transport from farm		
rail	2.1	
road	5.0	
grain handling	0.3	7.4
Factory processing		
bagasse as fuel	9.7	
other fuel	45.6	55.3
Food and drink packaging		
steel cans	10.8	
paper	8.5	
fuel value of paper packaging	4.3	
glass	5.5	29.1
Road transport from factory		7.7
Subtotal to retail store		99.5
Transport from store to home	33.0	
Domestic refrigeration	46.0	
Domestic cooking	42.0	
Subtotal store to dinner table		121
Grand total		220

Work, in progress, of converting the world's valuable fossil fuel reserves directly into food by growing microbes on the petroleum and harvesting them as food for livestock (or humans) has shown this to be feasible and economic. However it does not solve the problem of the much larger energy consumption past the farm gate. In the food chain, the internal combustion engine guzzles at least 40 percent of the total energy consumed in the total process. While shopping uses only 2 percent of the fuel going into petrol tanks of private cars, it represents 10 percent of the total energy cost of the food. Any improvement in transport would represent a substantial saving.

Our method of agriculture has been compared to that of the Tsembaga tribe living in the New Guinea highlands in 8.3 km^2 of tropical rainforest.[7] The comparison is difficult because of different cultural values but a very important difference is that their energy comes from renewable resources (trees) whereas ours comes from non-renewable fossil fuels almost exclusively.

A similar energy analysis can be done on uranium. If you assume that there is *no* inherent energy content in uranium then nuclear technology can convert about 1 MJ of oil into 1 MJ of electricity (where the oil is used to mine,

extract, transport, and upgrade the uranium). This shows an energy advantage over a conventional oil-fuel generating station which requires 4 MJ of oil (in this case burnt directly) to produce 1 MJ of electricity. Thus uranium is a component in a new technology that allows our oil reserves to last four times as long. If the uranium input to nuclear reactors is counted as a fuel input, with a theoretical energy content of uranium then nuclear reactors operate as poor energy converters (energy ratio of 1:100). Breeder reactors complicate the issue because they require 'burner' reactors to produce the plutonium.

SOLAR ENERGY

There has been a resurgence of interest in solar energy in recent years because of the realisation of the limitations of our present energy resources. An immense amount has been published. From the point of view of the consumer, a useful report is that of the Australian Senate Standing Committee on National Resources, *Solar Energy*.

For 1973–1974 the percentage of primary energy consumption of the various sectors of the Australian community was as follows:

	%
manufacturing	33
electric utilities	28
transport	27
domestic/commercial	5
mining	3
agriculture	2
other	2

These figures suggest that the thrust of Australia's solar energy research and development strategy should be aimed at manufacturing and liquid fuel applications. The more important applications in manufacturing are the generation of heat for industrial uses where process hot water and low pressure steam are required.[8]

The Committee, on examining the evidence put to it, came to the conclusion:

At the scientific level, debate indicates that some experts are more concerned with the promotion of their own projects than with the overall development of solar energy utilisation.

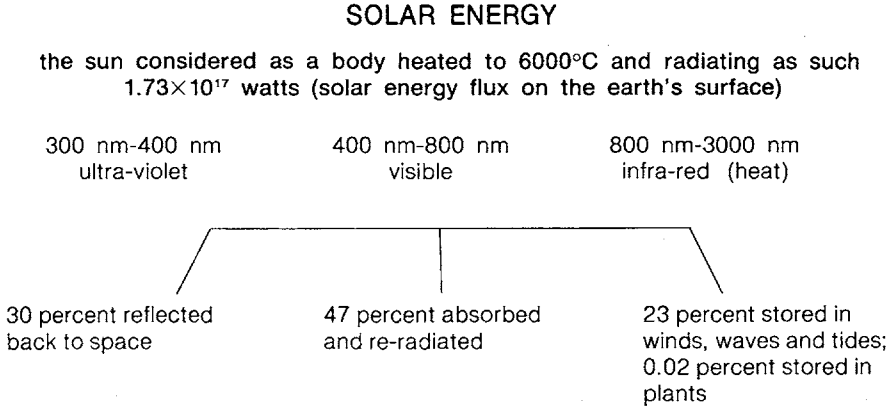
The use of collected solar energy in Australia represents less than 1 percent of total energy consumption with domestic water heating and heating of swimming pools as the major areas. Photovoltaic cells are being used in some remote areas to provide low power requirements for communications purposes.

Solar hot water systems consist of panels of collectors, generally copper pipes, installed to face north. The water heats up and circulates through collectors into a storage tank which generally has an electric booster for overcast days. The lifetime of commercial plastic collectors is believed to be

about ten years. The plastic used in pipes is a black acrylonitrile butadiene styrene (ABS) copolymer (see Chapter 6). It has a much lower thermal conductivity (heat transferring properties) than metals.

As solar heating generally competes with electricity, it is important to see how electricity is costed. The electricity authorities assume that coal (used for most generators) has *no intrinsic value* when they determine the rates. To them the cost of coal is simply the cost of digging it out of the ground, and because the big power stations are now located on coal fields, the cost of digging it out of the ground is very low. The export price of coal varies from $5.60 per tonne for steaming coal from mines tied to electricity authority power stations to about $40 per tonne for export high grade coking coal. Using this market value the electricity tariffs could be expected to be much higher and also provide an incentive to preserve coal rather than offer off-peak tariffs. Under changed accounting rules solar energy might be quite competitive. The off-peak rates are used to encourage consumers to use electricity outside the 7 a.m.–11 p.m. period to assist in balancing demand because boilers have to be kept idling on standby in coal-fired power stations. It is argued that the cost of providing the hardware for supplying electricity to consumers is about 70 percent of the total cost, so that the cost of the coal saved by solar heating is small (on present accounting). Charging for electricity may revert to the method used for telephones, namely a fixed rent to pay for a share of the overheads and then charge per use. A solar enthusiast will then need a co-operative neighbour, an extension cord and a private meter to take care of low usage domestic needs and cloudy days!

There are many interesting physical aspects of solar heating technology. One of these is highly developed at the NSW Institute of Technology and involves



11.3 The fate of the solar energy that reaches the earth

studying selective surfaces which have high absorbance (~ 90 percent) for sunlight but low emissivity for heat radiation (3–8 percent) so that the heat which is obtained from the sun is not lost again.

Readers should consult the report for further information.

PETROL, DIESOLINE, ETC.

With the demise of the steam engine Australia, following the path of most western so-called developed nations, has switched almost exclusively to *petroleum* as the fuel for its vital transportation industry. Current world usage is in excess of 10 million litres of crude petroleum oil and 3000 million cubic metres of petroleum gas *a day*. At this steady rate, not allowing for increases, the known reserves will be gone by the year 2000 A.D.

Petroleum is the fossilised organic remains of minute marine plants and animals that settled to the sea floor millions of years ago. Crude petroleum consists of a complex mixture of compounds, mainly hydrocarbons, but also of smaller amounts of organic molecules containing oxygen, sulphur, nitrogen, and even metals. The percentage volume composition of West Texas crude oil is:

	%
butanes	2
petrol	11
napthas (diesel, kerosene)	14
furnace oil	17
gas oil (heating oil)	39
residue (lubricating oil, asphalt)	17

(The standard 'barrel' is 42 United States gallons.)

The usual first step in refining petroleum is to separate the crude oil into fractions on the basis of their boiling points. Fractions of a typical crude petroleum, arranged in order of increasing boiling point, can be seen in Table 11.6. The petrol obtained in this separation is known as *straight-run gasoline* and is of too low a quality to be used directly in today's automobiles. The naphthas yield kerosene, and solvents for paints, varnishes, and lacquers. Furnace and gas oils are burned in oil heaters and diesel engines or are used to make more petrol (see later this chapter in the section on cracking). The residues furnish a great variety of common products, ranging from waxes, mineral oils, and paraffin to asphalt for paving.

TABLE 11.6 *Petroleum oil fractionation*

Fraction	Composition	Boiling range,°C	Principal use
Gas	C_1–C_4	Below 20	Heating fuel
Petroleum ether	C_5–C_6	20–70	Solvents, petrol additive for cold weather
Petrol (straight-run)	C_6–C_{10}	70–200	Motor fuel, solvent
Kerosene	C_{10}–C_{18}	175–320	Jet and diesel fuel
Gas–oil	C_{12}–C_{18}	Above 275	Diesel fuel, heating fuel oil, cracking stock
Lubricating oils	Above C_{18}	Distil under vacuum	Lubrication
Asphalt	Above C_{18}	Non-volatile liquid	Roofing and road materials

Petroleum oil fractionation

Before the advent of electricity as a utility about 1900, the most useful fraction was kerosene, used for home lighting. The advent of electricity and the automobile then made gasoline the most important fraction. Straight-run gasoline (octane rating is about 70) consists mainly of straight-chain hydrocarbons, which cause engine knock and are relatively poor fuels for today's modern automobile. To get a smooth constant push on the piston you need a *slow* explosion. When detonation occurs you have *pinging* or *knocking*. Furthermore, until the advent of jet engines, the kerosene fraction had much less use than gasoline. Over the years the petroleum industry has made high octane gasoline by *reforming* the structure of the C_4–C_{18} fractions to give a highly branched C_6—C_{10} fraction with octane ratings of 90–110.

Alkanes vary greatly in their ability to burn in an engine without knocking. The *octane ratings* of a number of alkanes are presented in Appendix 11. These are relative values of the ability of a fuel to burn smoothly and not to cause knocking or pinging; they are determined under carefully defined engine conditions. It was discovered that 2,2,4-trimethylpentane (called industrially *iso-octane*) caused little knocking, whereas *n*-heptane caused a great deal (Figure 11.4).

11.4 Iso-octane and n-heptane

A scale was therefore devised on which the octane rating of any hydrocarbon was defined as being equal to the proportion of iso-octane in an iso-octane–n-heptane mixture that knocked under the same conditions. Methylcyclohexane, for example, knocks under the same conditions as a mixture of 75 percent iso-octane and 25 percent *n*-heptane, and hence has an octane rating of 75. A similar system is used for diesel fuel with the *cetane* number which is set by comparing a fuel with a mixture cetane, 100, and α-methylnaphthalene, 0. A high cetane number indicates a greater ability of the molecules to continue a burning process.

The twin problems of low quality and low quantity of petrol from direct distillation of crude petroleum were solved by a variety of processes known as cracking, alkylation, reforming, and isomerisation, and by the addition of additives.

Cracking (thermal, catalytic, hydro-)

By heating the high boiling (C_{10} and above) fractions with a catalyst to 400–500°, the larger molecules 'crack' into the smaller hydrocarbons and at the same time tend to rearrange into the branched-chain hydrocarbons. (The reason for this transformation lies in the fact that the branched chain products are more 'disordered'—i.e. they have a higher entropy than the straight chain ones.) This not only increases the amount of petrol from crude oil but also improves the octane rating (see Appendix 11.3), typically into the 85–95 range. For example,

$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{cracking}} CH_2{=}CH_2 + CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3 \text{ etc.}$$

Alkylation

Alkylation involves heating isobutane with the low boiling alkenes (C_3–C_6) under acid conditions which causes addition of the isobutane to the alkene —leading to a larger branched alkane, e.g.

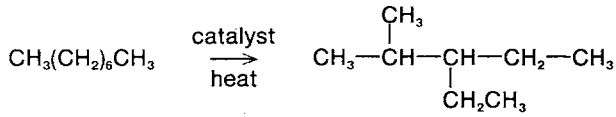
This converts some of the lower boiling gas fractions into high octane (typically 90–95) fractions.

$$CH_2{=}CH{-}CH_3 + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\begin{matrix} H \\ CH_3 \end{matrix} \xrightarrow{H^+} \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!C{-}CH_2{-}CH_2{-}CH_3$$

an alkene isobutane branched chain alkane

Isomerisation

Relatively low temperature heating with special catalysts causes rearrangement or isomerisation of straight-chain hydrocarbons into their branched-chain isomers, e.g.



This improves the octane rating to the mid-eighties and is used primarily on the straight-run gasoline fraction.

Reformation

This is by far the most important change process in refining and involves heating with special catalysts similar to cracking and isomerisation. By careful choice of conditions however, C_6 and above hydrocarbons are converted into aromatic compounds, mainly benzene, toluene, and xylenes. The improvement in octane rating is marked—into the mid- to high nineties. However the aromatic compounds on incomplete combustion in an engine can produce larger molecules in the exhaust which are known carcinogens.

With all this refining of the crude oil the average petrol produced today has the broad composition:

	%
butane	10
paraffins	60–65
aromatics	25 (up to 40)
alkenes (olefins)	small

and the average octane rating is in the high eighties for the 'pure' hydrocarbon mixture. Since the modern car usually has a compression ratio of 8.5–9.5:1 this requires 93–96 octane fuel, and the petroleum industry needed to upgrade its product.

The answer to this problem was found in the early 1930s—the addition of relatively small amounts of some compounds such as iodine, I_2, iron carbonyl, $Fe(CO)_5$, methylaniline, $C_6H_5NHCH_3$, can improve the octane rating of a petrol quite markedly. In this area of anti-knock additives the only ones commercially used are lead tetra-ethyl, $Pb(C_2H_5)_4$, and lead tetra-methyl, $Pb(CH_3)_4$. These tetra-alkyl leads, whose precise mode of action is not completely known although it is linked with the inhibition of 'branching' reactions occurring during the explosion, can raise the octane rating from the average 88.5 to 96.5 by the addition of only *0.5 g per litre.*

The two lead tetra-alkyls are not equally effective with all petrols—they are most effective in raising the octane of predominantly straight-chain fuels and have less effect on petrols with high aromatic content. The improvement is also non-linear—i.e. there is a diminishing return for the addition of larger amounts of lead anti-knock.

The solution to one problem, however, often creates others. Lead compounds, mainly oxides, are formed in the engine and these foul the spark plug (conducting electricity and allowing spark leak) and the cylinder walls. Some ethylene chloride, CH_2Cl–CH_2Cl, and ethylene bromide, CH_2Br–CH_2Br are added to avoid these deposits and to convert the lead to the volatile lead chloride and bromide which are then exhausted. Not all the lead is removed this way, so other additives are also necessary (see Ignition Control Additive).

At present MMT (methylcyclopentadienyl manganese tricarbonyl) is added to 40 percent of unleaded gasoline refined in the United States. Reports that it fouls catalytic converters appear unfounded.[9] MMT disperses the less toxic manganese rather than lead into the environment. At least there is some evidence for the reconcentration of manganese from sea water by nodules on the ocean floor.

TABLE 11.7 *A summary of lead in petrol*

Reason for lead in petrol—introduced 1923	to raise octane rating approx.
World production of lead (1971)	3,000,000 tonnes
Lead used for petrol additives (1971)	
whole world	750,000 tonnes
United States	250,000 tonnes
Australia	6,000 tonnes
New South Wales	2,000 tonnes
Lead content of petrol (1971)*	
Australia—super	0.55 g/litre
standard	0.15 g/litre
United States—super	0.75 g/litre
standard	0.60 g/litre
low lead	0.13 g/litre
no lead	0.004 g/litre
Petrol Consumption†	
Australia (1971)—super	13,200 million litres
standard	2,300 million litres
United States (1969)—total	327,000 million litres

*1 g Pb = 0.946 ml tetra-ethyl lead.
†5×10^5 million litres/year $\times$ 0.5 lead/litre = 2.5×10^5 tonnes lead per year (10^6 g lead per tonne).

Source: Smythe.[10]

Lead levels in Australian petrols are detailed in Table 11.8. The amount of lead and bromine in petrol is most readily determined quantitatively by X-ray fluorescence. Because the lead tetra-ethyl and ethylene dibromide are supplied together, the molecular ratio is found to be constant. More surprising-

TABLE 11.8 *Maximum legal lead content of petrol (g/litre)*

	Pre-control	1975	1976	1977/8	1979	1980
New South Wales	0.84	0.64	*	0.45	*	0.40
Victoria	0.84	0.60	*	0.50	0.45	*
Tasmania	0.84	*	0.64	0.55	0.45	*

*No change

ly, more lead is often found in standard petrol than super grade, because of the poorer hydrocarbon mix used in some standard petrols. The higher levels of lead used in the country compared to the city are seen from the table of typical petrol consumption given in Appendix 11.6.

An Australian Standard for petrol (AS 1876–1976) sets the anti-knock value, expressed as the Research Octane Number of the petrol (method ASTM D2699–IP237), at not less than 98 for premium grade petrol and 89 for regular grade. When the standard was set up in 1976 it was hoped that standard grade petrol would contain an identifying agent so that an admix of 10 percent or more of standard could be detected in super by the use of a dye developing agent. This was to prevent fraud but turns out to be expensive.

The anti-knock compounds are not the sole additives used. ICA (ignition control additive) is tricresylphosphate, $(CH_3C_6H_4O)_3P{=}O$, added to change the lead compound deposits on the spark plug (both lead and lead oxide are conductors and would cause short circuits in the spark plugs) and cylinder walls by converting them to the refractory lead phosphate (a white deposit which is an electrical *insulator*). Methanol and ethanol are added as 'de-icers' and to dissolve any water which might lodge in the carburetter. Antioxidants (see Chapter 3) stabilise the alkenes (unsaturated hydrocarbons) in petrol; dyes are added, yellow for standard and red for super for identification and aesthetic reasons, and so on. Further, the actual blend of hydrocarbons is varied according to the weather and altitude; more of the highly volatile butane is added in winter to facilitate 'cold starting'.

LUBRICATING OILS

Lubrication serves to reduce friction and wear between moving surfaces. The familiar petroleum lubricating oils are complex mixtures of hydrocarbon molecules blended for specific purposes by mixing long-chain and ring hydrocarbons. Important characteristics of oils are the viscosity and stability.[1]

Viscosity

Viscosity varies widely from oil to oil. For car engines, viscosities on the SAE scale lie between 10 and 50, while gear box oils have SAE values lying between 75 and 250. The viscosity of a particular oil also varies markedly with temperature. When an engine starts from cold, particularly in the winter, it needs a light mobile oil to provide instantaneous lubrication at the normal running temperature of the engine. No single oil is capable of satisfactory performance over this wide temperature range, but mixtures of oils with a few percent of a viscosity index improver—a linear polymer such as polyisobutylene or polymethacrylate—do not change markedly in viscosity with temperature. These are the multigrade or summer–winter oils such as SAE 10W–30 which has the viscosity characteristics of both grade 10, for cold starting, and 30, for hot running.

Oil additives

Most oils have small amounts of additives to control oxidation, corrosion, foaming, and sludge-deposition.

At the running temperature, oxidation of hydrocarbon oils by atmospheric oxidation would occur rapidly by mechanisms similar to those by which butter and margarine turn rancid. The consequences of such oxidation, besides degradation of the oil, are deposition of engine varnish and sludge, and the production of corrosive acids. Antioxidants consume the oxygen preferentially and stabilise the oil.

Rust inhibitors, antiwear agents, and dispersants are usually heavy metal soaps, e.g. barium alkyl benzene sulphonates. As discussed in Chapter 2, their surface-active properties come from the polar ends attracting themselves to the metal surfaces, leaving the non-polar chains to provide a protective oily film on the surfaces. The dispersants present deposition of the oil-insoluble sludge—particles of metal and compounds of lead and carbon—on the surfaces of the engine.

The constant churning of the oil with air would rapidly produce foams with conseqent overflow and loss of oil. To prevent this traces of silicones are added.

Synthetic oils

To meet the special requirements of heavy-duty engines or to operate in extreme conditions of temperature, special oils have been tailored to meet exacting requirements. These are silicones, esters, or polyglycols.

Solid film lubricants

Where operating conditions are extreme—very heavy loads or high temperatures—solid lubricants are used. These are substances such as graphite, molybdenum disulphide, and boron nitride which have unusual arrangements of atoms in the solid. The atoms are connected together in sheets which slide over one another, providing lubrication.

Recycling

Approximately 1.3 million litres of waste oil is produced in the Australian Capital Territory each year.[11] Almost all of this is lubricating oil drained from the sumps of engines during routine oil changes. The oil may be contaminated with water, cotton wastes, food scraps and may also contain products of combustion and petrol additives such as lead (~1 percent), sulphur, barium, vanadium, and phosphorus. At present some oil is transported to Melbourne for reprocessing.

Used sump oil can be filtered and added to fuel oil. The Petroleum Industry Environment Corporation Executive allows a self-regulated limit of 3.3 percent because of the lead content which was set in September 1973. The Victorian Environmental Protection Agency allows used sump oil to be used in bunker oil for ships at sea. Some is reprocessed and re-used as engine oil. The rate of recovery depends on the initial quality of the oil, varying from 60 percent to 90 percent. However re-refining is made more difficult by the presence of the many additives and has to be done on a fairly large scale. Collections of old oil represents the largest cost.[11,13]

HYDRAULIC BRAKE FLUIDS[14]

The hydraulic brake fluids used until just after World War II were essentially a solution of castor oil in *n*-butanol or diacetone alcohol. The availability of synthetic lubricants at a stable price helped the change to higher performance fluids based on ethylene oxide derivatives. These new fluids had a boiling point

of about 190°C in contrast to 140°C of the earlier fluids. A typical formulation for the new brake fluids was

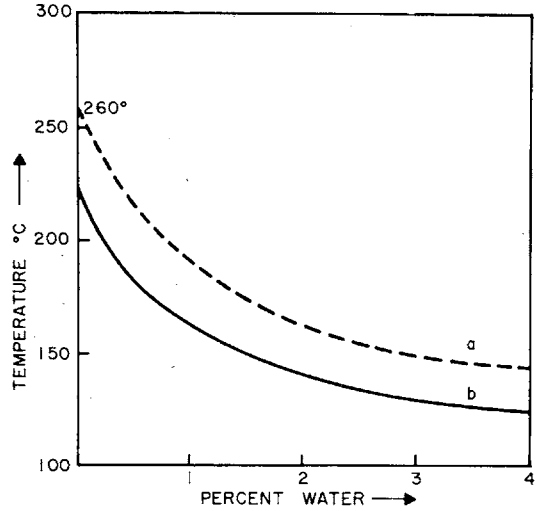
solvent	60 percent	(a mixture of mono alkyls usually either methyl, ethyl, or *n*-butyl, of mono-, di- and tri- ethylene glycol)
antiswell	20 percent	(a mixture of mono-, di- and triethylene glycol)
lubricant	20 percent	(a condensate of *n*-butanol and a 50:50 mixture of ethylene oxide and propylene oxide)
additives	minor amounts	(corrosion inhibitors and antioxidants)

ICI Australia developed its own brake fluid technology and commenced manufacturing in 1964.

The trend has been for cars to become more powerful and heavier and to travel faster, and when these factors are combined with the increasingly widespread use of automatic transmissions which provide less engine braking, the demand for more efficient braking systems becomes more pressing. However, these trends have resulted in more energy having to be dissipated as heat in the braking system. The introduction of disc brakes with intrinsically higher operating temperatures accentuated the effect of vapour formation and resulted in car manufacturers finding that more of their vehicles were experiencing brake failures due to vapour locking. Vapour locking is the effect produced by the local boiling of the brake fluid producing sufficient vapour in the system to allow the brake pedal to be depressed thereby compressing the vapour without accentuating the brake.

At the request of some of the car manufacturers in the early sixties, ICI Australia developed brake fluids with boiling points of 260° and 290°C which overcame this problem. These compounds are similar to some of the non-ionic surfactants but of much lower molecular weight. One type is a copolymer of ethylene and propylene oxides (compare non-ionic surfactants) and belongs to a group called polyglycols. However, these new brake fluids absorbed water from the atmosphere more readily, thus lowering the boiling point, so that after about one year in service the boiling point in many cases would be in the danger area where vapour locking might occur. In one experimental exposure of a simulated braking system to 80 percent relative humidity at 32°C for 141 days, the water concentration reached 3.85 percent in the front wheel cylinders and 1.65 percent in the diaphram-protected master cylinder. Much of the water enters *through* the brake hoses (see gas permeability of plastics).

The effect of water on the vapour locking temperature of a brake fluid as measured by two different procedures is shown in the graph in Figure 11.5 (see also experiment, ch.14). In interpreting this it should be noted that trials in the Rocky Mountains in America showed that the highest operating temperatures brake fluids reached were 148°C, while high speed pursuits by London police have achieved fluid temperatures of 188°C. The safe operating temperature has been nominated by the United States Department of Transportation in their federal specification at 155°C, and this roughly corresponds to about 1.5 percent water in the brake fluid. Field trials with fleets of vehicles in Britain as well as laboratory experiments suggest that water uptake by brake fluids will reach this level in about twelve to eighteen months so that the brake fluid should be changed before this danger zone is reached.



(a) boiling point; (b) vapour formation temperature

11.5 Vapour locking temperature of brake fluids (*Stop* (ICI))

Recently ICI Australia has developed a brake fluid which is tolerant of moisture absorption as it is able to react with the water chemically and the products of the reaction are normal brake fluid components. Australia is one of the first countries in the world to use this new safer brake fluid.

Details of this new brake fluid were not available from ICI at the time of writing. For the curious consumer chemist the next step is a glance at the subject index of *Chemical Abstracts* under—**hydraulic fluids, brake**. Here we find:

water scavengers for
orthoesters as P,208313a

The Chemical Abstract reference gives United States patent 3903006 (Castrol Ltd England, 2 September 1975) and details of the orthoesters used, e.g. $C_2H_5C(OCH_2CH)_3$. Orthoborates (ICI), orthophosphates, and orthosilicates are also seen in the patent literature (see Chapter 14 for the use of Patent Information Services).

This particular patent turns out to be more informative than most. Among the patent 'rhubarb' there is in fact a table which shows that the compounds do actually work (patents often give no indication that they are in fact feasible). The drop in boiling point of a 'base' brake fluid with the addition of 1 percent of water is compared to the case where it contains 10 percent orthoester as well. To quote the United States patent,

> This demonstrates the ability of the orthoesters to counteract, at least in part, the boiling point reduction caused when water is present in the hydraulic fluid, for example as a result of absorption of water vapour from the atmosphere by hydroscopic absorption of water vapour from the atmosphere by hydroscopic components of the fluid.

It is difficult to keep water out of brake fluid because it can diffuse through hoses and seals, so this does represent a real advance.

ANTIFREEZE

Water freezes at 0°C and in so doing it expands (ice is less dense than water and floats on it—there are very few other materials which have this strange property). The expansion can damage the chambers in which radiator water flows. When water has other materials dissolved in it, the freezing point is lowered and the boiling point is raised. The amount by which this happens depends only (to a first approximation) on the *number* of molecules of the added material—not on its weight or the type of molecule. So for a given *weight* of material, light molecules are more efficient than heavy molecules. For this reason methanol—methyl alcohol CH_3OH, MW 32—was commonly used but it has the disadvantage that it tends to boil away, so that ethylene glycol, $HO—CH_2—CH_2—OH$, MW 62, is generally used—but it is half as effective.

Antifreeze solutions tend to be quite corrosive and so corrosion inhibitors are added which protect, to a certain extent, the metals found in an engine cooling system, namely copper, solder, brass, steel, cast iron, and cast aluminium. The inhibitors used are generally sodium nitrite with sodium benzoate although other materials are occasionally quoted. (Ethylene glycol is sweet—see sweetners, Chapter 12—and poisonous—death on swallowing probably occurs however from nitrite poisoning. This is unfortunate because the antidote for ethylene glycol is alcohol! Reason? The alcohol keeps busy the enzymes that would otherwise convert the glycol into the toxic oxalic acid, which is the real poison . . . 'but offischer I just shwallowed some antifreeze'.)

An Australian standard (AS 2108–1977) calls for a depression of freezing point of −12°C when used according to the manufacturer's recommendations and requires that when an engine manufacturer recommends a particular product specification, that recommendation should be followed. One hopes such statements will not appear as recommendations of a particular brand name. The British standard calls for a depression of freezing of approximately −12°C from a 25 percent v/v antifreeze solution making the quality of the product independent of the manufacturer's recommendation (e.g. to use more of an inferior product to maintain adequate production). The effects of some highly corrosive antifreeze solutions were reported in the *Choice* issue of June 1976.

CORROSION INHIBITORS

Concentrations in g/litre except where stated otherwise	Original pH
1. 1.0 $NaNO_3$, 2.0 $Na_3PO_4 \cdot 12H_2O$, 2.5 NaMBT, 3.0 $Na_2B_4O_7$, 1.0 $Na_2SiO_3 \cdot 9H_2O$, 1.0 NaOH	11.5
2. 4.0 $Na_3PO_4 \cdot 12H_2O$, 2.0 $Na_2SiO_3 \cdot 9H_2O$, 4.0 NaMBT	11.7
3. 1.5 $NaNO_3$, 2.0 $Na_3PO_4 \cdot 12H_2O$, 2.5 NaMBT, 4.0 $Na_2B_4O_7$	9.4
4. 1.5 $NaNO_3$, 2.5 $Na_3PO_4 \cdot 12H_2O$, 4.0 NaMBT, 2.0 $Na_2SiO_3 \cdot 9H_2O$	11.6
5. 1.4 Na_2HPO_4, 2.4 MBT, 6.2 $Na_2B_4O_7$	9.4
6. 50 percent v/v in water 'permanent type anti-freeze' (ethylene glycol base).	10.1
7. 12.0 $NaC_7H_5O_2$, 1.0 $NaNO_2$	8.1
8. 1.0 Na_2CrO_4	9.0
9. Uninhibited test water—i.e. normal water	8.2–5.0
10. 50 percent v/v in water uninhibited ethylene glycol	8.4
11. Same as No. 1 without the NaOH	9.7

$NaNO_2$—sodium nitrite
$NaNO_3$—sodium nitrate
$Na_2B_4O_7$—sodium borate
Na_2SiO_3—sodium silicate
Na_3PO_4—trisodium phosphate
$NaC_7H_5O_2$—sodium benzoate
Na_2CrO_4—sodium chromate
NaOH—sodium hydroxide
Na_2HPO_4—disodium hydrogen phosphate
MBT—mercaptobenzothiazole
NaMBT—sodium mercaptobenzothiazole (50 percent solution)

Source of data: T.S. Humphries and G.E. De Ramus, 'Corrosion inhibitors for solar heating and cooling systems.' NASA, Washington DC, February 1977. Consult this reference for further details, particularly if you want to design your own experiments.

VISUAL DESCRIPTION OF CORROSION OF ELEVATED TEMPERATURE TEST SPECIMENS (82°C)

Inhibitor	Alloy	Visual Description	Weight loss (mg) after 1 year
1.	Al	— One deep pit on the bottom edge and several shallow pits on the bottom and one side edge	26
	Fe	— Mild non-uniform attack mainly on the bottom edge	83
2.	Al	— Scattered areas of moderate non-uniform attack with deep pits around the screw	552
	Fe	— Scattered areas of mild to moderate non-uniform attack	385
3.	Al	— No visible corrosion; specimen coated with adherent black film	749
	Fe	— Mild non-uniform attack in vicinity of the screw with moderate attack on bottom edge	279
4.	Al	— No visible attack.	0
	Fe	— Scattered moderate to severe pitting and non-uniform attack.	1293
5.	Al	— Scattered areas of mild non-uniform attack. Specimen coated with adherent black film	292
	Fe	— Scattered areas of mild non-uniform attack	385
6.	Al	— Mild to moderate pitting of edges with severe pitting of bottom edge.	126
	Fe	— Scattered areas of mild to moderate non-uniform attack.	197
7.	Al	— Moderate non-uniform attack	309
	Fe	— No visible corrosion	5
8.	Al	— Several deep pits around screw	229
	Fe	— Several scattered moderate to deep pits	268
9.	Al	— Scattered areas of deep pitting	436
	Fe	— Severely etched plus non-uniform attack	5172
10.	Al	— No visible attack. Specimen coated with loosely adherent dark film	0
	Fe	— Severely etched, 50 percent weight loss	5562
11.	Al	— Moderately deep pits on all edges	300
	Fe	— Moderate non-uniform attack with severe attack of bottom edge	1609

NOTES: 1. The terms mild, moderate, and severe refer mainly to depth of attack.
2. Stainless steel specimens were unaffected and copper specimens were only tarnished.
3. Tests under quiescent conditions—no effects of fluid flow.

ACCUMULATORS (BATTERIES)

Normally car engines rely on electricity stored in the battery for starting purposes. During running, the electricity drawn from the battery is returned by the generator (or alternator) and the battery fails only through mechanical breakdown. Batteries of this type are called secondary or storage cells; electricity is stored by driving a set of chemical reactions in one direction by connecting the battery to a charger. Current may then be drawn from the battery when the reactions proceed in the reverse direction.

Lead-acid accumulator

The familiar 12-volt car battery contains 6 cells, each providing 2 volts. Each cell contains two series of plates—positive and negative—immersed in sulphuric acid. The positive plates are made by forcing a paste of lead dioxide, PbO_2, into a grid made of lead alloy, while the negative plates contain lead in a highly active spongy form. The overall reactions that occur are:

at the positive plates

$$\underset{\text{lead dioxide}}{PbO_2} + 4H^+ + SO_4^{2-} + 2e \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2H_2O + \underset{\text{insoluble}}{PbSO_4}\downarrow$$

and at the negative plates

$$\underset{\text{spongy lead}}{Pb} + SO_4^{2-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4\downarrow + 2e$$

Ideally these reactions can be recycled indefinitely, but in practice material is gradually lost from the plates and falls to the bottom of the cell where eventually it may short circuit the plates, rendering that cell useless. The state of charge of a lead battery can be estimated readily by a hydrometer which measures the density of the sulphuric acid. As can be seen from the reactions above, sulphuric acid is consumed by both reactions during discharge and so the density of the electrolyte falls from about 1.28 (about 37 percent sulphuric acid) in the fully charged cell to about 1.15 (about 21 percent sulphuric acid) in the flat battery. If the water is allowed to evaporate from the battery, the concentration of the electrolyte rises to a value which can adversely affect the performance. Thus the electrolyte should be topped up with pure water as often as necessary—distilled water is preferable but *some* domestic water supplies are sufficiently pure.

Batteries may be classified according to the amount of electricity stored in them. An SAA standard for starter batteries (AS 1981) defines a number of important parameters.

1. *Rated capacity—the number of ampere hours a battery is capable of delivering during continuous uniform discharge over a period of 20 hours at a current of one-twentieth of the 20-hour capacity (from 11.2V to 10.5V for a 12-volt battery at 25°)*

A 12-volt battery that can supply 2.5 A for 20 hours has a rated capacity of 50 amp-hours. This test is used because the capacity of a battery depends on how it is discharged. Because a battery has an internal resistance, some of its power is dissipated inside. This heats the battery up so that, except for a quick start, the battery is hotter than the outside temperature.

The chemical reactions which occur to drive electricity through the starter motor are sensitive to temperature and starting a car on a cold morning places heavy demand on the battery; not only does the battery not function as well but the engine oil is more viscous and the engine turns over with greater difficulty. The starter motor draws over 150 amps for a short period so that we need to define a parameter for this aspect.

2. *Rated current—the constant (A) a battery is capable of delivering for 3 minutes before the battery voltage is halved. This is to be carried out at −7°C (Australian Capital Territory winter conditions).*

A third parameter measures the time a battery survives when supplying a high current intermediate to that used for rated capacity and starting conditions.

3. *Reserve capacity—the period in minutes during which a battery is capable of delivering a constant current of 25 A ± 0.25 (at 25°C) before the voltage drops to 10.5V (for a 12-volt battery).*

Parameters 1 and 2 are to be marked on the battery or be elsewhere available. *Choice* October 1976 based an article on the discussion in the first edition of this book and carried out some battery tests. These tests mirrored typical battery usage patterns and showed a difference between different products much larger than is usual in such comparative testing.

Since, for a variety of reasons, charged batteries will slowly discharge on standing, new batteries are nowadays usually supplied in the dry-charged form. During manufacture they are fully charged, but the acid is then drained off. The cells are rinsed and then dried quickly. These dry-charged batteries should retain their charge for many years. When the battery is to be put into service, sulphuric acid of the proper density is added.

There are two major causes for the deterioration of a lead accumulator. The first is physical breakdown of the plates, accelerated to a certain extent by movement of the car. The second cause is a chemical one. On standing, the lead sulphate produced by the discharge reactions tends to recrystallise into a form which is less soluble, making it difficult to recharge the battery properly. It has often been suggested that the addition of magnesium sulphate (Epsom salts) reduces the crystallisation of the lead sulphate, but there is no real evidence for this and it is unlikely that any of the commercial battery 'dopes' will improve the life and performance of the battery. What may help resuscitate a battery with a shorted cell is to empty out the electrolyte, and flush the battery, and then replace with fresh acid.

BATTERIES FOR ELECTRIC CARS, AND A 'FUEL GAUGE'.

H.P. Cantor, of the Australian National University Department of Engineering Physics, dissected 138 used lead-acid car batteries in 1975. In most cases, failure had been due to disintegration of the positive plate or 'paste shedding'; in 21, inter-cell connectors had failed; and Mr Cantor put down 18 to 'excessive cell stack looseness'. Negative plates were generally in excellent condition. He is now planning a much larger program of examination of batteries with known histories, assisted by Consumer Cooperatives.

Cantor believes that, in spite of intensive research on other kinds of battery, the lead-acid cell remains the only possible power source for electric cars for many years to come. The economics of electric vehicles therefore depends critically on the cost and lifetime of lead-acid batteries. He told the 2nd Australian Conference on Science Technology, held in Adelaide in August 1975

—cases should be of clear plastic with removable lids, for re-use—'At present, the aim of a modern plastic-cased battery production line is certainly "to get that non-see-through lid on to the non-see-through case" ';

—cells should be encased separately, to avoid the wastage due to discarding a complete battery of which one cell has failed;

—positive plates could be strengthened with a nylon grid at little extra weight penalty;

—the plates themselves could be replaceable.

Cont. next page

On the basis of his experience with a simple electric vehicle in Canberra, Cantor believes that running costs per kilometre would be better than those of a 15 km/litre petrol driven car if battery life could be doubled. He does not believe that this will happen without government assistance for the research and development because manufacturers see no incentive for altering their present products. 'Why spend a cent improving a product that conveniently has a very short life and can, therefore, be replaced constantly at great profit? This short life has now become shorter.' Cantor mentioned what he called 'the unmentionable—the so-called guarantee for 2, 3, or 4 years life from a battery. In all cases that I know of . . . these batteries are of exactly the same type. The only difference is that the customer has paid . . . a sort of insurance premium.'

For industries that require them, Cantor pointed out, most manufacturers in fact provide batteries that are 'very well produced, in clear, see-through containers and do generally last for 10 to 30 years in stationary use. What is needed, and needed urgently, is a light weight low cost battery closer in weight and price to the automotive than to the heavy industrial battery.'

It was one of these industries that funded a recent innovation by the Electric Vehicle Group at Flinders University: a dashboard 'fuel gauge' to indicate how far a bank of batteries has to go before it needs recharging. The usual method is too cumbersome for routine use on an electric road vehicle. The Flinders team, whose vehicle was described in *Search* volume 5 no. 5, and who were recently awarded $50,000 by the South Australian Government for further development, described at the Adelaide conference a simple gauge based on the direct relationship between charge state and the refractive index of the electrolyte. A U-shaped glass rod projects into the liquid (through one of the filling holes); there is an infra-red light-emitting diode at one end of the rod and a phototransfer at the other. The amount of light leaking out of the rod at the U-bend, and thus the amount reaching the sensor, is governed by the refractive index of the liquid.[15]

H.P. Cantor, 'Batteries for Electric Cars, and a "Fuel Gauge",' *Search* **6**, no. 10, October 1975, 399.

Other accumulators

The lead accumulator has a number of advantages—cheapness, ease of manufacture, a cheap electrolyte the density of which serves to indicate the state of change, and a relatively constant voltage over most of the discharge range. However it is heavy—the 'energy density' in watt-hours per kilogram

is consequently low—and the electrolyte is corrosive and the battery cannot be sealed as gas is generated during the charging process from the electrolysis of water.

Several other systems are known and some of these have special applications. In particular, the nickel-cadmium accumulator, which can be sealed, is now commonly used for rechargeable domestic devices—electric toothbrushes, portable razors and radios, and so on. The simplified overall cell reaction is

$$2NiOOH + Cd + 2H_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_2 + Cd(OH)_2$$

with the cadmium plate being the negative one. Because the electrolyte, potassium hydroxide, does not enter into the cell reaction, its density does not vary with the state of charge. Methods for determining the charge are accordingly somewhat more complex and so these accumulators are usually recharged after a set period of use or are continually 'trickle' charged.

Primary batteries

As a contribution to the fight against pollution by car exhaust, much research is currently being devoted to the production of primary batteries to drive cars. These primary cells produce electricity from the reaction of chemical substances—they are not rechargeable. Many different types have been developed for special purposes, such as military use and space flight.

One of the most promising types is the fuel cell. Most of these rely on the controlled reaction between oxygen and a fuel substance—i.e. controlled combustion—although other mixtures have been investigated. Thus in the hydrogen fuel cell, gaseous hydrogen and oxygen are bubbled over electrodes (carbon may be used, as well as certain metals) immersed in potassium hydroxide solution. The cell reaction is

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e$$
$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$
$$\overline{2H_2 + O_2 \longrightarrow 2H_2O}$$

The maximum theoretical voltage is 1.23 volts. One advantage of the fuel cell is that it generates electricity directly from chemical reactions without going through the intermediate phase of a (heat) engine. The theoretical limitations on efficiency of conversion thus do not apply. Other cells use alcohol or hydrocarbons in place of hydrogen. The products are water only, or water and carbon dioxide, and so the cells do not produce the pollutants carbon monoxide and oxides of nitrogen associated with the internal combustion engine. However, these cells have certain difficulties—e.g. the water must be removed or the electrolyte will become too dilute—and none has yet been developed to the stage where, whilst still being of a reasonable size, it can provide sufficient power to drive a car.

APPENDIX 11.1

Tariffs for Electricity in Various Parts of Australia

Authority	*Domestic tariffs (charge per kWh)*		*Off-peak tariffs (and other water heating tariffs) (charge per kWh)*		*Tariff restrictions and special conditions applicable to electrically boosted solar water heaters*
New South Wales					
1. Sydney County Council	1st 30kWh/quarter	8.74c	Off-Peak 1	1.37c	No tariff restrictions
	next 70kWh/quarter	5.95c	Off-Peak 2	1.96c	No special conditions
	next 400kWh/quarter	3.14c			
	Remainder	2.61c			
2. Prospect County Council	1st 50kWh/quarter	7.54c	Off-Peak	1.24c	Off-peak tariff is not available
	next 200kWh/quarter	4.06c			
	next 250kWh/quarter	2.61c			
	Remainder	2.24c			
3. Illawarra County Council	1st 120kWh/quarter	6.3c	Off-Peak 1	1.2c	Off-peak tariff is not available
	next 390kWh/quarter	3.8c	Off-Peak 2	1.53c	
	Remainder	2.4c			
4. Shortland County Council	1st 100kWh/quarter	5.517c	Off-Peak B4	1.314c	Off-peak tariff is not available. Continuous water heating tariff is.
	Remainder (domestic)	2.839c	Off-Peak B3	1.761c	
	OR (domestic cooking)	2.654c	Continuous Water Heating	2.654c	
5. Northern Riverina County Council	1st 20kWh/month	14.00c	Off-Peak	1.40c	No tariff restrictions
	next 60kWh/month	6.00c			No special conditions
	Remainder	3.25c			
6. Namoi Valley County Council	1st 60kWh/quarter	23.08c	Off-Peak	1.60c	No tariff restrictions
	next 100kWh/quarter	8.25c	Extended Off-Peak	2.60c	No special conditions
	Remainder	3.48c			

Queensland					
1. Brisbane City Council (Dept. of Electricity)	1st 30kWh/water next 150kWh/quarter Remainder	7.68c 3.01c 2.59c	Restricted Hours (Option 2) Controlled Storage Hot Water Continuous Water Heating	1.28c 1.58c 2.49c	Restricted hours and controlled storage hot water tariffs are available; continuous water heating tariff is not
2. Southern Electric Authority of Queensland	1st 90kWh/quarter next 450kWh/quarter Remainder	9.94c 3.84c 2.78c	No Off-Peak Tariffs Continuous Water Heating	2.47c	Continuous water heating tariff is not available to electrically boosted solar water heaters: but electric water heaters supplied at the continuous water heating tariff may be connected to a solar pre-heater
3. Cairns Regional Electricity Board	1st 30kWh/month next 150kWh/month Remainder	13.08c 4.95c 3.61c	Off-Peak Tariff H Continuous Water Heating Tariff J	2.10c 3.46c	Neither the off-peak nor the continuous water heating tariff is available
Victoria					
State Electricity Commission of Victoria (and Melbourne Metropolitan Supply Authorities)	1st 90kWh/quarter next 450kWh/quarter Remainder-Tariff GB OR Tariff GC	9.95c 3.17c 2.58c 2.09c	Off-Peak Tariff 1 (water heating) Off-Peak Tariff J Combined Space & Water Heating 1st 1200 kWh/quarter Remainder	1.26c 1.26c 1.02c	No tariff restrictions No special conditions
Tasmania					
Hydro-Electric Commission, Tasmania	56c/room/quarter plus 1st 300kWh/quarter next 900kWh/quarter Remainder	 3.33c 2.72c 2.30c	Off-Peak 1st 2000kWh/quarter Remainder Continuous Water Heating	 1.16c 1.01c 1.60c	Neither the off-peak nor the continuous water heating tariff is available, except with the written consent of the HECT

APPENDIX 11.1—contd

Tariffs for Electricity in Various parts of Australia

Authority	*Domestic tariffs (charge per kWh)*		*Off-peak tariffs (and other water heating tariffs) (charge per kWh)*		*Tariff restrictions and special conditions applicable to electrically boosted solar water heaters*
Western Australia					
State Energy Commission of Western Australia	Fixed charge $2.04 per quarter. All metered kWh	 3.83c	No Off-Peak at present. (new off-peak tariff expected 1.1.77)		No tariff restrictions No special conditions
South Australia					
Electricity Trust of South Australia	1st 48kWh/quarter next 120kWh/quarter Remainder	7.4c 4.13c 2.69c	Off-Peak Tariff J Off-Peak Tariff K	1.46c 1.46c	Off-Peak tariff J is not available Off-peak tariff K provides for a minimum $1.50 per month charge and restricted (7 hours) heating hours
Northern Territory					
Department of the Northern Territory	1st 200kWh/quarter next 800kWh/quarter Remainder	5.0c 4.4c 3.7c	No Off-Peak		No tariff restrictions No special conditions

Tariffs as at 1 October 1976.
Source: *Solar energy* the report of the Senate Standing Committee on National Resources, 1977

APPENDIX 11.2

AUSTRALIA'S SPACE HEATERS PERFORMING POORLY

This winter millions of Australians are spending their evenings in rooms warmed by conventional space heaters—and most of us are not experiencing a satisfactory degree of thermal comfort. In other words our heaters are not doing the job we expect of them!

Even with oil, gas or electric space heaters turned to 'high' many people will find that their feet are too cold for comfort. Some householders may decide—on the basis of this discomfort—to insulate their ceilings, and although this may reduce their fuel bills it will not solve their cold feet problems.

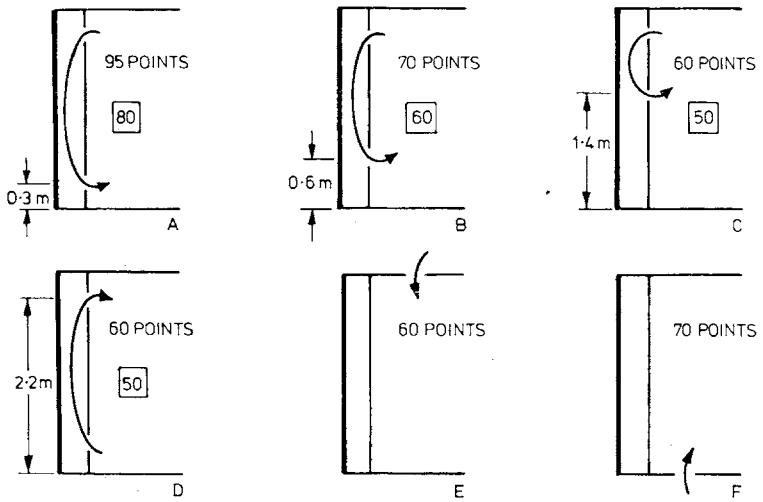
What 'everybody knows'—but it still took quite some work to prove to them—is that our feet get cold if the air near the floor is cold. Medical science has proved that once our feet get cold our bodies switch off the flow of warm blood to that region in an effort to conserve heat for the vital organs contained in the trunk. Frostbite is an extreme example of this 'switching off'. Because of this bodily reaction we can say that the temperature of air a few centimetres from the ground largely determines the comfort of a person in the normal sitting position. It is not uncommon for people in a heated room to feel 'stuffy' and nod off to sleep. Work in the UK has described this 'stuffiness' as a condition caused by a temperature gradient—hot near the head, and cold near the floor—and attributed sleepiness to this variation.

The aims of effective room heating must include the elimination of this temperature gradient. If we are to overcome cold feet and sleepiness our heating systems need to warm the air near the floor and maintain an even temperature from floor level to ceiling. Most popular space heaters do not achieve this—they pour out warm air at too great a height above floor level and we get a high temperature at head height or higher, and an unnacceptably low temperature at feet level.

In an effort to determine how to achieve optimum room heating DBR [Division of Building Research] scientists set up a test room with an area of 20 m^2 (240 sq. ft.) —the size of a large living room. They experimented with heated air being blown into the room at different heights above floor level, and rated each against a scale of zero (poor heating) to 100 (excellent). This score was achieved by taking the temperature rise recorded near the floor and dividing it by the average temperature rise recorded in the room. The result was then multiplied by 100 to give a workable figure.

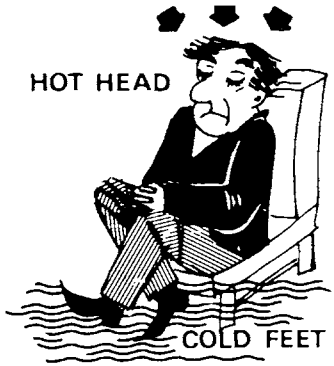
The diagrams show that the best performance was achieved when air was blown into the room at a height of 0.3 m above floor level. It can be assumed that a similar result would have been achieved at any height below 0.3 m. In these experiments the incoming air was kept at a temperature of 17°C above that of room temperature. The figures appearing in boxes (in diagrams A–D) indicate the performance change which occurred when the incoming air was 30°C above that of room temperature. This increased temperature always reduced heating effectiveness—thereby indicating that there must be an adequate volume of circulating air to keep the incoming temperature within about 17°C of the room air. More precisely, this means about 50 litres per second per kW.

Tests were also done with convection 'stoves' of both fan and fanless types (65 points); hot water radiators of the stand-up variety (60 points); and hot water baseboard radiators (80 points when placed opposite a window, and 90 points when placed under a window).



The results indicate that few methods are well suited to room heating, and that much present equipment is unsatisfactory. The only reasonable possibilities appear to be:—

- Heating of the actual flooring material (not tested). This generally has to be installed during house construction. Heating systems installed in a concrete floor can pose another problem: that of very slow response to change.
- convection 'stoves' using oil, gas or solid fuel with forced air flowing in the opposite direction to normal so that air intake is at say waist level, and the forced air outlet is almost at floor level. (Such units may not be available commercially.)
- hot water baseboard radiators.
- fan-assisted heaters blowing air horizontally near the floor.
- radiant heaters (gas, electric, fuel, oil) facing the people to be kept warm.



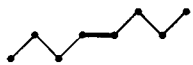
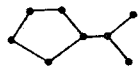
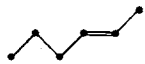
While conventional space heaters continue to pour out warm air at the wrong height above floor level we will not solve our hot head and cold feet problem.

Source: Rebuild, June 1977. Reprinted with permission.

APPENDIX 11.3

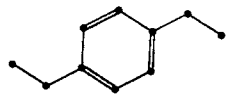
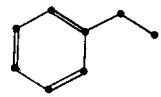
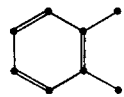
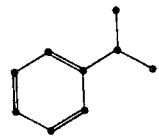
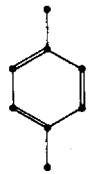
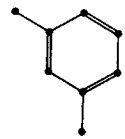
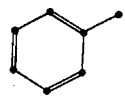
Octane Values for Hydrocarbons

Octane values vary widely with hydrocarbon branching, unsaturation, and size

Hydrocarbon	Structure	Unleaded research octane number RON
n-Octane		−19.0
n-Heptane		0.0
n-Hexane		24.8
n-Propylcyclopentane		31.2
Octene-2, cis-isomer		56.2
n-Pentane		61.7
isopropylcyclohexane		62.8
2,4-Dimethylhexane		65.2
Octene-4, trans-isomer		73.3
iso-propylcyclopentane		81.1
Cyclohexane		83.0
Pentene-1		90.9
Hexene-2, trans-isomer		92.7
n-Butane		93.8

Octane Values for Hydrocarbons

Octane values vary widely with hydrocarbon branching, unsaturation, and size

Hydrocarbon	Structure	Unleaded research octane number RON
Propane		97.1
Butene-1		97.4
2,2,4-Trimethylpentane (iso-octane)		*100.0*
Cyclopentane		101.3
Propylene		102.5
2,4,4-Trimethylpentene-1		102.5
Benzene, technical grade		105.8
1,4-Diethylbenzene		106.0
Ethylbenzene		107.4
o-Xylene		107.4
isopropylbenzene (cumene)		113.1
p-Xylene		116.4
m-Xylene		117.5
Toluene, technical grade		117.8
Toluene, chemically pure		120.1

Source: 'Gasoline', *Chemical and Engineering News*, 9 November 1970, p. 52.

APPENDIX 11.4

Octane Number Requirements of Automobile Engines

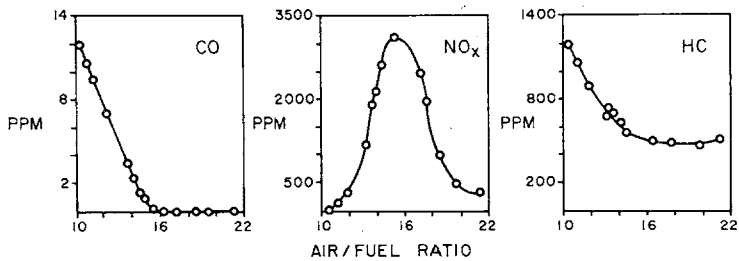
Octane number requirements of automobile engines increase as compression ratio increases.

Engine compression ratio	Typical Research Octane no. required for knock-free operation
4:1	60
5:1	73
6:1	81
7:1	87
8:1	91
9:1	95
10:1	98
11:1	100
12:1	102

Source: 'Gasoline', *Chemical and Engineering News*, 9 November 1970, p. 52.

APPENDIX 11.5

Pollution by Exhaust Materials as a Function of Fuel Mixture Setting



Effect of air-fuel mixture ratio of pollutant emissions. Best ignition occurs in the range A/F = 10 to 14.5 and the overall ratio must allow for variations within the cylinder and from cylinder to cylinder. Uncontrolled engines are thus usually tuned to an A/F of about 13. The stoicheiometric ratio (where in the theory the exact amount of air is present for the fuel) is 15.5.

Source: R. W. Bilger, 'The War against Air Pollution', *Current Affairs Bulletin* no. 49, 1973, p. 347.

APPENDIX 11.6

Typical Petrol Specifications

Brand Name X Super Premium Petrol
Date Effective October, 1975
Newcastle

Test Method	Tests	Specification		Typical Values	
Visual	Appearance	Clear & Bright		Clear & Bright	
Visual	Colour	Red		Red	
ASTM D 2267	Benzene content (% vol.)	5.0	Max.	<5.0	
ASTM D 130	Copper strip corrosion, 3 hrs @ 50°C	1	Max.	1A	
ASTM D 381	Gum, Existent (mg/100ml)	4	Max.	<1	
ACM 17.05	Lead Content(g/l)	0.64[1]	Max.	0.60	
ASTM D 2699	Octane number, research	98.0	Min.	98.2	
ASTM D 2700	Octane number, motor	—		88.0	
	Odour	Marketable		Marketable	
ASTM D 525	Oxidation stability (minutes)	240	Min.	300+	
ASTM D 1298	Density @ 15°C (kg/l)	—		0.743	
ASTM D 1266	Sulphur, total (% mass)	0.2	Max.	0.2	
	Volatile characteristics	Summer[2]	Winter	Summer	Winter
ASTM D 86	Distillation,				
	10% Evap. (°C max.)	60	60	52	50
	50% Evap. (°C)	80–115	85–110	95	93
	90% Evap. (°C max.)	180	180	160	158
	End Point (°C)	—	—	200	203
	Evap. @ 70°C (°C)	—	—	29	32
	Recovery (vol. %)	—	—	98	98
	Residue (vol. %)	2	2	1	1
ASTM D 323	Vapour Pressure, Reid (kPa max.)	69	83	62	72

*American Society for Testing Materials

Additional blending and testing notes

[1] For supply outside Sydney, Newcastle, Wollongong areas, lead content may be 0.84 g/l Max.

[2] Summer: 16 October to 1 March
Winter: 2 March to 15 October

Appendix 11.6—contd

Typical Petrol Specifications

Brand Name X Regular Petrol
Date Effective December, 1975
Southern Queensland

Test Method	Tests	Specification			Typical Values		
Visual	Appearance @ 20°C	Clear & Bright			Clear & Bright		
ASTM D 2267	Benzene content (% vol.)	5.0[1] Max.			0.8		
Visual	Colour	Yellow			Yellow		
IP 17	Colour lovibond 1″ cell	—			2.5Y 1.OR		
ASTM D 130	Copper strip corrosion, 3 hrs @ 50°C	1 Max.			1A		
ASTM	Gum, Existent (mg/100ml)	4.0 Max.			0.1		
ACM 17.05	Lead content (g/l)	0.84 Max.			0.18		
ASTM D 2699	Octane number, research	89.0 Min.			89.0		
ASTM D 2700	Octane number, motor	—			81.5		
	Odour	—			Marketable		
ASTM D 525	Oxidation stability (minutes)	240 Min.			1500+		
ASTM D 1298	Density @ 15°C (kg/l)				0.734		
ASTM D 1266	Sulphur, total (% mass)	0.15 Max.			0.05		
	Volatility characteristics[2]	Sum.	Int.	Win.	Sum.	Int.	Win.
ASTM D 86	Distillation,						
	10% Evap. (°C max.)	60	57	57	53	52	50
	50% Evap. (°C max.)	116	107	85–107	97	97	96
	90% Evap. (°C max.)	180	180	180	171	171	172
	End Pt. (°C max.)	218	218	218	207	206	205
	Recovery (% vol. min.)	96	96	96	98	98	98
	Residue (% vol. max.)	2	2	2	1	1	1
ASTM D 323	Vapour Pressure, Reid (kPa max.)	69	72	76	52	54	56

Additional blending and testing notes

[1] For supplies to N.S.W. only

[2] Summer: 16 September to 31 March
Winter: 1 May to 15 August
Intermediate: 1 April to 30 April
16 August to 15 September

APPENDIX 11.7

Pamphlets available from the Southern Electricity Authority of Queensland.
Independent advice on domestic electrical appliances can be obtained from electricity authorities. Some examples of what is available are given here from the Southern Electricity Authority of Queensland as a customer education service (which is constantly updated).

1. *Air conditioners*
   types: room, split system, vertical and horizontal, ducted system. What size air conditioner do you need?: average living area 25 m^2 (270 sq ft) would need about 3500 watt; bedroom 15 m^2 (160 sq ft) 1650 watts needed; vertical-type unit for dining-living room 40 m^2 (430 sq ft) needs about 6000 watts. Note however aspects of house, size and slope of windows and doors, insulation, etc. Gives average installation times.
2. *Dishwasher*
   Why buy a dishwasher; types of dishwasher; how they work; points to consider; features available; hints on use.
3. *Refrigerators and deep freezers*
   types available; defrosting; features to look for.
4. *How to prepare, freeze and store frozen food*
5. *How to buy an electric range*
   includes microwave ovens; somewhat uncritical of 'continuous cleaning' ovens.
6. *Washer and dryer guide*
   types available; wringer washers, twin tub washers, automatic washers—top loading automatics, front loading automatics. Minimum features a machine should have, additional features.
7. *Space heating* (electrical only!)
8. *Operating costs of domestic electric appliances*
   This is a very useful little pamphlet. Something one could use as an interesting exercise.
   There are five columns:

Household appliance	Average input wattage	Weekly hours of use	Estimated kWh per quarter	Estimated cost per quarter @ 2.78 cents/kWh ($)
Cooking appliances				
Range—4 persons	11250[T]		320	8.9
Microwave	1300[T]	4	70	1.9
Frypan	1350[T]	4	64	1.8
Crockpot, etc.	150	20	35	1.0
Kitchen appliances				
Dishwasher (cold water type)	2000[T]	13	114	4.0
Coffee percolator	600	3.5	30	0.8
Jug or kettle	1800	3	75	2.0
Toaster				
manual	600	1	12	0.3
Automatic	1500	0.5	10	0.3

Appendix 11.7—*(continued)*

Household appliance	Average input wattage	Weekly hours of use	Estimated kWh per quarter	Estimated cost per quarter @ 2.78 cents/kWh ($)
Refrigeration				
250–320 litres one-door manual	150[T]	cont	100	3.0 (9–12 c.ft)
475–600 litres 2 door frost free	600[T]	cont	530	15.0 (18–20 c.ft)
Freezers				
220–330 litres upright more expensive than chest freezers	280[T]	cont	160–250	4.0–7.0 (7–12 c. ft)
Laundry appliances				
clothes dryer (4 kg)	2000	5	150	4.0
Washing machine				
wringer and tub	500	5	30	1 0
automatic				
Water heating				
30 gal (4 persons)	1800[T]	cont	630	18.0 (less if there is a special rate)
Other appliances				
blanket—single	65	63	28	0.8
—double	138	63	50	1.6
hair dryer	300	1	3	0.8
lawn mower	1200	1(av.)	20	0.6
large radiator	2400			6 cents/hour
TV colour 22″	200	35	86	2.4
vacuum cleaner	600	2	14	0.4
Lighting				
incandescent				
3 on average	300w	30		3.0
fluorescent				
3 on average	150w	30		1.5

(T) when calculating for thermostatted appliances (T), consider only the time when the power is being used by the appliance

Source: Southern Electricity Authority of Queensland.

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Chapter 12

CHEMISTRY IN THE DINING ROOM: FOOD ADDITIVES

PLATE 12.I *Junk Food.* © 1975 United Feature Syndicate Inc.

INTRODUCTION

There is nothing new in the idea of food additives. The man who first smoked a herring was putting an additive in his food. Thousands of years ago the Chinese used ethylene and propene (produced by the incomplete combustion of oil shale) to ripen bananas and peas. Pliny the Elder records that wines from Gaul were artificially coloured and flavoured (shades of the recent Bordeaux wine trials!). Pickling in salt, and fermentation processes resulting in the production of lactic acid, alcohol, or acetic acid are methods of food preservation that date from ancient times. In salt caves near the Dead Sea there is evidence of even prehistoric preservative processes. Human and animal droppings containing protein and hence nitrogen on the salt floor produced both sodium nitrate and sodium nitrite, which preserve meat. This accidental (but perhaps socially undesirable) piece of chemistry was apparently put to good use. Curing meat with brines containing nitrites and nitrates is thus a long established process. The nitrites apparently fulfil an essential role in the curing process; they certainly give ham a pleasing colour, which has been attributed to the conversion of myoglobin and haemoglobin into their nitroso-derivatives. The nitrite also prevents the development of the bacterium

Clostridium botulinum that causes botulism, a most deadly form of food poisoning. However in the last few years there has been some concern at the possibility of a reaction in processed food or in the digestive system, between nitrite and secondary amines to form nitrosamines which are highly carcinogenic (i.e. cancer inducing).[1] Small concentrations of nitrosamines (parts per billion) have been found in raw, but particularly smoked, fish and less so in meat.

Flavouring and seasoning were arts in many ancient civilisations, with the result that spices and condiments were important items in commerce. The spices were originally added as preservatives when refrigeration was not available. They contain antioxidants which are currently under study by CSIRO.[2] They were also used to hide the off-colour of food that had been kept too long. No doubt many of us would prefer to eat food straight from the farm, orchard, or sea. But, in societies with large, heavily populated urban areas that import food produced, perhaps, on the other side of the world, some form of processing if only for preservation is necessary. However, people do feel uneasy about 'chemicals' in their food because they are worried about the possible effects of eating substances which we do not eat 'naturally', or simply because their food tastes different. All food, of course, consists of chemicals. The chemicals people are worried about are traces of substances that are not themselves foods, and that may not be present in foods in their natural or traditional state. The presence of these substances may be either accidental or deliberate. Before allowing ourselves to become carried away by this concern let us consider a few 'natural' culinary disasters.[3]

In 400 B.C. an army of Greek mercenaries 10,000 strong became intoxicated and finally unconscious after eating honey in some villages on the shore of the Black Sea. In 1596 members of an expedition to Novaya Zembla in the polar wastes all became ill after eating bear liver, and three of them lost their skin. Much the same thing happened again in 1913 to another expedition to the Arctic. In 1816 Abraham Lincoln's mother died after drinking milk from a cow that had fed on snakeweed. Abraham was then 7.

What happened was that the bees had fed on the nectar of rhododendrons which contained a poison that had been deposited in the honey. Mrs Lincoln's cow had acquired a poison from the pasture. The case of the bears demonstrates that a necessary component in our diet, essential to our health, when eaten in excess can be disastrous. In this case it was Vitamin A stored in the bear liver. These instances of normal foods being toxic are rare; that of Lincoln's mother is the only one recorded, but outbreaks of honey poisoning do occur from time to time.

However, there are foods which appear to lead to disease in the long term. In Nigeria the starchy root, *cassava*, is widely eaten and is believed to be responsible for a nervous disease resulting in deafness, difficulty in walking, etc. The cassava root contains compounds which produce *cyanide* when the

root is prepared as food. Although it is customary to wash the food well—the toxic substances pass out of the root on soaking—it appears likely that enough cyanide remains to cause disease over a period of years. It is relevant to note that we have evolved culturally to avoid the dangers from natural poisons (e.g. the Nigerians wash their cassava without ever having done chemistry or having heard of cyanide!). On the other hand it is hardly possible to pick up a woman's magazine or weekly journal without finding some horrific story of the additives we are all consuming. The classic in this regime is probably the Ralph Nader publication *The Chemical Feast* and I quote here a section dealing with baby food:

> Twenty years ago a jar of baby food contained a given amount of fruit, vegetables or meat. As the costs of these ingredients rose, baby food companies began to replace part of them with starch and sugar—each of which is less expensive than the ingredient it was replacing. Naturally, foods thinned out with starch or sugar tasted blander or sweeter than the originals, so baby food makers began adding salt and monosodium glutamate to please mothers who tasted their babies' food. Then it was discovered that the starches added to the food would break down and become watery if a mother fed her baby some of the bottle's contents and let the remainder sit, even in the refrigerator, overnight. The baby's saliva, which got into the food on the spoon the baby fed with was 'digesting' it. The answer provided by the baby food companies was to find a starch that saliva could not break down and add it to the bottles' contents. So now baby food contains not only added sugar, salt and monosodium glutamate, but also added modified starch which baby saliva does not break down in the jar or the mouth and which some researchers fear may not be completely digested even by the rest of the baby's system. None of these additives in the food for purely economic reasons has been proven safe for consumption by babies.[4]

FOOD TECHNOLOGY AND THE LAW

The first modern processes for preservation were developed empirically some half a century before the true cause of food spoilage was known.[5] In 1795 the embryonic revolutionary republic of France was beset by enemies on all sides and the government was desperate to seek ways of preserving food for its troops. A prize of 12,000 francs was offered and it was won, after many years of patient experimentation, by a Parisian confectioner Nicolas Appert. He published, in 1810, *The Book for all Households on the Art of Preserving Animal Substances for Many Years.* That's how it all started.

The legal situation in Australia has been described by Madgwick (then Chief Food Inspector with the New South Wales Health Commission) in an article in *Food Technology in Australia.*[6] In New South Wales, people were rather pleased with their rich creamy milk, which seemed to keep so well. The colour, it appears, was by courtesy of the milkman rather than the cow, and formalin acted as a preservative. The state of Victoria enacted the first general food legislation in 1905 followed by New South Wales in 1908. Other states followed

shortly after and there is hope that the Australian Capital Territory will also get a food law soon. The Australian states adapted a system of prohibition (in contrast to a system of abuse). In our system all substances which are not expressly authorised are prohibited in food—in contrast to allowing what is not expressly prohibited. Food products thus have to be defined by 'specifications of identity' known as Food Standards. Additives have to be defined separately as they are not foods and this causes difficulty. While the 1908 New South Wales Act prohibits preservatives unless specifically allowed it does not define *preservative* except to state that common salt, sugar, spices, wood smoke, vinegar, and acetic acid are *not* included in the term. Other additives such as flavours, colours, essences, and spices were originally defined as foods. After describing these first Australian food laws, Madgwick then goes on to follow the legal development of the food law through to today.

There are still areas of confusion. The labels *artificially flavoured* and *artificially coloured* refer to the colour or flavour being artificial to the product to which they have been added and not, as many appear to believe, that the flavour or colour is necessarily of non-natural origin. The allowed list of colours includes chemical dyes as well as 'natural' vegetable colours but the same legal requirements apply to the whole set. 'Naturally' dairy products such as butter and cheese are exempt (provided harmless vegetable colouring matter only is used). The definition of *food* in the current New South Wales Pure Food Act is:

> 'Food' or 'article of food' means article used for food or drink by man, and includes confectionery, and any article that enters into or is used in the composition or preparation of food, and *any spices, flavouring substances, essences, and colouring matters so used* and any substance or article used for consumption by man which the Governor may by proclamation declare to be food or an article of food [my italics].

Madgwick then explains that the *additives* which I have italicised can be used as food when they are added to a food for which there is no standard. A food product for which no standard has been defined by regulation and which does not occur in nature cannot be said to be artificially coloured and/or flavoured. The colours and flavours then used are considered to be an integral part of the food. Function defines legal status. Ascorbic acid (vitamin C) can be used as an antioxidant (as in beer) or as a vitamin (as in orange juice). Sorbital can be used as a humectant or as a sweetener. Sucrose (cane sugar) when added to sweeten a product should, according to Madgwick, have the same status as other sweeteners such as cyclamate and saccharin when a product in its standard state does not normally contain sucrose.

Thus *additive* is not defined directly in Australian food law.

By now you should be completely disoriented—thinking either of giving up food altogether or not worrying at all about these things and assuming that the 'authorities' will look after us. The first alternative does not appear to

show much promise in the long term and the second unfortunately is just not good enough because those authorities need to be continually prodded to ensure action within a reasonable time. The problem, like many in our lives, is one of cost versus benefit.[7] We must, however, be careful as to exactly what we mean. Is it consumer *health* benefits weighed against consumer *health* risks? Or consumer *economic* benefit against consumer *health* risk? Or consumer *convenience* benefit against consumer *health* risk? And on the other hand when manufacturers use the term *cost/benefit*, does it mean *industry economic* benefit against *consumer health* risk? These very different factors are often covered by the same expression.

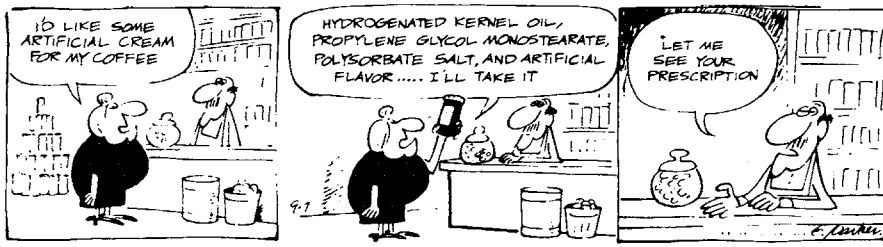


PLATE 12.II *Food additives*

Types Of Food Additives

In this section I give brief definitions of the different types of food additives before describing the major groups in more detail. Classes of additives which I have not covered include antibiotics, radioactive irradiation (not allowed for food but used for sterilising pharmaceuticals), release agents in confectionery, starch modifying agents, and water correcting agents (used in brewing to give a uniform mineral content), and many others.

GRAS. A group of additives included in the United States Food and Drug Administration's list of additives 'generally recognised as safe', including a large groups of natural flavours and oils which are not specified.[9] To be on this list an additive must have been in use before 1958 and have met certain specifications of safety. Additives brought into use since 1958 must be approved individually. Occasionally substances are removed from the list by the FDA in the light of new evidence, a recent example being the cyclamate sweeteners.

Preservatives. Substances used to prevent spoilage caused by bacterial activity, fungus and mould, and thus to prolong the keeping quality of foods.

Antioxidants. Substances used to inhibit the oxidation of fats during storage —i.e. stop them becoming rancid.

Colouring matter. Substances used to colour foods.

Flavouring agents. Aromatic substances, both natural and synthetic, used as components of food flavours or directly in foods, and artificial sweeteners.

Sweeteners. Substances to make food taste sweet.

TABLE 12.1 *United States classification of intentional food additives by technical effect*

General classification	Detailed classification	Estimated $ sales 1970 (in millions) MCW*	CW†	Number in category
Nutritional	Nutrient supplements			85
Aesthetic	Flavor enhancers	185	83	1580
	Flavoring agents, adjuvants			
	pH control agents	34	33 (acidulants only)	
	Colours, coloring adjuncts			
	Non-nutritive sweeteners			
	Enzymes			
	Surface-finishing agents			
Preservative	Preservatives	14	36	110
	Antioxidants			
	Sequestrants			
	Fumigants			
Texturizing and Stabilizing	Emulsifiers	62	52	340
	Surface-active agents			
	Stabilizers, thickeners	71	104	
	Humectants, etc.			
	Firming agents			
	Texturizers			
Processing Aids	Processing aids			430
	Propellants, aerating agents, etc.			
	Solvents, vehicles			
	Anticaking agents			
	Curing, pickling agents			
	Dough conditioners			
	Drying agents			
	Flour-treating agents			
	Formulation aids			
	Leavening agents			
	Lubricants, release agents	Total of all others		
	Synergists	118	58	

* Mallinckrodt Chemical Company
† *Chemical Week*

Source: The President's Science Advisory Committee[8]

Sequesterants. Substances that react with traces of metal ions, tying them up in a manner which prevents their normal reactions such as catalysing the decomposition of food. Sequesterants such as phosphates are used in detergent formulations to tie up metal ions in water.

Gelling agents, stabilisers, and emulsifiers. Substances used to produce or maintain a certain consistency in foods.

Acids and bases. Substances used to impart a certain tartness to foods or to alter the acidity of the medium (i.e. to lower the pH in canned products or to prevent the crystallisation of jams and jellies). Some are used as ingredients of baking powders used in pastry production and in powders for effervescent beverages.

Improving agents. This group includes chemical compounds which enhance one or more of the quality criteria of foods (flavour, consistency) and substances used for polishing and glazing confectionary products.

Acceptable daily intake, ADI

This is the amount of a food additive, calculated on the basis of body weight in mg/kg, that can be eaten daily for a lifetime without adverse effect. For a 70 kg man the amount would be seventy times the ADI. Where there is some doubt about the safety of an additive, a time limit on its use is set (e.g. five years) in which further work is to be done and a conditional (or temporary) ADI is set. The method of establishing the ADI is to carry out experiments on animals—increasing the quantity of the additive to establish at which level acute and chronic toxicity occurs in any animal. (That is the level at which an immediate poisonous effect is observed and the one at which long-term effects occur.) At least two species of animals are used and the most sensitive species is taken for determining the level. The quantity so determined is divided by 100—the usual safety factor—to set the ADI. Sometimes such a factor cannot be afforded. In the case of mercury the ADI based on *human* studies was set with a safety factor of only 10. If we consider a natural poison such as *solanine* which occurs in the green patches of sprouting potatoes (it is a glyco-alkaloid and inhibits cholinesterase enzyme—see Chapter 5) then we find that concentrations of solanine of 380–480 mg/kg have been obtained from potatoes implicated in fatal poisoning whereas the normal levels in potatoes are 30–60 mg/kg. Solanine is not destroyed by cooking but it is washed out to a certain extent.[10]

The final task is to look at all the foods in which the particular additive under consideration occurs and to calculate the likely consumption of the various foods. It is then possible to calculate what the actual daily consumption of the additive might be. This knowledge allows a variety of decisions to be made.

SOFT DRINKS

Arguments based on thirst suggest a limit on the average daily consumption of soft drink at about 25 ml of beverage per kilogram body weight. For a 50 kg reference individual, 25 ml/kg corresponds to 1250 ml/day or 456 litres/year. The Australian average for consumption of soft drinks is 70 litres/year. The question remains as to what the average consumption is for those consumers who drink a lot of soft drinks. This does not influence the question of what level of food colour should be allowed in soft drink, given an accepted rate of consumption and an accepted no response dose.

For the food colour amaranth, a temporary acceptable daily intake has been set at 0.75 mg/kilogram body weight.* With the usual assumption that 50 percent of intake will occur in food other than soft drinks, this level fixes a maximum level for soft drinks at 15 mg/kg.

The current (1977) allowed level in Australia is 70 mg/kg.

*World Health Organization. *Evaluation of Mercury, Lead, Cadmium, and the Food Additives Amaranth, Diethyl pyrocarbonate, and octyl Gallate* (WHO Food Additive Series No. 4), Geneva, 1972.

1. In the case of an intentional additive—e.g. a preservative—should it be allowed in more types of foods or not? Should the level allowed presently in foods be reduced? Is there a chance of an abnormal diet—someone who drinks a couple of litres of, say, Glugga each day getting too much of an additive such as SAIB (sucrose acetate isobutyrate), which is a replacement for the more dangerous brominated vegetable oils. Should technology be improved to reduce the need for the additive?
2. In the case of unintentional additives—such as pesticide residues—should the *withholding* period (see Chapter 5) be increased so as to reduce the amount of additive in the food when eaten?

Substances used in a wide range of food, such as the preservative sorbic acid, are very difficult to calculate for. Most toxicological data are based on laboratory mammals. Unfortunately such results are not necessarily transferable to man, there being examples of compounds which are very toxic to some animals but not man and *vice versa*. Infants and children cannot be considered simply as small adults, but reliable clinical data are generally unavailable. For a start the energy intake of children per body weight is about three times that of adults. Very young infants are especially vulnerable to foreign chemicals because the mechanisms that provide protection against these substances in adults are as yet absent or not fully developed. Although the evidence for this derives mainly from studies with drugs rather than with food additives, it is likely that such very young infants are less efficient that older

children in metabolising some food additives and may therefore accumulate them to excessive levels. If this occurs at a time when sensitivity to toxic effects is critical because of delicately balanced growth and differentiation processes, there may be deleterious consequences that may not appear until much later in the child's development. Very young infants may also differ from older children in relation to physiological barriers protecting sensitive tissues, such as the blood brain barrier or the protective barriers for retinal or lens tissue. In the case of food additives the immediate danger of poisoning is not nearly as important as the long-term chronic, carcinogenic, and mutagenic effects. Even less information is available on these effects.

LD_{50}—HISTORICAL PERSPECTIVE

. . . Until about 50 years ago, the toxicity of a substance was usually expressed as the lowest dose which had been observed to kill an animal —even though it was realised that another animal might survive after a much larger dose. In 1926, however, it was shown that the individual minimal lethal doses of digitalis for 573 cats followed a normal distribution, and in 1927 Trevan, who got similar results on an enormous number of frogs, plotted percent mortality at each dose and interpolated a value for the dose that would kill 50 percent of the animals. This dose he designated as the LD_{50}. After another quarter century, in the early 1950s, the value of this measure of toxicity had been completely accepted and the methods necessary for obtaining it had been well worked out. The practical value of this approach is now being questioned —again on grounds of biological variability. It has been shown, for example, that the LD_{50} for a drug on a single species of laboratory animal varies with strain, sex, age, diet, litter, season, social factors, and temperature. It seems hardly worth standardising all these variables, however, when LD_{50} variation between species is so great—sometimes more than hundredfold between rats and mice.

It is clear, moreover, that man differs very greatly from the rat and other experimental animals in his response to some toxins. Some species of animals used in routine laboratory toxicity testing can live happily all their natural days on the seeds of a vetch that when consumed by man in amounts of a few hundred grams a day produces irreversible paralysis of the legs. Much concern was recently aroused by the demonstration that lysinoalanine—a compound formed in foodstuffs treated with alkali as in the preparation of protein isolates, or, more traditionally, in the primitive use of maize—is quite strongly toxic to rats, producing kidney damage when fed at levels of 100 ppm in their diet. It has now been shown that ten times this level in the

diet of quail, mice, hamsters, rabbits, or monkeys has no discernible effect. Thus it appears that the rat is quite unusual in its susceptibility and that in retrospect, the primitive Middle Americans who developed maize as a staple of the diet using alkali treatments in its preparation were not foolhardy. Unfortunately there is no convenient escape from the truism that the proof of the pudding is in the eating—and that must be by man, for it is clear that lack of effect of a new food on experimental animals does not guarantee harmlessness for man nor does toxicity in an animal species mean that man must at all costs avoid it.

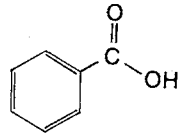
The variability of response between animals of the same species occurs in humans too, and ignorance of this principle has led to many unsuccessful murder and suicide attempts, in which the presumed lethal dose of toxic substance has turned out not to be enough for the purpose envisaged. With very toxic substances the lethal dose resulting in death in 99 percent of a population may be several times the LD_{50}, but it is still a very small amount, and the distinction is perhaps not very important. It is, however, interesting to speculate on the application of this biological phenomenon to the long-term deleterious effects of particular diets on individuals. Let us suppose, for example, that the consumption of a total of 2.5 tonnes of saturated fatty acid could be shown to result in the death of 50 percent of those consuming it from coronary heart disease. It would take about 100 years to consume that much on a normal Australian diet and we would be perhaps entitled to say that therefore it could not be regarded as toxic as no one (or *almost* no one) would have an opportunity to consume that much. We might, however, be wrong to make this judgment, for in a highly variable population such as ours, one could expect death to result in *some* individuals in half or a third of the time. What I am suggesting is that with the articles of diet present in major amounts, it is not possible to test for indications of long-term human toxicity using animals, simply because to multiply the dosage of the suspect material in the diet enough to give reasonably clear-cut experimental results in animals is impossible, for to do this the component would have to amount to all or more than the total weight of the diet. Still less is it possible to make such tests on man, for the institution of slavery was abolished in advanced societies half a century before the emergence of human nutrition as a science—which is one reason we know so much less about human nutrition than about the nutrition of domestic animals.

Source: M.V. Tracey. 'The Price of Making our Foods Safe and Suitable', *Food Quality in Australia.* (Academy Report no. 22), Australian Academy of Science, Canberra 1977.

Preservatives or antimicrobials

Benzoic acid

Benzoic acid and its sodium salts are among the bacteriostatic or germicidal agents most widely used in foods. Many berries (e.g. raspberries) contain appreciable amounts (~0.05 percent) of benzoic acid. Benzoic acid is included on the permitted lists of at least thirty countries throughout the world for a great variety of foods, particularly soft drinks. Benzoic acid preserves food by inhibiting the growth of bacteria. As it is only the free acid which is effective it can only be used in foods of pH less than 4.5.

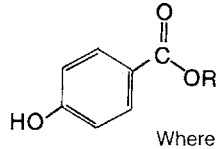


12.1 Benzoic acid

At the international level, the Joint FAO/WHO Expert Committee on Food Additives considered benzoic acid in a report in 1962. They stated that benzoic acid is rapidly and completely excreted in the urine. Long-term tests in rats showed that no accumulation in the body occurs. The body excretes benzoic acid as hippuric acid within 9–15 hours of eating food containing it.

p-hydroxybenzoic acid esters

The *p*-hydroxybenzoic acid esters are other compounds in use overseas but not in Australia.



Where R = CH_3, C_2H_5, C_3H_7, C_4H_9

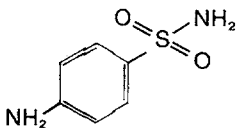
12.2 Structure of the *p*-hydroxybenzoic acid esters

Sulphur dioxide and sulphites, SO_2, SO_3^{2-}

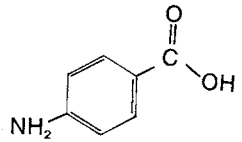
These substances were used by the early Egyptians and the Romans. Sulphur dioxide is unique in being the most effective inhibitor of the deterioration of dried fruits and fruit juices. It is used widely in the fermentation industry to prevent spoilage by microbes and as a selective inhibitor. It is also used as an antioxidant and antibrowning agent (for *casse brune*) in wine making. Sulphur dioxide destroys thiamine (a vitamin) so its use is restricted to foods

which are not important sources of thiamine. Thus it is forbidden in meat except for manufactured meat (e.g. salami, etc.) where it is allowed because it protects against the danger of bacterial contamination during processing at elevated temperatures.

It is interesting to note that a common vitamin (i.e. essential food requirement) for microbes is *p*-aminobenzoic acid—PABA—while the basic antibacterial sulpha drug, sulphanilamide, has a closely related structure, and also approximately the same distribution of electronic charge.



sulphanilamide



p-aminobenzoic acid

Propionates, $CH_3.CH_2.COOH$

Flour contains the spores of the bacterium *Bacillus mesentericus* which are not likely to be killed by the baking temperature. Under summer conditions, these bacteria become active and produce a condition called *rope* which renders bread inedible. The calcium and sodium salts of propionic acid are used in bread (0.2 percent) to inhibit the growth of micro-organisms.

Sorbic acid

Sorbic acid, 2,4-hexadienoic acid,

$$CH_3—CH=CHCH=CHCOOH,$$

is naturally present in some fruits. It is a selective growth inhibitor for certain moulds, yeasts, and bacteria. It is used in cheese products, pickles, fish products, cordials, and carbonated drinks.

Nitrates and Nitrites

As indicated in the introduction to this chapter, these substances occur naturally in many foods, particularly vegetables. The human infant is extremely sensitive to nitrites because of low ability to deal with a modification of blood haemoglobin caused by nitrites. Additional nitrite is derived from nitrate by bacterial activity in the gut which is particularly efficient in the very young infant because of the inadequacy of acid production in the stomach.

Diethylpyrocarbonate, $C_2H_5OCOOCOOC_2H_5$

This preservative *decomposes* rapidly in water to form ethyl alcohol and carbon dioxide. It is thus useful in the preparation of wines, beer, and other drinks. However, because it has been alleged to produce a urethane with some food products it has recently been removed from the NHMRC permitted list. This removal has yet to be incorporated into legislation in Australia.

Miscellaneous

Sodium diacetate is another rope inhibitor in baked goods.

Biphenyl is a fungistatic which migrates from the wrapping material to inhibit growth of mould causing decay of citrus fruits. Often chlorinated biphenyls are used.

Hexamethylenetetramine is a preservative for certain fish products (but is not used in Australia).

In our cost-benefit decision making process, preservatives would probably score well on the benefit side. Whenever there is a choice, however (price and convenience being comparable—such as for say tomato sauce), it would seem sensible to opt for the unpreserved product. There is no case for the indiscriminate use of preservatives. It is often better to encourage the use of refrigeration and good handling techniques.

Antioxidants

Preservatives for fatty products and oils are called antioxidants.[10–12] They prevent the occurrence of oxidation which is the cause of *rancidity*. Vitamin C (ascorbic acid) is commonly used for water-soluble fatty products but the most common antioxidants are the fat-soluble BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene). They have similar properties to the 'natural' oxidant, vitamin E—α-tocopherol. The word *butylated* is not widely used in chemical nomenclature. It is applied here because the usual names for BHA and BHT include the words *cresol* or *phenol* which are generally known to imply toxicity. To avoid consumer rejection of these 'safe' compounds, the names were made 'safe' as well. Various esters (propyl, acetyl, and dodecyl) of gallic acid—3,4,5-trihydroxybenzoic acid—are used in margarine, oils, cream cheese, instant mashed potatoes; etc. The new polymeats, polycheese and polymilk developed by CSIRO require fairly large doses of antioxidants because metallic contamination in the dairy (traces of copper, etc.) catalyse the oxidation of the polyunsaturated fats (see Chapter 3).

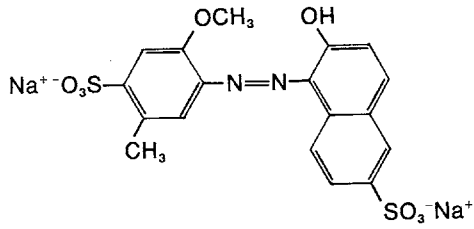
Antioxidants are additives we shall probably have to accept if we want convenience and reasonable shelf-life. On the other hand we should expect

producers to use the maximum technological skill to reduce the required amount to a minimum.

Colouring matter

Colours are put in food mainly for aesthetic reasons on the established pattern that the way the food looks has an effect on its palatability. Both natural and synthetic colours are used. The synthetic colours are mainly coal-tar dyes, many of which have been found to be carcinogenic. The list of permitted red dyes has halved in thirty years. No two countries seem to agree which colours are safe.[13] The USSR puts its faith into natural colours and allows only three synthetic ones (although the distinction is questionable when a natural dye is synthesised). When the British had to conform with the EEC norm (1 January 1977), the 'gold' in the kippers and 'pink' in the sausage had to be changed.

A typical example of the type of compound used as a food dye is Allura Red, now (1977) added to allowed food colours in Australia and shown in Figure 12.3



12.3 Allura Red

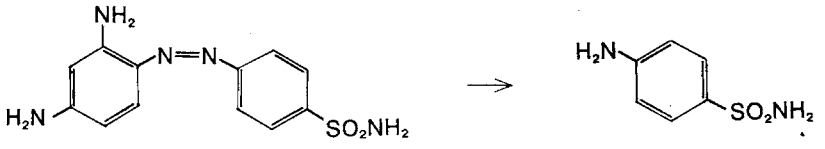
The coal-tar designation comes from the presence of aromatic rings, mainly benzene and naphthalene (see Figure 12.4). The colour is basically introduced by one or more *diazo* (dinitrogen) groups: —N=N—. To make the dyes soluble in water one or more sulphonic acid SO_3^- groups are attached with Na^+ or NH_4^+ as the other ion. The dyes are generally made from two halves which are brought together by joining the nitrogens in a diazo coupling reaction.

benzene naphthalene

12.4 Aromatic hydrocarbons

A case was reported of a young boy passing red stools who unfortunately was subjected to extensive hospital diagnostic procedures before it was concluded that the source of the red was *erythrosine*, which was used to colour the cereal he was fond of.[14] Apparently very little of the colour is absorbed —most is excreted in the faeces—which explains its lack of toxicity.

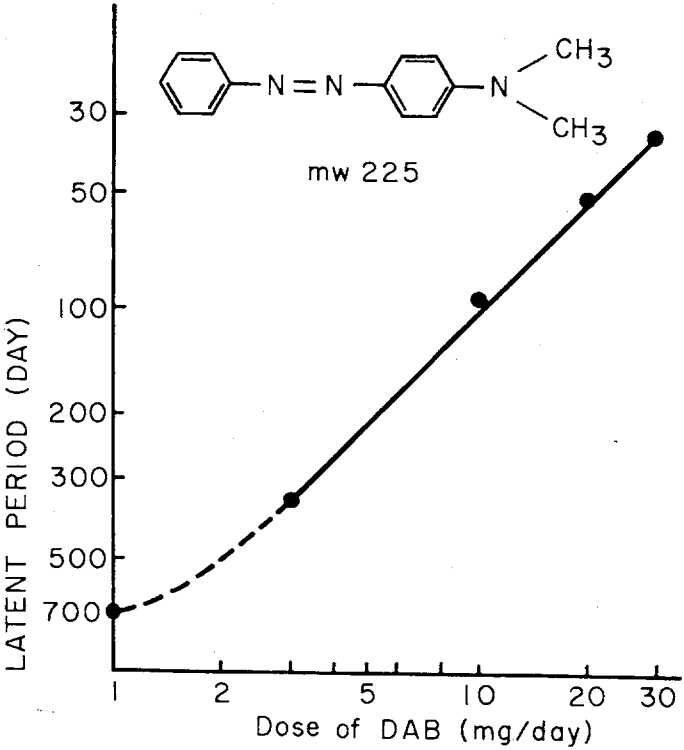
This metabolic inertness is not found with the food azo dyes described above. The azo linkage is split by the bacteria in the gut of humans and animals and it is probable that the products are the problem. The process has been known since the discovery of the first antibacterial sulpha drug[15]—Prontosil in 1935—which was later found to form the active drug sulphanilamide in the bowel:



prontosil sulphanilamide

The less toxic members of the azo series are sulphonated on *both* aromatic partners of the azo link (see Figure 12.3). When split both bits will still be sulphonated and hence poorly absorbed. The more toxic members split with one part not sulphonated and hence are probably more easily absorbed. The triphenylmethane colours (these are chemically a different family—see Appendix 12.2) are all sulphonated and highly water-soluble. They do not break up metabolically and are poorly absorbed.

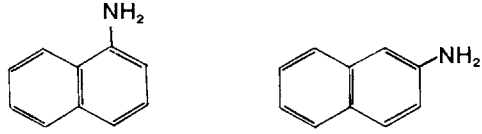
Prior to the Australian 1955 list some forty coal-tar dyes were approved as food colours. The reduced list (twenty-two) excludes all *fat-soluble* dyes (and other suspect dyes) including the notorious carcinogen *butter yellow 11020*—*p*-dimethylaminoazobenzene (see Figure 12.5) which had already been deleted (along with the colour Sudan I) by Canada in 1934. The $SO_3^-Na^+$ group which makes these dyes soluble in water also reduces its physiological activity. The Australian 1955 list was 'known to include some dyes which were, to some extent, suspect but which were included for the time being to prevent undue embarrassment to the food industry, it being understood that they were subject to removal at any time'.[13] In 1966 this number was still twenty-two —8 red, 1 orange, 6 yellow, 1 green, 2 blue, 1 violet, 2 brown (of mixed composition), 1 black. In 1969 two yellow dyes were removed. At the present time another four colours have been deleted because of lack of technological need (see Appendix 12.2). A new red colour has been added (see Figure 12.3). In 1960 the United States had fourteen permitted food dyes, the United Kingdom had thirty and yet nine of the permitted United States' dyes were



12.5 Log-log plot of latent period for the appearance of liver cancer in rats fed *para*-dimethylaminoazobenzene (butter yellow) against dose levels. The larger the dose the shorter the time for the cancer to appear. Curves of this type are used to justify the use of high dosages in testing for carcinogens which at the levels in normal use take long times to show an effect. It was as a result of such tests that this colour was removed from the list of allowed food colours.

Source: International Agency for Research on Cancer 'Evaluation of Carcinogenic Risk of Chemicals to Man.' Vol.8 1975. (WHO Lyon).

banned in the United Kingdom. Because the chemical structures are very similar one might imagine that there is not much to choose between them from the point of view of danger to health. However, two of the basic materials in the preparation of some of these dyes are the naphthylamines (Figure 12.6).



1-naphthylamine 2-naphthylamine

12.6 Naphthylamines

The 2-naphthylamine is a very potent carcinogen and causes cancer of the bladder with an induction period between intake and disease of about 20–30 years. On the other hand the 1-naphthylamine is less potent (i.e. compared to the 2-) and its greatest danger is that it may be contaminated by the 2-compound. This of course all raises another point—most toxicological testing is done with massive overdoses of the material over a relatively short time span. Commercial enterprises are unhappy at waiting thirty years for the release of their latest find on the general public. There is little reason to believe that dose can replace time as an experimental variable. In fact if high concentrations of a possibly potent test chemical are used then the effect can be to *kill* the exposed cells which would not then reveal mutagenic or carcinogenic responses. This also applies to the effects of radiation. Large concentrations can also act as physical irritants leading to tumour formation. On the other hand, large concentrations can reveal the presence of a potent impurity, present in very low concentration, as in the herbicide 2,4,5-T and in saccharin.

The purity of the food colours is based where possible on the relevant British Standard. The standard method of analysis is given in BS 3210–1960. For a typical colour the following specifications are set:

1. The colouring matter shall be essentially the chemical specified and impurities should be no greater than are to be found in good manufacturing practice
2. . . . no more than 10% w/w of volatile (135°C) matter
3. . . . no more than 0.1% w/w of water-insoluble matter
4. . . . no more than 0.2% w/w of ether-soluble matter (di-isopropylether)
5. . . . no more than x% w/w of subsidiary dyes (e.g. amaranth x = 3%)
6. . . . no less than 85% w/w of the dye that it is meant to be. The standard differs for the different colours. For example with tartrazine a specific level of 0.1% w/w is set for phenylhydrazine-*p*-sulphonic acid.

The use of healthy animals as an indication of the toxicity of chemicals for human beings of a variety of ages and states of health (liver and kidney function, etc.) is also questionable. This explains why, with three exceptions (4-aminodiphenyl, nitrogen mustard gas, and vinyl chloride monomer), the carcinogenic action of various industrial compounds was detected primarily by exact medical observations on man, and not in animal experiments. Confirmation by *animal* experiments has often lagged several decades behind the medical observation, e.g. over forty years in the case of 2-naphthylamine (man 1895; animals 1938). Other examples are tar (1775, 1918), asbestos (1930, 1941), chromates (1912, 1958), benzidine (1940, 1946).

Although it can be argued that preservatives are essential under modern conditions, the case for adding colours is not strong. While the reasons for using colouring agents are to restore colour that may have been lost in processing or to standardise the final look of a product which may be made from varying ingredients—the matter is really a question of what you are used to. A Dutchman faced with a can of green peas would be most suspicious —he is used to their natural cooked colour of bluish-grey. There can be no justification for exposing the most sensitive section of our community, the children, to relatively large concentrations of dyes in soft drinks, ice confectionary, and sweets, where no natural colouring is being restored. It was reported that, for 1976, Australians drank 70 litres of soft drink per head of population, about one-third of which were cola-type drinks (and that beer consumption was about 140 litres a head). The permitted concentration of dyestuff in drinks as consumed (NHMRC Food Standards) are 70 mg/kg (double in cordials and four times in solid foods). Because it may take decades for these substances to be cancer-producing, protecting our children should be a minimum objective. In addition drinks of the cola variety can contain caffeine (a stimulant) and phosphoric acid, the use of which has never really been examined and justified.

Flavour

Flavours constitute the largest class of food additives—1100 to 1400 natural or synthetic flavours are estimated to be available. This represents a tremendous task of checking for dangerous effects—which needless to say has hardly been attempted (many synthetic flavours are identical to the natural ones). Some countries publish lists of permitted and prohibited flavours; some have a short list of prohibited flavours, many of which are natural, and others allow flavourings that are found only in the aromatic oils of edible plants.

The following classification is likely to be adopted.

1. Natural flavour added (extracts and concentrates)
2. Nature identical (synthetic or chemically isolated) flavour added, e.g. vanillin and citral
3. Artificial (non-nature identical, synthetic) flavour added, i.e. compounds which simulate natural 'notes'.

Australia will probably start to develop a list of both specifically allowed and specifically forbidden flavours.

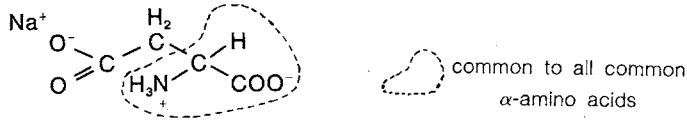
Many natural flavours are complex mixtures often of more than 20 different ingredients[16]—e.g. strawberry and raspberry. Apple contains at least 8 alcohols, 21 carbonyls, 17 acids, and 62 esters, and the list for tea includes 12 hydrocarbons, 27 alcohols, 31 carbonyls, 23 acids, 7 esters, 4 sulphur compounds, and 22 other miscellaneous substances including phenol and cresol.

Synthetic imitations are usually limited to a few components and these may not necessarily include any of the natural flavour components.

Brominated vegetable oil, BVO, has been used for more than thirty years for weighting of flavour oil blends to produce cloudy fruit flavoured beverages. It has a high density (1.33) and keeps the lighter flavour oils in suspension. Following some indication that the ingestion of BVO could lead to the accumulation of brominated metabolites in the human body the Food Standards Committee recommended its prohibition and replacement with sucrose acetate isobutyrate (SAIB). The subject may be reopened in the light of new evidence.

Monosodium glutamate

Related to flavours are the additives known as *flavour enhancers*. The commonest of them is monosodium glutamate, MSG, which is the monosodium salt of glutamic acid, one of the natural amino acids. It is illustrated in Figure 12.7.



12.7 Monosodium glutamate

In excess, this compound can give rather unpleasant symptoms known as *Kwok's disease* or more commonly *Chinese restaurant syndrome* because of the generous application of MSG in the dishes of these establishments.[17] It was also used in baby foods but this has been discontinued although not specifically banned.

Cooks throughout south-east Asia firmly believe that a pinch of monosodium glutamate can bring out the flavour of every single ingredient in any complex dish they are frying up. Cans, jars, or plastic bags of this seasoning powder are found in every kitchen in the subcontinent and in Chinese restaurants throughout the world.

The most efficient form of production is by means of a fermentation of glycose or sucrose produced by the acid hydrolysis of any cheaply available carbohydrate such as (in Thailand where I spent three months on a Leverhulme fellowship preparing a chemistry syllabus 'relevant' to the country) molasses and tapioca, in a suitable nutrient medium containing nitrogen, e.g. urea. The organism involved is *Micrococcus glutamicus*. The product comes as short needle-like crystals which look dull. They smell like sauerkraut and taste sweet and a bit salty. The reason for this detailed description is that adulteration by shopkeepers in the region is widespread. In spite of its relative cheapness

(~$1 per kilo in Thailand), similar looking crystals of borax or sodium metaphosphate (and sugar and salt), are often added, with disastrous results for the consumer in the case of borax. Borax is such a common illegal additive in the region (in meatballs, fish, etc.) that methods for its detection suitable for local use must be publicised. One method involves the preparation of turmeric paper from turmeric tubers which are readily available in the marketplace. Ground turmeric is extracted into ethanol (or methylated spirits), and filter paper (or newspaper edges) are soaked in the solution and dried. The suspected crystals can be scattered on the paper and then drops of 1M hydrochloric acid, HCl, added. Alternatively the paper can be added to the borax acidified with HCl. In either case a pink colouration develops. In ammonia vapour turmeric paper turns from yellow to pink and the pink borax stain turns blue.

Artificial sweeteners

In a society that is becoming increasingly weight conscious, many people want a sweetening agent that will not add energy to their diet. Saccharin was discovered in 1879, by accident—a chemist did not wash his hands before eating. Its safety in food has been questioned on the grounds of possible carcinogenic properties and reaffirmed periodically. At the moment we are in a questioning state again.

In 1969 the United States FDA banned the sweetening agent *cyclamate* after about twenty years of use, when it was found that it could cause bladder tumours in rats after they had been fed large doses. (In Australia the NHMRC recommended that cyclamates should be continued at a low level (0.06 percent in beverages and no more than 2 percent in diabetic food) and that such food be labelled to the effect that they contain a non-nutritive *sweetening* substance. The States and the Territories did not incorporate the recommendation into law, but manufacturers have voluntarily complied.) Of chemical interest is the point that in most cases the rats which had tumors induced by cyclamate had in fact converted it to cyclohexylamine, which is a known carcinogen. Saccharin, the only non-nutritive sugar substitute permitted in the United States since the cyclamate ban, was itself ordered off the market on 10 March 1977 (it was later allowed to be sold by pharmacists) and cyclamate—the most successful sweetener, which at its demise was the basis of $1000 million a year industry, and had achieved annual sales of 7000 tonnes, and which in the manner of its going nearly wrecked the FDA and cost the Food, Drug, and Cosmetics Commissioner his job—*could be on its way back!* Such is the state of the art in testing the substances for cancer-producing properties!

A Dr Michael Sveda discovered cyclamates in 1937 during a Ph.D. project. He found that the compound possesses three important characteristics: a much

more sugar-like sweetness than saccharin; it stays sweet even in concentrated solutions, whereas saccharin is bitter; and it remains stable towards hydrolysis (decomposition in water) even in the presence of acids. A detailed history of its banning has been given in the *National Times*.[18] Dr Spike Langsford, first assistant Director General of Health stated therein that

> there were three main objections to the original cyclamate research with rats—the rats were of a kind which could have developed cancer anyway, the dosages fed to them were far higher than any human being would be likely to consume, and they were fed a *mixture* of drugs, not just cyclamates.

Further research with just cyclamates by Dr Schmahl in Germany in 1973 and at least twenty other studies have failed to turn up any evidence for implicating cyclamates. For diabetics and overweight people the possible risks are negligible in comparison with the benefits. However, it might be prudent to keep children clear of the additive, unless you feel that sugar is worse![19]

SACCHARIN

Canadian scientists fed saccharin as 5 percent of the diet (equivalent to 2.5g per kg body weight) to two generations of laboratory rats. Among the first generation 3 of 100 developed bladder tumours. Among the second generation rats exposed to saccharin *in utero* as well as during their lifetimes, 14 of 100 developed bladder tumours.*

'Absolutely' pure saccharin is not mutagenic in the Ames test (see Appendix 12.3) while the Canadian saccharin is. Saccharin is often contaminated with an intermediate in its preparation—*ortho*-toluenesulphonamide, OTS, which however, the Canadians found not to be carcinogenic—so a different impurity may be involved. There are three common methods of preparing saccharin, each with different purity problems.

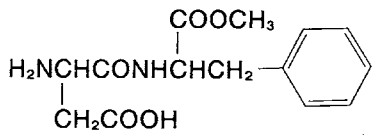
Saccharin is not metabolised by rats or humans and is excreted unchanged (most known carcinogens *are* metabolised). Rats concentrate their urine highly and so keep the chemicals in it in their bladders for long periods. Tests on hamsters and rhesus monkeys have so far shown up no ill effects from saccharin.

Saccharin has been shown to lower blood sugar levels which in turn is associated with increased appetite, and the few proper studies that have been done on dieters and diabetics do not appear to show up any benefit from the use of saccharin.

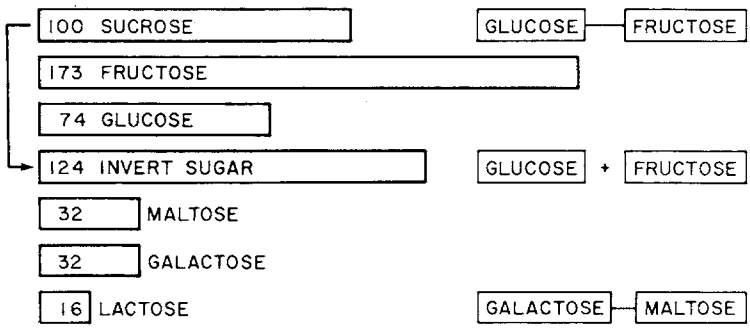
*'Saccharin: A Chemical in Search of an Identity', *Science*, 10 June 1977, 1179.

Meanwhile lots of things have been happening on the sweetener front.[20] Searle laboratories, whilst working on a peptide hormone, discovered a dipeptide (aspartylphenylalanine methyl ester) which was 100–200 times as sweet as sugar. It was named *aspartame* (Figure 12.9). (The United States FDA has approved aspartame for use on the table and in many ready-mix products, but not for soft drinks or foods that have to be cooked because when denatured a protein loses some of its properties—in this case sweetness! It is on the agenda of the Australian Food Standards Committee and a discussion is expected before the turn of the century.)

N-L-α-Aspartyl-L-phenylalanine 1-Methyl Ester



12.8 Aspartame



12.9 Relative sweetness of sugars. Sucrose is a chemical combination of glucose and fructose and lactose is a chemical combination of galactose and maltose. When sucrose is 'inverted' it breaks up into glucose plus fructose which is thus sweeter than the sucrose it came from.

Perhaps the most intriguing of the taste-active proteins is one that is tasteless itself, but has the capacity when eaten to make sour substances, eaten up to several hours later, taste sweet. The berry containing this protein grows in the coastal regions of West Africa and was first brought to European attention in the 1850s by an English surgeon. It was rediscovered by the United States Department of Agriculture in the 1920s, and in 1968 the active glycoprotein was isolated—called *miraculin*. There are two other taste active proteins—one, *monellin*, is (on a weight for weight basis) some 3000 times sweeter than sugar.

There is a line of thought which suggests that the additive industry needs ways of making its additives safer rather than new additives. The idea is to 'leash' active molecules (like sweeteners) to polymer 'controllers' that would carry the additive undigested through the digestive tract. The point is that the additive—whether it is to impart flavour, colour, or stability to a food —does its work in the food itself (or, in the case of taste, in the mouth) and need never be absorbed and metabolised along with the food: indeed, it is when it is absorbed that the trouble begins. There has been some recent success with this process of attaching a small sweetener molecule to a fragment of polymer without changing its sweetening properties.

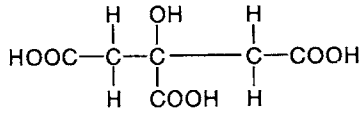
TABLE 12.2 *Relative sweetness of some artificial sweeteners*

	Relative sweetness (weight for weight)
Sucrose (cane sugar)	1.0
Glycerol (glycerine)	0.6
Ethylene glycol (antifreeze)*	1.3
Sodium cyclamate	30
Aspartame*	200
Dulcin (sucrol)*	250
Saccharin	500
Ultrasüss*	4100
Monellin*, Thaumatin*, Miraculin*	~3000

* Not permitted in Australia

Sequesterants

Metals such as copper, iron, and nickel get into food from processing machinery or chemical reactions. A sequesterant such as citric acid (chief acid in citrus fruit: 6–7 percent in lemon juice) thus acts as a synergist (a helping agent) for antioxidants. Sequesterants are used in shortenings, mayonnaise, lard, soup, salad dressings, margarine, cheese, etc.



12.10 Citric acid

Stabilisers and thickeners

These substances are added to improve the texture and blends of foods. An example is *carrageenin* (a polymer from edible sea weed) which belongs to a group of chemicals called polysaccharides (which are carbohydrates of high molecular weight and include sugars, cellulose, starch, etc.). They are particularly effective in icings, frozen desserts, salad dressing, whipped cream, confectionery, and cheeses.

Surface-active agents

The food 'soaps' are used to stabilise emulsions of oil and water components in foods.

Polyhydric alcohols

These additives are used as humectants—to prevent foods from drying out; tobacco is also kept moist by them. An added feature of these compounds is their sweetness. Two particularly effective alcohols added to sweeten sugarless chewing gum are *mannitol* and *sorbitol* (in special dietary foods with modified carbohydrate). These polyhydric alcohols have the same energy (Calorific) value as cane sugar—16.5 kJ/g.

Water retention agents

Polyphosphates are increasingly used in the processing of poultry and mammalian meats to bind water and to minimise 'drip', and as an aid to further processing. They are used to a large extent in processed fish. Phosphates are also used in soft drinks and in the production of modified starches. Because of these many uses, phosphate, although an essential mineral, is likely to be consumed in larger amounts than would be the case if the diet consisted of unprocessed foods. There are indications that an excessive daily intake can lead to the premature cessation of bone growth in children with a consequent significant reduction in adult height.[20]

The NHMRC Food Additive standards allow the following usages:

Sodium phosphate (soluble) including ortho-, pyro-, and metaphosphates and low molecular weight polyphosphates (analysis as P_2O_5)
Canned and processed meat products—0.3 percent; cheese and cheese products—3.0 percent; fish and fish products—0.5 percent; frozen fish and poultry—0.3 percent

As a member of Group II modifying agents (mineral salts), sodium phosphate is allowed in all foods in which these agents are allowed. There is a specified list, the last member of which is 'Foods not elsewhere standardised'. Permitted

concentrations are not set for most of the specified list and in particular not for its open-ended final member.

It is an interesting exercise to calculate the potential daily intake of phosphate on a typical Australian diet for children. It is also fairly straightforward to analyse for phosphates in food although some special reagents are required.

Packaging and other accidental additives

Finally there is the matter of accidental additives which enter food without any wish for their presence, for example residues of pesticides. An NHMRC standard sets a tolerance for various pesticides and substances derived from pesticides, being the maximum concentration that is permitted for about 160 compounds. The amount specified is different for different chemicals and for the same chemical may be different in different foods. For example dichlorvos (the active constituent in Shelltox insect strips) is allowed up to 0.1 mg/kg in fruit (except citrus), 0.3 mg/kg in vegetables and cereal products, 0.5 mg/kg in milled cereal products, and 2 mg/kg in raw cereals. The reason for this ought to be related to the average daily intake of these foods but could possibly be related to the *rate of use* of the pesticide or the difficulty of its removal (incidentally there is no level set for citrus fruit). Analyses of foodstuffs (particularly meat) have regularly shown levels in excess of the standard, so its enforcement will be politically embarrassing.

Another source of accidental additives comes from the material used for packaging and this has been an area of increasing concern. At the present time there are no general regulations which refer specifically to the control of the composition of packaging materials nor are there regulations which allow for the migration of substances from packaging materials to foods.[21] Indeed, current food regulations can be taken to specifically prohibit such migration. For example, the regulations of the New South Wales Pure Foods Act state that 'No substance may be added to food unless specifically permitted by these regulations'. The Act itself requires that 'the consumer is entitled to receive goods of the substance and quality demanded' and, so far as I am aware, consumers do not ask for chemical migrants in their food purchases. The two exceptions to these generalisations are regulations which set down the permissible levels of metals and of pesticides that may be present in foods, and some or all of the metals might be derived legally from packaging materials.

Despite the lack of regulatory permission to do so, a variety of materials are known to migrate from packages to foods. Paper and cardboard packages can be the source of inorganic and organic migrants from inks, pigments, dyes, and preservatives if the paper and cardboard have been produced using waste

paper recovery processes. Perhaps the most famous of the migrants from such sources were the celebrated PCBs (polychlorinated biphenyls), which have toxicities similar to chlorinated pesticides (DDT, hexachlor, etc.). The use of virgin wood pulps presumably would preclude any migration risks in paper and cardboard intended for food-contact use, but the economics of such processes may not always be acceptable to the industry.

Glass containers, despite statements to the contrary, can frequently contribute to food quantities of contaminants substantially in excess of those derived from plastic containers, but it must be admitted that, as yet, there has been no evidence of toxicity from this source. Nevertheless, re-saleable glass containers that are subject to sterilising chemicals and detergent processes could be a significant source of these materials in foods unless strict controls are observed. Metal containers, apart from metallic contamination derived from corrosion, may also contribute cadmium from lacquers and can linings, as well as the surface lubricants that are used in the rolling of metallic foil and sheet stock. The United States FDA has recently set limits not only on the amount of such materials on metal sheets intended for food containers but also on the nature of the lubricants as well. The use of electroplating to give a layer of tin on a steel can has produced a cheaper but less satisfactory product than the older dip process, as there are greater problems of ensuring a continuous cover.

It is generally conceded that the major area of regulatory interest centres upon plastics material intended for food contact use. This is because plastics are highly complex mixtures and the problems that they pose appear to be of much greater significance than for any other packaging material. The number of different packaging materials is very large, their individual characteristics differ widely, and a very large variety of substances may be used in their manufacture. New ingredients, new formulations and new packaging uses are introduced frequently. It has been estimated that from 5000 to 15,000 different chemical compounds may be available to the plastics manufacturer who supplies materials for both food and non-food packaging applications. Migrants may take the form of unpolymerised monomers, catalysts, surface active agents, and release agents; additives—such as antioxidants and plasticisers; lubricants—such as fatty acids and fatty alcohols; and antioxidants which do not necessarily figure in the permitted lists of additives for food. One recent survey showed that margarine generally contains about 0.2mg/kg of cadmium, while a margarine packed in a container with about 1.4 percent cadmium content gave a value of about 0.7 mg/kg cadmium. Despite the impressive list of migrants from packages that one could produce it has been argued that the hazard to health they constitute is small: where migration and adulteration do occur and the migrant is toxic, then the extent of migration is generally small in relation to the total diet and (it is hoped)

is below the acceptable daily intake. However the recent discovery that vinyl chloride monomer (for which there is no recommended acceptable daily intake) on inhalation is a potent liver carcinogen has raised doubts about such a complacent attitude. (For further details see Chapters 6 and 13.)

Contaminants of microbiological origin are even more critical. *Aflatoxin* is a naturally occurring toxic product of a common mould. There is usually no visual evidence of its presence. It has been found in greatest amounts in peanuts and other nuts, in corn and products manufactured from these commodities. It has been shown to cause liver cancer in some test animals and has been a suspected, but unproven, cause of liver cancer in certain African and Asian countries where high amounts of these toxins have been detected in foods normally consumed. Aflatoxin is one of a number of toxins (poisons) produced by various moulds. Not all moulds produce toxins, and some are useful in food processing, such as the moulds used to produce Roquefort cheese. Other moulds are used to produce antibiotics. Precautions to help control aflatoxins involve the prevention of mould formation by proper drying and storage of crops, removing damaged material before storage or processing, and providing adequate moisture and humidity control of stored foodstuffs.

Labelling

Everybody is an expert on food labelling (ingredient, nutrition, etc.) and there are as many systems as there are experts. Anyone who has bought Australian food products overseas will know that a lot of the technical problems held up against labelling food adequately in Australia have been overcome on export labels.

On the question of additives, however, the EEC has developed a simple rational system. Each additive is given a code number: E 100 to E 199 are colours; E 200 to E 299 are preservatives; E 300 to E 399 are antioxidants; E 400 to E 499 texture modification agents. Flavours have not been dealt with. The colours are further subdivided—E 100 to E 109 yellow; E 110 to E 119 orange; E 120 to E 129 red; E 130 to E 139 blue; E 140 to E 149 green; E 150 to E 159 brown and black; E 160 to E 170 unclassified; E 170 to E 189 unique surface colourants. Some specific examples are: ammoniacal caramel E 150; tartrazine E 102; benzoic acid (sodium benzoate, potassium benzoate, calcium benzoate) E 210 (to E 214); propylene glycol alginate E 405.

It is now possible to search for specific allergies due to food additives and to select a diet which avoids them. Technological improvement which results in the use of fewer additives can then be followed by the consumer who studies the labels.

In the summer of 1976 the French Federal Consumer Organisation declared

a boycott on food additives they regarded as unsafe and unnecessary, particularly food colours. I was in Paris at the time and spoke to François Lamy who was responsible for the assault. Contrary to popular belief the French take food much more seriously than sex and the boycott was an outstanding success. Unfortunately, the accuracy of the evidence on which the boycott was based was very poor in places. However, the consumers had been subject to so much delay and procrastination by the food industry that the industries' scientific protestations made no impact at all. Bastille day for colours had come!

Australia seems to have gone in the opposite direction. Whereas effervescent drinks etc. were once labelled with the preservative used this is apparently no longer required. To give readers some idea of how food standards are prepared in Australia it should be mentioned that the original draft is generally prepared by the industry concerned with the introduction of the food or additive. This is not so much a Machiavellian plot as the lack of any alternative source of expertise or concern. Many of the changes in food standards are designed to increase the benefit to the manufacturer with some spin-off (perhaps) to the consumer.

And now for a few stories. The most powerful 'food' industry in Australia must be the brewing industry. Their product is both revered and suspected. This attitude is best illustrated in the two articles reproduced here—one from the United Kingdom and one local. We are all experts on beer and bread and we resent the technological interference with our 'natural' products to an irrational extent. Or is it irrational?

More than barley and hops

Richard Boston examines the ingredients of British beer, *The Guardian* 1 February 1975. Reprinted with permission.

In 1516 Count William IV of Bavaria issued a Reinheitsgebot, or Purity Law, which allowed the use in brewing of only barley, hops, and water. This law remains in force to this day, not only in Bavaria but throughout Germany.

There are some who would have you believe that the situation here is not totally dissimilar, and will quote to you the old rhyme:

He that buys land buys many stones,
He that buys flesh buys many bones,
He that buys eggs buys many shells,
But he that buys good beer buys nothing else.

This doggerel, it must be obvious to anyone experienced in these things, was written by a brewer. Apart from the feebleness of the verse, it is completely misleading, this being an unmistakable hallmark of brewers' utterances. Unless we are to be told what the ingredients of good beer are considered to be, the last line is simply tautologous.

The brewers of today are more prosaic, but their statements have the same qualities. A few months ago the Brewers' Society announced that 'British beer today is brewed from the same basic ingredients as it has been for the past 500 years or more—barley

and hops.' It depends, as the late Professor Joad might have said, on what you mean by British beer, and what you mean by basic.

Apart from the presumably accidental omission from the ingredients of yeast and water, anyone who believed that particular statement was doubtless surprised to learn from recent newspaper reports that a shortage of sea weed was threatening the foaming head of his pint.

What, then, are the ingredients of British beer? Since the wicked W.E. Gladstone's Inland Revenue Act of 1880 brewers have been allowed to use not only sugar but virtually whatever they like provided it is not actually injurious to health. That was no small provision, considering some of the things that used to go into the beer. That neglected Tudor poet John Skelton, the Rector of Diss, who kept falcons in the church, among other things, penned the greatest ever denunciation of a brewer. This was the ill-favoured Eleanour Rummyng.

Droupy and drowsy,
Scurvy and lowsy,
Her face all bowsy,
Comely crynklyd,
Woundersly wrinklyd,
Like a roast pygges eare
Brystled with hare.

Apart from being physically repulsive, one of Eleanour's less endearing habits was that of allowing the hens to roost above her mash-vat so that the droppings fell into the beer.

And somtymes she blennes
The dung of her hens
And the ale together.

As far as I know no modern brewer follows this malpractice. However, in the eighteenth and early nineteenth centuries still worse things were used, such as a poisonous drug called *Cocculus indicus* and what H. Jackson described in 1758 as 'green vitriol called copperas or salt of iron.' When mixed with alum this was guaranteed to give a 'head like a collyflower' (to the beer, I assume, but possibly to the consumer).

Cobbett frequently denounced 'beer-doctors' and 'beer-druggists' and in *Cottage Economy* (1821) he quotes from a book on brewing a recipe for porter, of which the ingredients include 'one quarter of high-coloured malt, eight pounds of hops, nine pounds of treacle, eight pounds of colour, eight pounds of sliced liquoriceroot, two drams of salt of tartar, two ounces of Spanish-liquorice, and half an ounce of capsicum.'

Complaints of adulteration were by no means rare in that period as is shown by a ballad of about 1825.

The brewer's a chemist, and that is quite clear,
We soon find no hops have hopped into his beer,
'Stead of malt he from drugs brews his porter and swipes.
No wonder so oft we all get the gripes.

We find Dickens in 1856 also writing about the 'brewhous-chemist' and similar complaints continue well into this century. For example, Beachcomber in his 1930s' *Dictionary for Today* was defining beer as 'a drink made of various chemicals in various proportions.'

Of course that's all in the distant past. What of today? The answer is that the consumer has no way of knowing. If you buy a tin of soup the ingredients are listed on the label. If you buy a bottle of beer there's no way of knowing what's in it. This is not simply a matter of curiosity. Quite recently cobalt sulphate was used in brewing in the United States; it gave the beer a lovely head, but it gave the consumers lousy

hearts, and after more than 40 people had died its use was discontinued.

Many of the independent brewers could echo the words of Mr John Young, chairman of Young's of Wandsworth, in his company report this year: 'Our definition of beer is that it is brewed from malted barley and hops, and we have no use for wheat flour, rice, or potato starch.'

These last ingredients, along with such things as maize grits, and flaked rice, are called adjuncts. They are harmful to flavour rather than health and though some are used for specific properties, are mostly cheaper than malt. I have even heard of one large brewer who produces a so-called beer which contains no malt at all.

Many people feel that beer-drinkers should be allowed to know what they are consuming, and the Food Standards Committee invited interested parties to submit evidence on the way beer should be made, defined, and labelled. The Consumers' Association, which for at least 15 years has kept a vigilant eye on beer, proposed among other things that adjuncts should be limited to 30 percent—or, to put it the other way round, that the 'malt fraction' should be at least 70 percent.

They point out that the malt fraction has declined from 81.1 percent in 1953 to 76.6 percent in 1973. The Campaign for Real Ale has also submitted a report suggesting that the malt fraction should be at least 70 percent. I don't know what the Brewers' Society said in their evidence, because when I asked them they wouldn't tell me.

Whatever the Food Standards Committee finally recommends [this report has now appeared and has accepted to a large extent the submissions by the Consumers' Association[22]], there are the EEC regulations to consider. A good row could well develop here. While the Germans will resist any regulation that allows the use of any adjuncts and chemicals, the British brewers (at least the big British brewers) will doubtless resist anything that inhibits their ancient and venerable right to use them. In this particular argument it will be hard for even someone as fond of the big British brewers as I am to cast them in the role of the good guys.

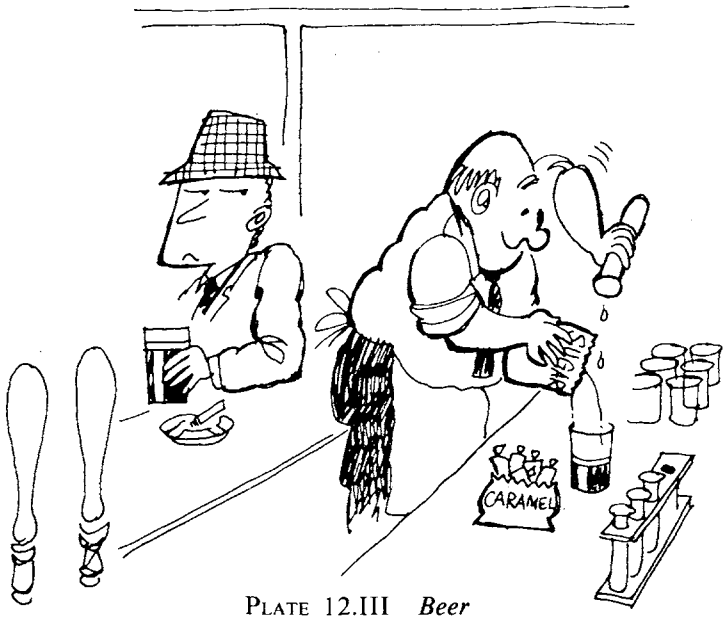


PLATE 12.III *Beer*

Legal aspects of alcoholic products

Beer was included in the rations of workers building the pyramids of Egypt and since ancient times alcoholic products have been a lucrative source of revenue for the tax gatherer. Taxes are based on alcohol content. *Proof* spirit was defined as 'that percent of pure alcohol, which when mixed with water and poured onto gunpowder of specified composition just permits the gunpowder to ignite.' In the United Kingdom this is 57.155 percent by volume at 20°C. The Americans earlier had adopted 50 percent by volume. Since 1972 *proof* has not been used in Australia and the measure is percentage by volume and taxes vary for different products.[23]

Brandy is distilled from grape wine and matured in wood for not less than two years. Apple brandy is distilled from grape cider. Whisky is distilled wholly from barley malt, while Australian blended whisky is distilled partly from barley malt and partly from other grains. Rum is distilled wholly from sugar, sugar syrup, molasses, or the refuse of sugar cane. Gin is distilled from barley malt, grain, grape wine, apples, or other approved fruit. All spirits must not contain more than 83 percent by volume of alcohol.

Various products are protected by law. *Cognac* under French law may only be manufactured from grapes grown in the Cognac region of France. *Scotch* is regarded as being a product of Scotland but has become a generic name for whisky whether the Scots like it or not. Hogarth's London was full of gin mills but by 1960 there was not one gin distillery left in the city of London proper as known to Hogarth, and London gin imported into Australia is now manufactured in Singapore. Spain has lost the legal battle to protect the name *Sherry*—now sherry.

In Australia today there are very few real liqueurs in spite of legal definitions in some states. Most are compounded and in fact purely synthetic. The excise definition requires alcohol of not less than 22.484 percent by volume (except Advocaat—17.136 percent v/v). Rye and corn whisky are defined but the definition is is analytically unenforceable! French brandies with names such as *Napoleon*, *VSOP*, etc., terms which have no legal standing in Australia, are usually regarded as being products of high quality. Ratios of amyl, propyl, and butyl alcohols give indications of the origin of the spirit and can determine that some French brandies are not legal brandies in Australia.

Australian wines exported to the EEC must be tested for density, alcohol content, total dry weight, total acidity, volatile acidity, total SO_2, and citric acid. There are no similar requirements for wine imported into Australia.

The *excise* definition of beer had to be changed several years ago to meet the changing technology in the brewing industry. The definition is:

any fermented liquor that—

1. is brewed from a mash, whether or not the mash contains malt, and
2. contains hops (including any substance prepared from hops) or other bitters, whether

or not the liquor contains sugars or glucose or other substance, but does not include liquor that does not contain more than 1.15 percent alcohol v/v.

This rather extended definition now permits the use of potato mash, sugars, enzymes, and lupinones which were not previously permitted.

Home brewing and home wine-making are now legal in Australia provided you do not produce more than 1,700 litres (400 gallons) per member of the family in any year and you do not sell the product. It seems an adequate allowance! See Appendix 12.4 for alcohol intakes in various countries.

NUTRITION

It would be difficult to find a topic within the ambit of consumer chemistry that is more confusing than nutrition. It is a topic which has a large coverage in the popular magazines, much of which is contradictory. The nutritional problems of the affluent society are also quite distinct from those of poorer societies. In our society fierce argument rages on just about every nutritional innovation, whether it be polyunsaturated oils or megadoses of vitamin C, the Feingold diet, allergies and hypersensitivity, fresh and processed foods . . . Then there are the capital Calories (equivalent to kilocalories) which are now metricated to kilojoules (big Joules anyone?). These are the numbers with which you do the arithmetic, remembering that some foods are not metabolised efficiently and so give the wrong answer. In the nineteenth century nutritionists recognised protein, fat, and carbohydrate but most of the emphasis was put on the accessory factors—the vital amines or *vitamins* (which are mostly not amines). The vitamin was a chemical which could be isolated and there was a one to one correlation between the insufficiency of this substance and a corresponding deficiency disease: thiamine—beri-beri; nicotinic acid (niacin in tobacco-conscious America)—pellagra; ascorbic acid—scurvy; and so on. The clinical classification of a single cause-and-effect relationship is useful but incomplete. A perfectly natural food amino acid, monosodium glutamate, when taken in excess causes severe reactions in some consumers of Asian meals.[17] Linus Pauling, twice Nobel laureate, argues persuasively that we, along with guinea pigs, fruit eating bats, the red-vented bul-bul and the anthropoid ape, have a species-wide genetic metabolic deficiency in not being able to synthesise ascorbic acid for ourselves. He therefore suggests that larger quantities than those just necessary to prevent scurvy are called for to maintain optimum health.

A large-scale nutritional survey in Canada involving 27,000 people showed widespread thiamine and iron deficiency in spite of the use of bread fortified with these additives. In France, refined flour contains no additives, neither to prolong the shelf life of baked products nor to restore vitamins and minerals discarded during milling. There are no reported deficiencies. Fortification does not compensate for poor diet. In fact it could be argued that the causative

foods, sugar, beer, soft drinks, etc., should be the ones fortified. Nutritionists are horrified at this thought, but. . . . Traditional foods also can change. An American variety of apple—Golden Delicious—is deficient in vitamin C, sugar, and fruit acid compared to French indigenous varieties. Yet the Golden Delicious now accounts for over 60 percent of apple production in France because of its apparent commercial advantage. The narrowing genetic base of foods is also shown by the fact that a single variety of hybrid corn covers most of the cornbelt of the United States.

When Margaret Mead discusses selection of food, she mentions a number of parameters, but not nutrition. Her argument is that culture determines diet and that our three meals a day and what they contain are set by upbringing and availability. This availability is to be interpreted in the widest sense: it includes price and packaging and positioning in the supermarket. The political punch of the producers, overseas prices, government subsidies, and import duties can be critical. In a free enterprise market, butter would have disappeared years ago. The fast food outlets are new determinants in our eating. How difficult it is to persuade people that school tuck-shops are part of the education process and not solely a financing institution! The upbringing includes influences such as religion and tradition. As Paul Hindson (Division of Health Education, Queensland) has said in making these points—who has liver for a barbecue or roast beef and baked potatoes for breakfast? Hilaire Belloc sums up this aspect in his classic poem on food.

From *On Food*

Alas! What various tastes in food
Divide the human brotherhood!
Birds in their little nests agree
With Chinamen, but not with me.
Colonials like their oysters hot,
Their omelettes heavy—I do not.
The French are fond of slugs and frogs,
The Siamese eat puppy-dogs.
The nobles at the brilliant Court
of Muscovy consumed a sort
Of candles held and eaten thus,
As though they were asparagus.
. . . . . .
And all the world is torn and rent
By varying views on nutriment.
And yet upon the other hand,
De gustibus non disputand–
–Um

Hilaire Belloc

In the introduction to his talk *The Myth of Pure Natural Foods* which was given at a public seminar on Nutrition, Health and the Consumer organised by the Queensland Consumer Affairs Council *et al.* in July 1977, Bill McCray, the director of the Biochemistry Animal Research Institute of the Queensland Department of Primary Industry, said:

To the nutritionist, and I quote, food is 'nutritive material taken into an organism for growth, work, repair, or the maintenance of vital processes.'—An objective view?—Agree?—It is not. It is the highly subjective view of the nutritionist. The truth is that food, for all holozoic creatures, like ourselves, consists of almost any readily available independently living fellow-creature and in our case often the carefully preserved remains of such fellow creatures. Further these unfortunate victims of the gratification of their fellow creatures are complex mixtures of chemicals, each victim containing a host of chemicals that are inimical to the 'growth, work, repair' etc. quoted in the so called objective definition.

George Bernard Shaw, the Irish wit and playwright of my youth said it for us. He said he refused to make his stomach a graveyard for dead animals. He was a confirmed vegetarian. Hence his stated wish was that his funeral cortege include little lambs, calves, and chickens to represent those dead animals for whom he had not made his stomach a graveyard. Though he did not admit it, he was forced to make his stomach a compost heap for dead plants.

It is easy to accept the predator-prey concept for the tiger or the eagle but even the gentle lamb devours the living grass. For ourselves, we can readily accept this thesis for meat and fish, but, consider the staff of life—bread. Here we take the grain into which a plant, our fellow creature, has poured all its reproductive energy; its hopes and aspirations for the future generation lie in the germ, the energy for whose early struggle is in the starch, and we crush both to flour snuffing out the life in the grain. Then into this bleached and whitened corpse we place our fellow creature, yeast, and when it has grown, reproduced, and prospered on the energy of the grain, we put it living into an oven at 400°F to die to make our daily bread.

In the multimillennium that man existed as a food gatherer, he existed as a fringe species under constant threat of the extinction that overtook many homonoid species, not the least threat was that posed by his food. Then as now eating provided the greatest exposure to exotic chemicals that most of us ever receive. Man evolved in an environment that provided many poisons produced by micro-organisms, plants, and other animals and is clearly not without biochemical defence mechanisms to protect himself. In his role as a sort of metabolic crematorium for his fellow creatures he manages to burn up on most occasions the harmful and the helpful with equal facility. Usually it is only when his defence mechanisms are overwhelmed by the sheer numbers of toxic molecules—the total amount of the toxin rather than its toxicity—is man adversely affected: the dose makes the poison.

That man's fellow creatures are often far from wholesome is a matter for history or prehistory; primitive men developed not only an extraordinary lore about the use and hazard of foods particularly plants, but also an extraordinary technology to render useful the more recalcitrant of their plant brothers. No

need to go to pre-history to study food gatherers—just go to the museum to learn how our own local aborigines worked the highly toxic seeds of the Moreton Bay Chestnut to make food of it in the absence of more prolific or less seasonal other foods.

While we have concentrated in this chapter on food additives, a proper balance requires a closer look at 'natural' foods. Some of the problems were discussed in the introduction and also when explaining ADI (acceptable daily intake), but the list can be extended greatly. Bananas contain *serotin* (one of the biologically active amines); chick peas while highly nutritious are also toxic—so that fad diets are to be avoided. One nutmeg is nice, two may abort you, while three at one sitting could be fatal. Avocados will poison animals, while onions cause anaemias in them. Half a kilo of horseradish (containing isocyanates) has slain a pig in three hours. Broad beans cause a disease (favism) in people with a particular genetic inclination. Aflatoxin is the most potent known carcinogen (in animals) and is formed by a fungus which attacks peanuts and other nuts when the humidity and temperature are right for it. It is believed that it causes liver cancer, which is prevalent in humans in parts of Africa and Asia. Along with other pesticides, the fungicides used to control fungi are becoming increasingly less effective, so that problems will arise in protecting our 'natural' food. Dairy herds in Tasmania were being fed on kale (1955) which transferred oxazolidene to the milk. This increased benign goitre amongst children in spite of the use of iodised salt. Today the problem is one of excess iodine in milk from iodoform disinfectants used in the dairies . . . I have quietly slipped back to an 'unnatural' additive. The difference in definition is marginal and the only sensible approach appears to be to spread any risk by spreading the diet to cover a large selection of foods.

Bread

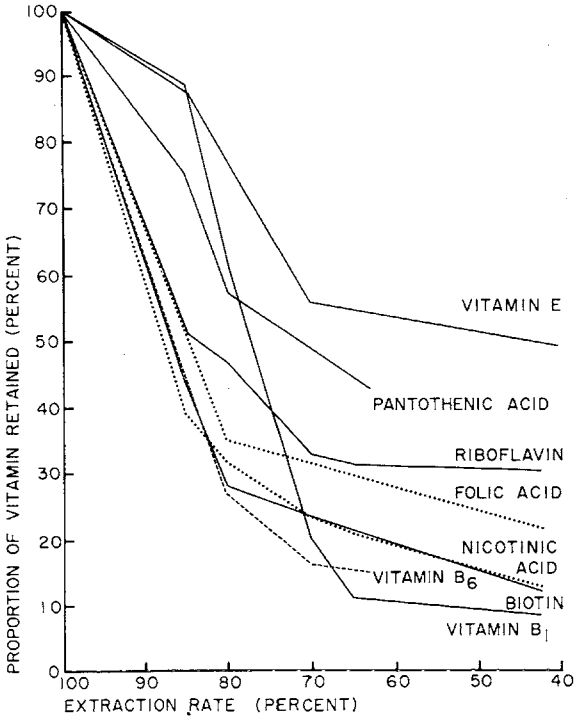
Magnus Pyke, in his book *Food and Society*, acknowledges that even those with 'knowledge and facts' fall short of objectivity on this topic: 'Few people are able to discuss the composition of bread temperately.'[24]

On the whole the (British) public seems to prefer white bread. At one time the demand was met by treating flour with *nitrogen trichloride*[25] but this agene process was abandoned some years ago after dogs fed large amounts of agenised bread developed running fits or canine hysteria. The toxic compound in the treated flour was later shown to be methionine sulphoximine which is formed by the action of nitrogen trichloride on methionine, an essential amino acid of proteins. Today over half the total flour production in the United Kingdom is treated with chlorine dioxide as a maturing and bleaching agent. Additional whiteness is achieved, if necessary, by bleaching with *benzoyl peroxide*, giving

benzoic acid as a final product. Various other improving agents are added, vitamins, buffers to control the acidity, surfactants to keep suspensions in the baking process, sequestrants to inactivate tiny amounts of possibly harmful metals, as well as preservatives such as propionic acid and sulphites to prevent spoilage.

Here are some details from the NHMRC (1977) standard for flours, meals, and bread. Bleaching of flour can only be carried out by ozone and/or oxides of nitrogen, chlorine, chlorine dioxide or benzoyl peroxide. The flour can contain:

	mg/kg
calcium acid phosphate, $Ca(H_2PO_4)_2$	700
ammonium chloride	600
bromates, $KBrO_3$	30
iodates, KIO_3	5
sodium and calcium stearoyl-lactylates	4
calcium sulphate $CaSO_4$	800
sodium metabisulphite	60



Source: Magnus Pyke, *Man and Food.* (World University Library 1970.)

12.11 Milling extraction rate and proportion of total vitamins retained in the grain in flour

Wholemeal flour (wholewheat, wheatmeal) contains all the constituents of the wheat. Wholemeal bread is made from 90 per cent (at least) wholemeal flour. It cannot be stored for long periods because the oil from the wheatgerm may become rancid. This makes it unpopular with millers and bakers. The bread must contain no more than 48 percent water. Brown bread must be made from at least 50 percent wholemeal flour and brown colouring (in the form of malt) can be added. Brown bread is *not* wholemeal bread. Rye bread must be made from at least 30 percent rye flour. Milk bread has at least 4 percent skim milk powder (non-fat milk solids) added, which makes the loaf bulkier and helps retard the staling process; protein-increased bread must have at least 15 percent protein (2.7 percent nitrogen $\times$ 5.5). (In both these cases it is percentage calculated on a *moisture free* basis.) Extra protein can be achieved by adding skim milk powder, soy flour, or gluten to the dough. Special grain breads such as soy contain a high proportion of wheat or rye flour because only these rise satisfactorily. There is no guaranteed minimum quantity of the flour named on the loaf. Preservatives in bread (generally propionates and sodium acetate/acetic acid) are not declared on the label. For a good discussion on bread see William Breckon's book *You are what you eat.*[5]

The current status of bread in the Australian diet was the subject of a very detailed research project carried out by Nobile and Woodhill, which they discuss in an article in *Food Technology in Australia.*[26] The results are complex and do not lend themselves to accurate condensation so readers are referred to the article. Wholemeal bread is nutritionally sound but a sample survey showed only 13 percent of people prefer it. The question that was asked in the research was whether the bread, biscuits, and snack foods consumed in Australia today contain vitamins in amounts sufficient not only to metabolise the carbohydrate, protein, and fat they contain, but also to compensate for the lack of these vitamins in the sugar, starch, and alcohol of the diet. It is possible today to monitor the sufficiency of some vitamins in the blood by testing whether their function in the body is being properly carried out. Nobile and Woodhill found significant deficiencies in the B group vitamins and to a lesser extent vitamin E. They appear to favour the American approach that our bread should be fortified rather than the French approach that we should eat properly.

Orange juice

Orange juice was discussed in the December 1975 issue of *Canberra Consumer* as a source of vitamin C (ascorbic acid), and in the March 1976 issue as a source of water. Some brands showed C minus (less than the required level of vitamin C). Consumers pay out \$15–20 million a year for water added to orange juice concentrate (H_2O plus). What is the present situation? The

NHMRC standard for fruit juices, etc. was gazetted in all states. Fruit juices shall not contain added water (except concentrates diluted to original). They may contain preservatives and added vitamins and minerals. Unless labelled sweetened they must contain no more than 4 percent of added sugar. A concentrated fruit juice has had at least 50 percent of the water removed. The minimum levels of vitamin C are:

	mg/litre
Orange juice	400
lemon juice	350
grapefruit juice	300
orange and grapefruit juice	350
blackcurrant juice	700
pineapple juice	100

Note that apple juice is not considered a source of vitamin C. Concentrated juices must have the required vitamin level on dilution and must have dilution instructions on the label. The preservatives used are sulphur dioxide (max. 115mg/litre) or benzoic acid (max. 400mg/litre) while sorbic acid can replace some of the benzoic acid. No other additives are allowed in fruit juices; neither colour nor flavouring shall be added.

The Trade Practices Commission issued Information Circular No. 16 on 25 June 1976 in response to complaints from consumers and the fruit juice industry.

Unless a product complies with the standard (as described above) it must not be sold as 'juice'. It may (depending on State law) be called a 'fresh fruit drink', a 'fruit juice drink', a 'fruit squash drink', a 'fruit drink', or a 'fruit flavoured drink'. A product reconstituted from concentrates should (according to the TPC) clearly state that it has been reconstituted. The word *pure* can only be used for a fruit juice without preservatives, artificial colourings (!), flavouring, or the like.

The word *fresh* should not be used for reconstituted juice. The word should convey a time lapse between production and consumption of not more than two or three days. Suppliers must be able to provide backing for their claims. The words *fresh picked*, *fresh chilled*, and *fresh delivered* should not be used to indicate non-existent freshness. Trade names should not be used to mislead.

Ascorbic acid is slowly destroyed by exposure to air. The results in Table 12.3 show the kinetics of the reduction of vitamin C content in orange juice with time. It should be stressed that concentrates are about 10 per cent citric acid and the ascorbic acid level is not stable in thawed concentrate. See also the experiment on vitamin C in Chapter 14. A point to note is that the titration actually measures ascorbic acid, whereas partially oxidised ascorbic acid may

TABLE 12.3 *Ascorbic acid levels in orange juice*

BRAND	Age after opening (days)	No. of determ-inations	Mean mg/litre	Standard Deviation	Comments
VITAFRESH* (concentrated)	0	25	149	1.7	Contains preservative.
	7	28	(25)	0.8	No correction made
	13	35	28	1.2	(this would be a -ve correction)
FARMLAND*	0	35	800	8.9	Contains preservative.
	7	36	649	5.2	No correction made
	15	26	331	2.9	(this would be a -ve correction)
BERRI	0	25	467	4.4	No preservative added.
UNSWEETENED	7	23	352	5.5	Metal container
(CANNED)	13	29	288	2.3	
100%(®)	0	36	256	5.9	No preservative added.
	7	37	434	2.8	Plastic container
	15	20	211	1.5	

*No information was obtained on the nature of the preservatives used in Vitafresh and Farmland juices. However, the only interfering preservative is SO_2 which gives an enormously high result for the determination of ascorbic acid. It is to be expected therefore that the results shown are higher than the true values (if SO_2 had been used as preservative).

Source: Australian National University Chemistry 1 students, December 1976, published *Canberra Consumer* **58**, June 1977.

also have vitamin activity. It is also suspected that other components in citric juice may have a synergistic effect on the vitamin C activity of ascorbic acid. In general parlance the two terms are used interchangeably.

Kinetics in the kitchen

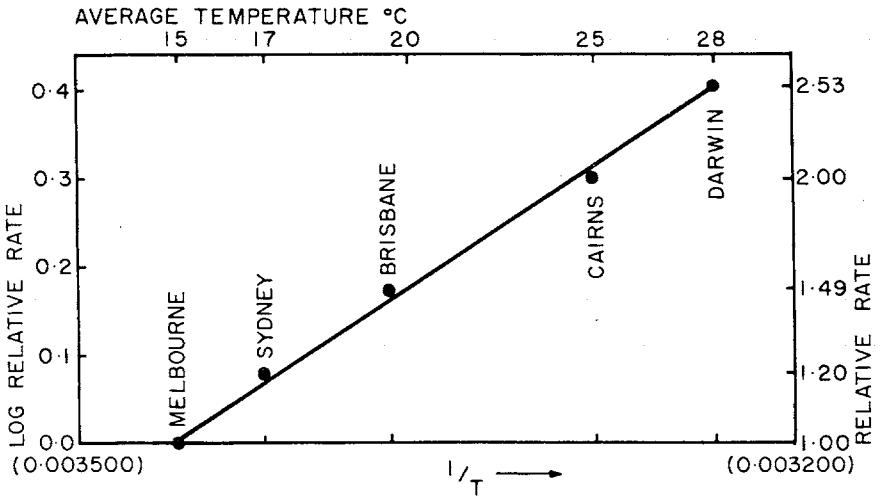
A paper published in the CSIRO *Food Research Quarterly* gives the relative effect of storage temperature on rates of chemical deterioration reactions in food (for different cities in Australia). Normally a physical chemist would plot the logarithm of the rate as a function of $1/T$, where $T = °C + 273$. Such a plot is shown in Figure 12.12.

This plot corresponds to a rule of thumb which says that chemical reactions go about twice as fast if the temperature goes up by 10°C. Later in discussing frozen food we will look at differences in the slope of the graph. Similar daily or seasonal changes in temperature in a shop at a particular location would

influence rates of deterioration in quality in the same way. The chemical reactions are not reversible, so that changes occurring in a food during storage at a temperature higher than recommended cannot be reversed by returning the product to the recommended temperature. The shelf life of food in a correctly hermetically sealed can which has been heat sterilised will be determined by the rate of corrosion of the can—for acid food such as fruits, but not for meat and vegetables where it is loss of flavour, texture, or colour that is rate determining.

Kinetics is the study of how fast chemical processes go and why. It is a subject to which much elegant mathematics has been applied. One aspect concerns itself with the principle of a rate determining step. Basically this says that if lots of things are happening, the slowest link in the chain acts as a 'bottleneck' and the speed of the whole process is determined by this single step.

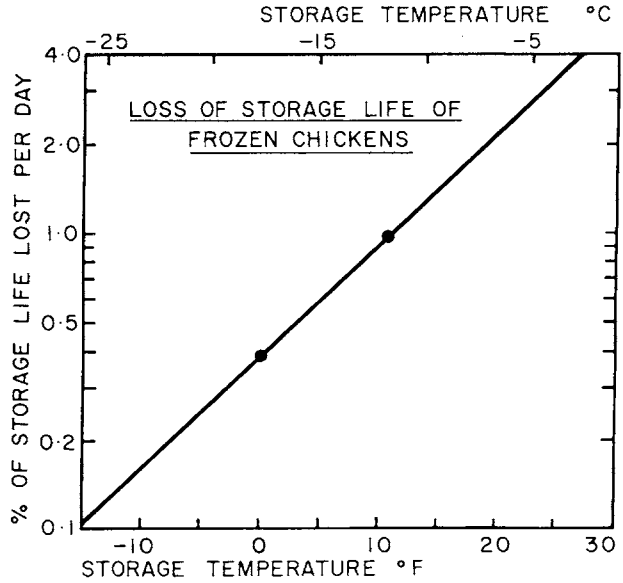
An interesting example is provided by the relative rates of cooking of potatoes and rice.[27] The cooking process in each case involves the contact of granules of starch with water at a sufficiently high temperature to cause gel formation. In the case of potatoes, large amounts of water are already present throughout the structure, and the turbulent action of boiling ensures the surface of each piece is effectively at the water temperature. The rate determining step is clearly the transfer of heat from the surfaces to the centre of the potato pieces. Further evidence for this is that undercooked potatoes are identified by hard, that is ungelatinised, centres and cutting the potatoes into small pieces reduces the cooking time.



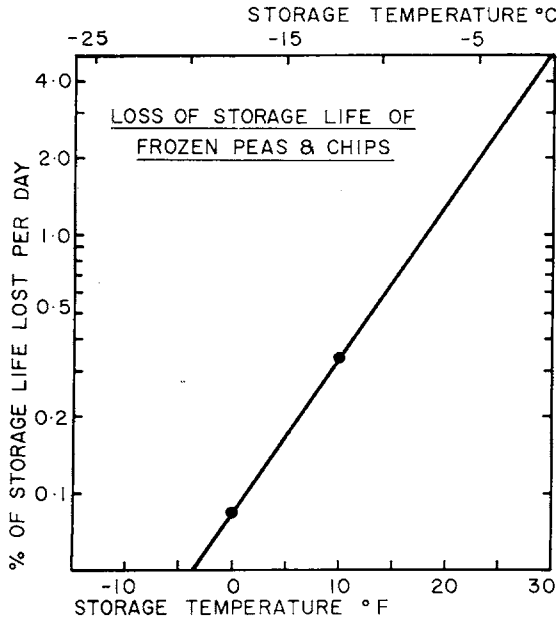
12.12 Relative rates of deterioration reactions in food for different cities in Australia

Rice is different because it starts out with very little water in the grain so that sufficient water must be absorbed, as well as heat transferred, to cause gelatinisation. The absorption of water is the rate determining step. It takes only a fraction of a second for the temperature at the centre of a grain to reach that of the boiling water when rice is thrown in. After about one minute a gelatinised film has formed around each grain. For ten minutes the film extends further into the grain and at twelve minutes the rice is largely cooked with only the odd grain still having a brittle centre. A quick cooking rice is produced by partly cooking rice and then drying which causes large scale cracks. Final cooking by the consumer then takes only five minutes.

At the other end of the temperature scale is freezing food. Foods continue the slow process of deterioration during the time they are frozen.[28, 29] There is considerable difficulty in setting standards of quality or of loss in quality of foods. There is reasonable agreement between trained food tasters in their assessment of the onset of the first detectable sign of degradation. This first onset can often be correlated with some measurable chemical change, e.g. reduction in ascorbic acid content of peas. Roughly six times this length of time (i.e. till detectable degradation) represents the end of 'high quality life' of the product and so the sixfold time is the 'storage life' of the food. After 100 percent of the storage life, the product is no longer 'high quality' but is still considered as not objectionable when confronting the average consumer.



12.13 Loss of storage life of frozen chickens. The dots (●) refer to Table 12.4.



12.14 Loss of storage life of frozen vegetables. The dots (●) refer to Table 12.4.

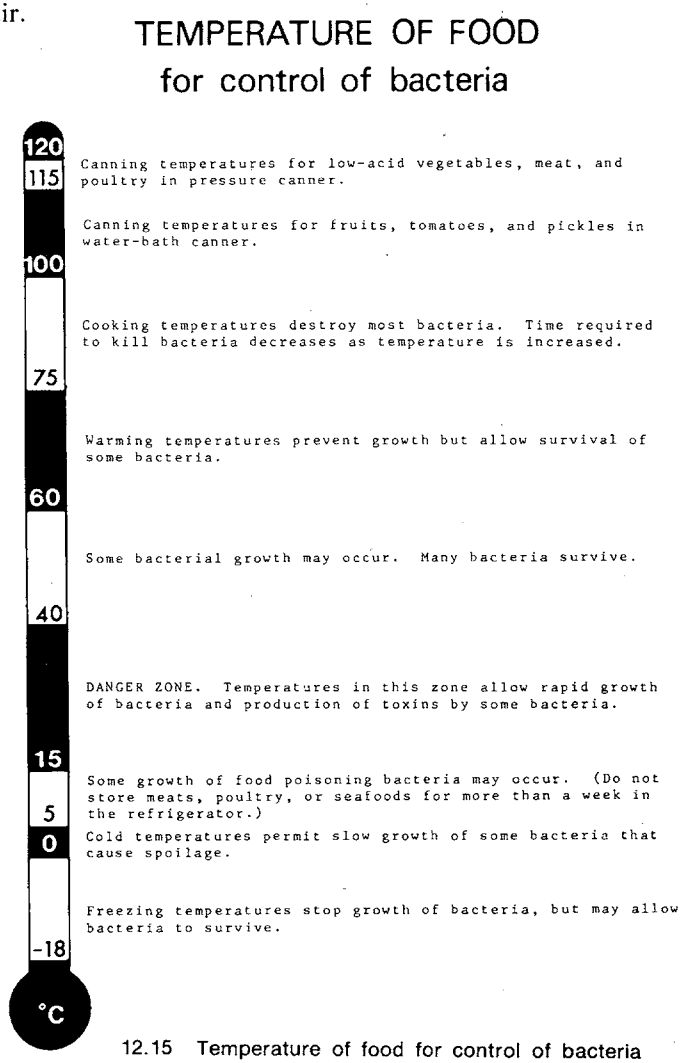
It is found empirically that a plot of the percentage of the storage life lost —on a *logarithm* scale—against the temperature is roughly a straight line[28] (see Figure 12.13). The slope of this line will be different for different foods (compare Figure 12.14 and note the difference in horizontal scales).

Thus a freezer operating at −12°C rather than −18°C will cause the loss of storage life to increase by a factor of two and a half for chicken, and four for frozen peas and chips (see Table 12.4). If the temperature is raised from −20°C to −4°C the frozen chicken still appears frozen but its storage life is reduced by a factor of ten. In the case of bad warehousing, the chickens would have reached the end of their storage life before they left the warehouse. In *absolute* terms, however, the percentage of the storage life lost is much smaller for peas and chips than for frozen chickens.

TABLE 12.4 *Storage of frozen food*

	Percentage of storage life lost per day	
	−12°C	−18°C
Frozen Chicken	1.0	0.4
Peas or Chips	0.35	0.08

Determine what percent storage is lost if the product is stored on the floor of the supermarket (25°C) for two hours instead of being placed in the frozen food retail display cabinet (par for the course). What about storage for a fortnight above the load line of the retail freezer cabinet temperature say −5°C —particularly if the top is not covered. An aluminium cover used just during non-selling hours (shop closing to shop opening) can more than double the storage life of the food in the cabinet. Most vertical retail frozen food cabinets are unable to keep food at anywhere near −18°C because of continuous loss of cold air.



12.15 Temperature of food for control of bacteria

Another interesting kinetic problem involves the monitoring of frozen food. The initial effort in this direction was the development of irreversible warm-up indicators (iwi). These little devices were designed to change colour if the package to which they were attached warmed above a preset temperature for more than a short period. The temperature for the colour change could be chosen from a reasonable range. If the package was refrozen they would not change back. They therefore provided evidence of mishandling in the history of the package.

As we have seen, it is a combination of time and temperature which is the decisive factor in loss of storage life. We need a combination device. An obvious choice is a chemical reaction of the same characteristics as the one we are monitoring. One such device, called *i-point TTM* (Time Temperature Monitor) is based on an enzyme reaction.[30] Reacting at a relatively slow rate at low temperature and at accelerated rates as the temperature rises, the indicator chemically integrates and accumulates the length of time and all temperature change experiences. When preselected time–temperature limits have been exceeded, a distinct irreversible colour change will occur indicating that action is required. A number of indicators of different 'length' can be used in one unit, so that they indicate consecutively after say 20 percent, 50 percent, 100 percent of the storage life has been exceeded. Table 12.5 gives the life spans for particular monitors. Which ones correspond to the behaviour of any of the frozen foods we have discussed?

TABLE 12.5—*Preliminary Standard Assortment of i-point TTM*

TTM No.	Time to colour change at a temperature of				
	+20° C	+10° C	0° C	−10° C	−18°C
2026	13 h	26 h	2.6 d	7.6 d	20 d
2040	20 h	40 h	4.0 d	11.6 d	32 d
2048	24 h	48 h	4.8 d	14 d	38 d
2080	40 h	3.3 d	8.0 d	23 d	63 d
2110	55 h	4.6 d	11 d	32 d	87 d
2140	70 h	5.8 d	14 d	41 d	110 d
2180	90 h	7.5 d	18 d	53 d	140 d
2220	108 h	9.0 d	22 d	63 d	171 d
2280	140 h	12 d	28 d	82 d	221 d
2340	7.0 d	14 d	34 d	98 d	266 d
2430	9.0 d	18 d	43 d	126 d	342 d
2530	11.0 d	22 d	53 d	154 d	418 d

C= °Celsius, h = hours, d = days

Source: Kockums Chemical, Malmö, Sweden, 6 December 1976.[30]

KINETICS AND HYPERKINETIC KIDS

As a follow-on to their book *The Magic Bullet*,[31] the Society for Social Responsibility in Science (ACT) held a symposium titled The Impact of Environment and Lifestyle on Human Health.[32] This conference included a paper by Peter Cook on his work with Joan Woodhill on the Feingold dietary treatment of the hyperkinetic syndrome[33] which was later published in the *Medical Journal of Australia*.[34] In their introduction to the paper the authors say:

a satisfactory explanation of the hyperkinetic syndrome in children has been lacking. Feingold has advanced the hypothesis that naturally occurring salicylates and artificial food additives may cause this (overactivity) syndrome in certain children who have a genetically determined predisposition. Following Feingold's dietary prescription, an elimination diet relevant to foods available in Sydney was developed. The treatment regime is described, and the results of the application to 15 hyperkinetic children are presented. The parents of 10 children are 'quite certain' and those of three others 'fairly certain' that their children's behaviour not only improved substantially with the diet, but also relapsed promptly when significant dietary infringements occurred—a possible ecological implication of these findings is discussed.

The authors go on to say:

In essence the diet consists of putting children on a diet which eliminates naturally-occurring salicylates and all artificial food colourings and flavourings for a trial period. Some of them seem to respond rather dramatically, others more slowly and some not at all. If the child appears to have improved then the next step is to test him with a 'challenge' substance that has been excluded from the diet, and see if he appears to relapse.

In a guest editorial in the *Medical Journal of Australia* one month later, John Werry of Auckland wrote in derogatory terms of Dr Feingold and cast aspersions on Cook and Woodhill and the editor of the journal for accepting their paper.[35] He attacked the method as unscientific. However, Cook and Woodhill themselves do point out:

A relevant and interesting point about this treatment is that this regime is unusual among diets, in that its value can be disproved, in a way that is visible to both the subject and to other observers within 24 hours. So any child who wishes to prove that these dietary restrictions are unnecessary, has only to eat a coloured ice-cream or have a soft drink and demonstrate that his behaviour is unchanged for the rest of the day, to discredit the basis of the treatment in his particular case.

This argument led to an entirely new concept for the *Medical Journal of Australia*, called 'Follow up'. The first example was an answer by Cook and Woodhill to the criticism in the Werry guest editorial.[36] In the meantime a double blind cross-over study has been carried out which strongly suggests that the diet does reduce the perceived hyperactivity of some children. Provided the diets are carried out under nutritional supervision so that no imbalance

occurs there seems little reason to discourage attempts at testing their effect in individual cases. Even a small rate of success is rewarding.

There is recent preliminary evidence that some food colours can dramatically build up the population of particular micro-organisms normally present in the human gut. These in turn can produce chemicals which are absorbed into the bloodstream, and a greater than normal concentration could cause behavioural changes.

In his chapter in *The Price of Making our Foods Safe and Suitable*,[37] Michael Tracey discusses two types of food safety. First is the safety of food for society as a whole, which is well covered in Australia and other developed countries. Second there is the suitability of food for an individual—here the variability of humans is important, as discussed in another abstract from this paper on the changing concept of LD_{50}. Research can reveal the influence of dietary components on the expression of genetic potentialities of both acute and chronic disease conditions for each individual. This is what the Feingold exercise is all about.

The implication of food colours in skin allergies is better documented[38]. Some experiments on the common housefly fed dyes and subsequently exposed to light (both sun and artificial) showed the rather dramatic result of producing 100 percent mortality in the light exposed flies.[39] In flies fed the highest concentration (1 percent) of the most effective dyes, loss of co-ordination occurred within 5–10 minutes and mortality within one hour. Other dyes were inactive. The flies were fed a number of different dyes used in food, drugs and cosmetics. One type of dye (xanthenes), of which the food dye erythrosine is an example, caused the 'photodynamic killing'. The flies were fed the dyes at 0.25 percent and 1 percent w/w concentration in liquid and solid food and *then* exposed to light. The time taken for the flies to die after feeding is given in Table 12.6

TABLE 12.6 *Mortality in erythrosine-fed house flies (%)*

Concentration in food*	Hours of exposure after feeding Artificial light					Natural light	
%	1	3	6	8	24	1	3†
0.25 L	20	77	100	—	—	47	100
0.25 D	6	23	48	77	98#	27	77
1.00 L	57	97	100	—	—#	87	100
1.00 D	12	32	68	80	100#	79	100

*L = liquid diet; D = solid diet

† No mortality occurred in control milk-sugar-fed flies

Mortality in darkness occurred in these cases and did not exceed 4 percent

Source: P.T. Yoho, L. Butler, and J.E. Weaver,[39]

There is still a lot to be learnt about the action of food additives on organisms. The sensitivity of flies could give us some clues on photo-allergic responses in humans.

Allergy testing

Sometimes the difficulties and uncertainties involved in testing situations where the method of test is subject to error are underestimated. If we consider a criminal court, it has certain procedures which it uses to determine guilt. These procedures are less than 100 percent certain. In a 'free' society the philosophy is to reduce to a small fraction the probability of convicting an innocent suspect. This must simultaneously increase the probability of acquitting a guilty suspect. (Type 1 and type 2 errors in a mathematical sense.)

Let us set up a simple model. We shall take a population of recalcitrant kids which has 1 percent of members who are allergic to a particular food additive. We do not know, however, who the individual members are who have this allergy, but we attempt to find this out by a test. We assume that the test is 80 percent accurate. This means that it will pick up an allergic child eight times out of ten and it will say that a particular child is allergic when in fact he is not two times out of ten. (These two factors need not be complementary—you can use 80 percent for the first and 5 percent for the second if you like—the possibilities just become a bit more numerous.)

Well, we now apply our test. The probability of detecting an allergic child from a group of totally allergic children is the conditional probability:

$$P[\text{detect} \mid +] = 0.80$$

As the fraction of actually allergic children is 0.01, the probability of correctly detecting an allergic child in our population is

$$0.80 \times 0.01 = 0.08 \qquad \mathbf{1}$$

In a similar manner, the probability of detecting an allergic child from a group of totally non-allergic children is

$$P[\text{detect} \mid -] = 0.20$$

As the fraction of non-allergic children is 0.99, the probability of wrongly detecting an allergic child in our population is

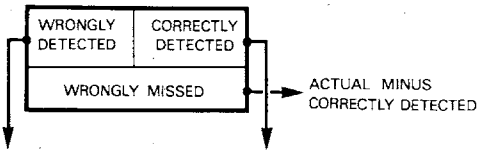
$$0.20 \times 0.99 = 0.198 \qquad \mathbf{2}$$

For 1000 children then we will have correctly detected eight allergic children —equation **1**—but wrongly detected 198 children—equation **2**. We also know that there were ten actual allergic children; so we have missed two of them. This result is tabulated along with a number of others in Table 12.7.

PROBABILITY TABLE PER 1,000 MEMBERS

TEST ACCURACY	NUMBER OF ACTUAL OR TRUE ALLERGIC MEMBERS IN THE GROUP TESTED							
	10		50		100		500	
90%	99	9	95	45	90	90	50	450
	1		5		10		50	
80%	198	8	190	40	180	80	100	400
	2		10		20		100	
70%	297	7	285	35	270	70	150	350
	3		15		30		150	

CODE AND CALCULATION



$$P[-] \times P[\text{detect} \mid -],\ P[+] \times P[\text{detect} \mid +]$$

TABLE 12.7 *Probability table for given test accuracies*

This method of screening was in fact discussed in terms of detecting chemicals present in our environment which are carcinogenic.[40] The result would be reported as a sample of 1000 chemicals in which the test detected 216 positive carcinogens (**1** plus **2**) of which however only eight were in fact carcinogens and 198 were picked up incorrectly. Of the remaining 784 chemicals which were cleared, two would have in fact been carcinogenic and not picked up.

Repeated measurement on the same sample will not change the detection success if the failure to detect is systematic rather than statistical in nature. For statistical uncertainties, increasing the number of replications increases the accuracy as the square root of the number of replications.

As an exercise make up some charts where the accuracy of correct detection and correct rejection are different.

STANDARDS

The Commonwealth Department of Health has commenced the publication of notices in the Commonwealth *Gazette* to inform the public that the NHMRC Food Standards Committee intends consideration of certain food standards. The public is being invited to submit written comment directly to the Food Standards Committee (FSC) Secretariat on the various FSC proposals. Submission via the Australian Federation of Consumer Organizations (AFCO) is unofficially recommended so as to co-ordinate comment on

particular topics. The standards in particular food groups such as dairy products will be revised as a group over a period of, say, twelve months together with urgent requests. Completed food groups would then not be routinely reviewed again for a period of some years, except for special reasons.

The NHMRC Recommended Standards will be in general terms not written for legal incorporation and they will not be restricted to health criteria. There will be three stages of review.

1. FSC will issue a Statement of Intention advising its intention to prepare or amend a standard on a particular commodity. Commonwealth *Gazette,* AFCO, Consumer Affairs Councils, State/Territory departments of Health and of Industry.
2. FSC will prepare an *Initial Draft Standard for Public Review* which will be presented for comment as in stage 1.
3. A Draft Standard is drawn up and forwarded to the State and Territorial Departments of Health for 'concurrence'.

The NHMRC then approves the standard and recommends its incorporation into State (Territorial) Law as a uniform standard. The FSC documentation remains 'confidential' throughout. It is my opinion that without general access to the working papers, useful comment from consumers cannot be expected at a stage earlier than the published draft standards. Even here comments made in the absence of working documents will tend to be assessed as irrelevant. The success will depend entirely on AFCO's willingness to present the industry argument to consumers in sufficient detail.

CONCLUSION

This chapter on food additives and the chemical aspects of nutrition has grown to become a dominant part of the book, extending its tentacles of influence into other chapters. Food is the most intimate chemical contact we have with our environment and our reaction to it is a peculiar one (in the strict sense of the word)—'one man's meat is another man's poison'.

Food allergies are quite common and I have ventured into the area where these are associated with behavioural problems. Because of this individual response, the responsibility for avoiding these problems is thrown much more on the consumer. With inadequate information there is no way in which this responsibility can be assumed. In the first edition I suggested that where labelling created problems, detailed information should be made available by the manufacturer or producer so that particular products known to cause personal problems can be avoided. This was just a natural extension in the provision of specified foods for rather larger sections of the population, such as diabetics (no sugar), coeliac (gluten free), phenylketonuria (low in the amino acid phenylalanine). It is pleasing to report that the pressure for legislation is moving in this direction. There will still be a need for ingredient labelling

(including additives which I believe can best be done by a system akin to that of the EEC—with a code number for each additive). Some mechanism must also be introduced into the scheme to provide incentives for manufacturers to use a minimum amount of additive and not necessarily the legally allowed maximum. The work of the Food Standards Committee must move much more into the area of providing information on the components (and their variability) in 'natural' foods as consumed in Australia. The emphasis on synthetic additives is due to industry wanting them and dominating the working of committees with their submissions.

Finally, consumers who found this chapter interesting should extend their reading (as suggested in the large Further Reading list) and keep it and their eating habits as broad as possible. Eating a narrow selection of foods in excess or reading only articles with which you agree are both undesirable.

DISCUSSION TOPICS

(Acknowledged gratefully to Bernie Keefe, Lecturer in Health Surveying, QIT)
Here is a check-list on the laws and regulations covering the sale of food. The situation is broadly similar in each State (and Territory).

1. What is the law?
2. Who frames it?
3. How is it framed?
4. What does it say?
5. Can it be clearly and simply *interpreted* by the consumer? If not—why not?
6. Who polices the law?
7. How well is it policed (a factual assessment).

Suggestions for answers

1–3: It is the State Act that is relevant, although there is now a move for a model Commonwealth Food Law. You may need to invite someone from the Department of Health or an institution teaching in this area for help. Obtain a copy of the local regulations on margarine. You may begin to wonder *who* indeed frames some of our food laws.

4. Various types of foods are defined in a series of standards (approx. 1000) which define: the qualities of the food; the detailed labelling requirements (including size of lettering, colours, etc., plus a list of prohibited statements about the product); what *can* be added to the food; what *cannot* be added to the food.

5: The answer to this is probably No more than Yes. For example, does the absence of the statement: 'preservative added' indicate the absence of preservatives? No—the reason differs slightly from State to State—because certain foods are exempt from this labelling requirement, e.g. packaged bread, beer; and certain preservatives are exempt from mention, e.g. nitrates and nitrites.

6–7: Again your local Department of Health is the place to ask.

APPENDIX 12.1

Food law in Australia

In Australia food law is a State matter, although there is a move towards a Federal Food Law. In order to achieve some measure of uniformity the National Health and Medical Research Council has set up a Food Standards Committee which co-ordinates the activities of the States (and Territories) and produces a list of approved food standards for incorporation into State (and Territory) legislation. Reference in this chapter is made to these standards. They are produced by the Australian Department of Health in the form of a book which also gives the approximate current status of the law in the various States (and Territories). *The NHMRC Food Standards have no legal significance until such time as they are incorporated into the legislation of the States and Territories of Australia.*

NHMRC Principles for the Evaluation of Food Additives—May 1977

1. The use of a food additive is justified only when it serves one or more of the following purposes:
   (a) to maintain or improve the nutritional quality of a food;
   (b) to improve the palatability, storage life or appearance of a food;
   (c) to render a food more appetising;
   (d) to provide aids in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, holding, or storing foods;
   (e) as a preservative only when necessary because there is no alternative practicable means of preservation of the food.
2. The use of a food additive is NOT justified:
   (a) if the proposed level of use constitutes a hazard to the health of the consumer;
   (b) if it causes an appreciable reduction in the nutritive value of a food;
   (c) if it disguises the faulty or inferior qualities of a product or the use of processing and handling techniques which are not permitted;
   (d) if it deceives the purchaser or consumer;
   (e) if the desired effect can be obtained by another method of processing which is economically and technologically feasible.
3. Approval for the use of a food additive should be based on anticipated intake in relation to consumption patterns of the community. Special regard should be given to vulnerable groups with special diets such as infants and the elderly.
4. Where it is necessary to use a food additive for any purpose, the purpose must be specific and in the best interests of the consumer. It must be

established that there are no alternative means of achieving the purpose more consistent with the best interests of the consumer.

5. Approval for the use of a food additive shall not be general but shall be limited to specific foods for specific purposes under specific conditions, unless otherwise determined.
6. A food additive must be:
   (a) used in the minimum amount necessary to effect the intended purpose under good manufacturing practice;
   (b) acceptable at the level approved on toxicological grounds.
7. A food additive must be in conformity with an acceptable standard of purity.
8. (a) All food additives proposed for use shall have had adequate toxicological evaluation;
   (b) Permitted food additives are subject to continuing observation and are re-appraised in the light of changing conditions of use and new scientific information.
9. Incidental food additives shall not exceed the lowest levels that are technologically feasible.

An applicant wishing to introduce a new food additive must make a detailed submission to the NHMRC Food Science and Technology Subcommittee. The information must include (*inter alia*) the following:

1. The proposed minimum and maximum level of use.
2. The limits of the probable daily intake of the additive in the diet.
3. Any evidence of rejection of the additive by any statutory body or authority.
4. Details of the precise chemical structure and physical details of the additive.
5. Details of the nature and amounts of impurities present.
6. The advantages which will accrue to the consumer from the use of the additive.
7. Analytical methods that can be used for verification.
8. Method of manufacture.
9. Results of pharmacological and toxicological investigations including acute, short-term and long-term (chronic) toxicity studies. Chronic toxicity data should be given for at least two species, one of which should be the dog and carried out over the major portion of the life span of the experimental animal. Chronic toxicity experiments should aim to give the data needed to establish a 'no effect' level.
10. Reports of any physiological effects and any abnormal reactions, including carcinogenesis, teratogenesis in pregnant species, sensitivity, tolerance, or idiosyncrasy in response to additive.
11. Biochemical information on the possible mode of action if available; metabolic studies to show rate, extent and mode of elimination.

Note

Details of any reports which could bias an evaluation of the safety of the additive should NOT be omitted.

The information supplied should be attested to by a statutory declaration.

Item 10 is of interest to people who believe they have sensitivity towards particular food additives. As presently allowed food additives are continually under review, and submissions can be made to The Secretary, NHMRC, P.O. Box 100 Woden, Australian Capital Territory 2606 at any time. If the list of requirements for food additives (of which the above is a selection) is to be regarded as more than a pious hope then additives must be continuously tested against its criteria. At the same time it should always be remembered that 'natural' foods should be subject to equally stringent scrutiny. It is probable that potatoes and chick peas could have a rough passage if re-examined!

A historical view—up to 1960—of Australian Food Standards is provided by F.H. Reuter in his chapter entitled 'National Problems in Australia' in A.J. Amos (ed.), *Pure Food and Pure Food Legislation*, Butterworths, 1960.

A critical study of the mechanism by which food standards are set in Australia has been produced by Murray McInnis in a thesis for B.Juris entitled Food Standards in Australia—Need for Reform (Monash University, November 1974).

APPENDIX 12.2

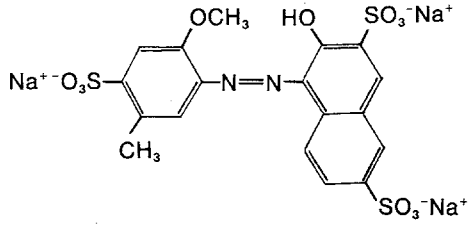
Synthetic food colours in Australia (NHMRC 1977)

The food colours fall into different chemical groups. All the reds, oranges, and yellows are *azo dyes* having the —N=N— linkage, except erythrosine which is a *xanthene*. The green, blue and violet are *triphenylene* dyes, while the browns and black are azo dyes again. Indigo carmine is a different type again. Where there is a sensitivity to azo dyes, there is often no reaction to food green and blue (unless the colour is a mixture).

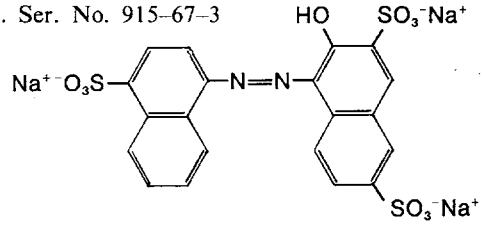
The *Chemical Abstracts* Registered Serial Number allows you to search the chemical literature. E numbers refer to the EEC. FD & C (Food, Drugs and Cosmetics) refers to the United States. CI is the code used in the Colour Index Volumes.

Red Shades

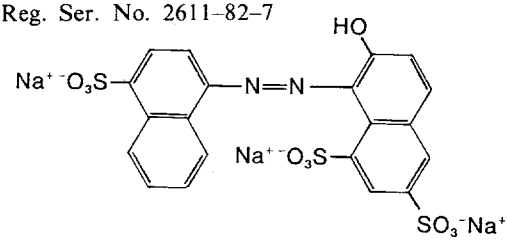
CI 16035 Allura Red AC
FD & C Red No. 40
CI Food Red 17 *Chem. Abs.* Reg. Ser. No. 2956-17-6



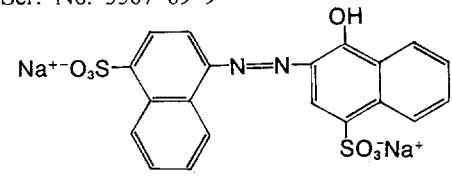
CI 16185 Amaranth
FD & C Red No. 2
CI Acid Red 27
CI Food Red 9
E123
Chem. Abs. Reg. Ser. No. 915-67-3



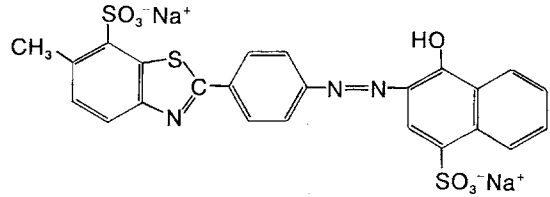
CI 16255 Brilliant Scarlet 4R
CI Acid Red 18
CI Food Red 7
E124
Chem. Abs. Reg. Ser. No. 2611-82-7



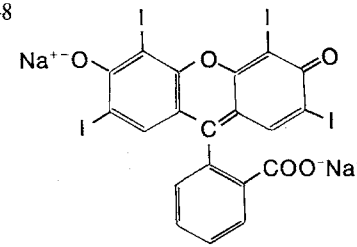
CI 14720 Carmoisine
CI Acid Red 14
CI Food Red 3
Chem. Abs. Reg. Ser. No. 3567-69-9



CI 14780 Chlorazol Pink Y
(Hexacol Red FB)
CI Direct Red 45
CI Food Red 13
Chem. Abs. Reg. Ser. No. 2150–33–6

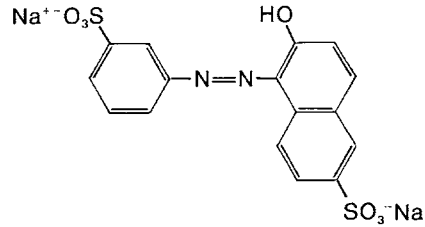


CI 45430 Erythrosine
(tetraiodinate fluorescein)
CI Acid Red 51
CI Food Red 14
E127
Chem. Abs. Reg. Ser. No. 568–63–8



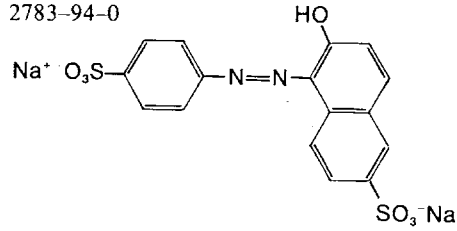
Orange Shade

CI 15980 Orange GGN
CI Food Orange 2
Delisted in the EEC (E111)
Chem. Abs. Reg. Ser. No. 2347–72–0

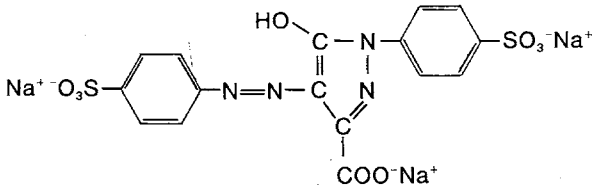


Yellow Shades

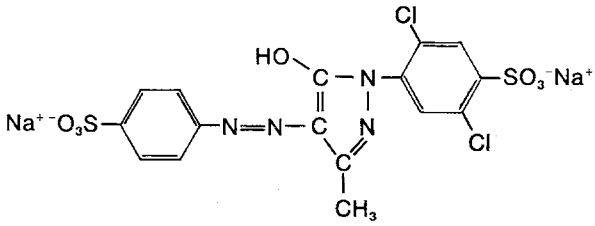
CI 15985 Sunset Yellow FCF
FD & C Yellow 6
CI Food Yellow 3
E110
Chem. Abs. Reg. Ser. No. 2783–94–0



CI 19140 Tartrazine
FD & C Yellow 5
CI Acid Yellow 23
CI Food Yellow 4
E102
Chem. Abs. Reg. Ser. No. 1934–21—60

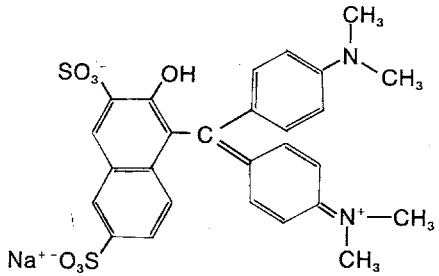


CI 18965 Yellow 2G
CI Acid Yellow 17
CI Food Yellow 5
Delisted in the EEC
Chem. Abs. Reg. Ser. No. 6359–98–4



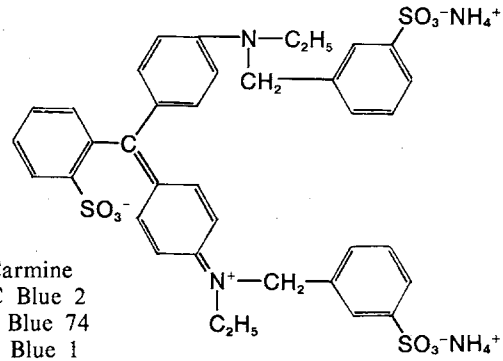
Green Shade

CI 44090 Green S
CI Acid Green 50
CI Food Green 4
E142
Chem. Abs. Reg. Ser. No. 3087–16–9

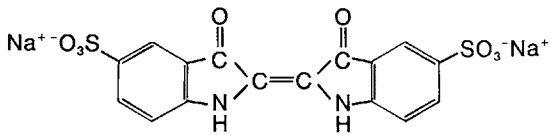


Blue Shades

CI 42090 Brilliant Blue FCF
CI Acid Blue 9
CI Food Blue 2
CI Pigment Blue 24
Delisted in the EEC
Chem. Abs. Reg. Ser. No. 2650–18–2

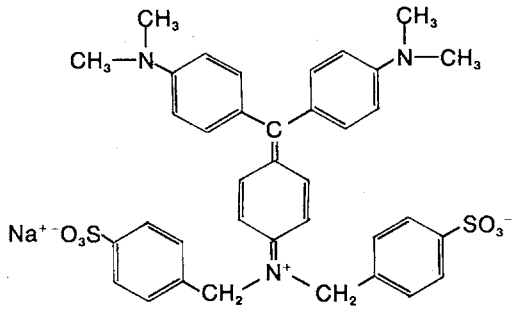


CI 73015 Indigo Carmine
FD & C Blue 2
CI Acid Blue 74
CI Food Blue 1
E132
Chem. Abs. Reg. Ser. No. 860–22–0



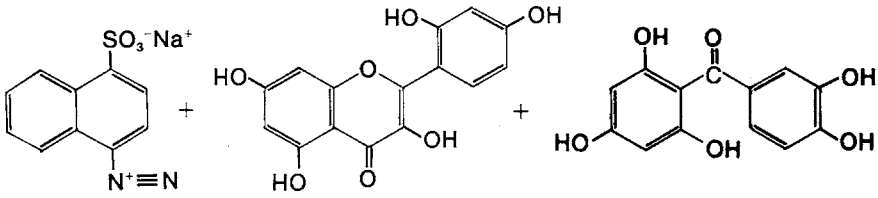
Violet Shade

(Sodium salt of 4,4′-di(dimethylamino)-4″-di(*p*-sulpho-benzylamino) triphenylmenthanol anhydride.
CI Acid Violet 21
Chem. Abs. Reg. Ser. No. 5905–37–3



Brown Shade

Chocolate Brown FB
(The product of coupling diazotised naphthionic acid (1-naphthylamine-4-sulphonic acid) with a mixture of morin and maclurin.)
No *Chem. Abs.* Reg. Ser. No. Delisted in the EEC—not allowed in U.S. or Canada
CI Food Brown 2



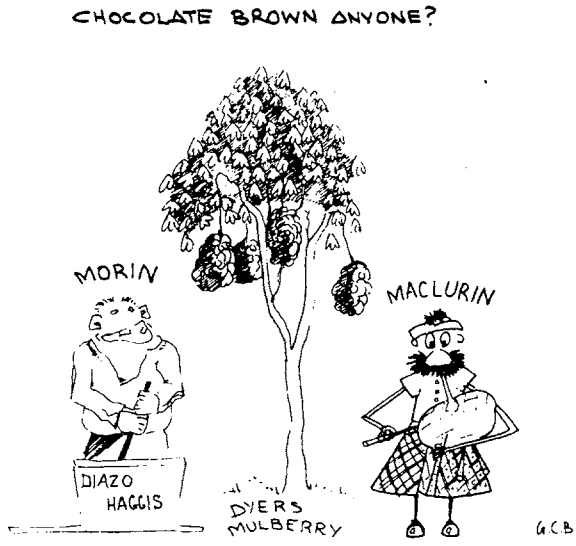
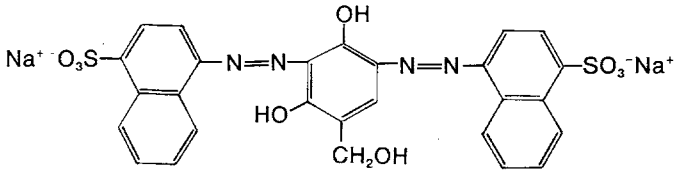


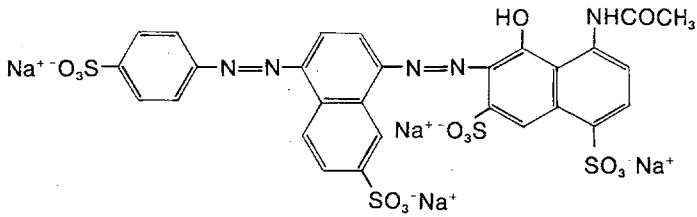
PLATE 12.IV *Chocolate Brown, anyone? Morin and Maclurin are found in the wood of the Dyer's mulberry, Chlorophora tinctoria. Morin is also found in the wood of the Osage Orange tree, found in the United States and as an ornamental tree in Australia. They are reacted with 1-naphthylamine-4-sulphonic acid to give Chocolate Brown FB, a colour allowed in Australia presumably because it is needed. However, this colour is no longer available commercially!*

CI 20285 Chocolate Brown HT. Delisted in the EEC—not allowed in U.S. or Canada.
CI Food Brown 3
Chem. Abs Reg. Ser. No. 4553–89–3



Black Shade

CI 28440 Brilliant Black BN
CI Food Black 1
(blueish-violet in water)
E 151
Chem. Abs. Reg. Ser. No. 2519–30–4



APPENDIX 12.3

History of approved synthetic colours in Australia

1955*	1967†	Since 1967#
16185 Amaranth	16185 Amaranth	
16255 Brilliant Scarlet 4R	16255 Brilliant Scarlet 4R	
14720 Carmoisine	14720 Carmoisine	
14780 Chlorazol Pink Y	14780 Chlorazol Pink Y	
45430 Erythrosine	45430 Erythrosine	
—	16045 Fast Red E	deleted 1975
45435 Rose Bengale	45435 Rose Bengale	deleted 1975
14815 Scarlet GN	14815 Scarlet GN	deleted 1975
14700 Ponceau SX	removed *c.* 1965	16035 Allura red added 1975
45170 Rhodamine B	removed *c.* 1961	
15980 Orange GGN	15980 Orange GGN	
13015 Acid Yellow G	13015 Acid Yellow G (kond)	deleted 1975
15985 Sunset Yellow FCF	15985 Sunset Yellow FCF	
19140 Tartrazine	19140 Tartrazine	
added *c.* 1961	13011 Yellow RFS	deleted 1968
—	18965 Yellow 2G	
—	14330 Yellow RY	deleted 1968
	44090 Green S	
42095 Light Green SF	removed *c.* 1961	
42090 Brilliant Blue FCF	42090 Brilliant Blue FCF	
73015 Indigo Carmine	73015 Indigo Carmine	
42045 Patent Blue	—	
added *c.* 1961	Violet BNP	
42650 Acid violet 5BN	—	
added *c.* 1961	Brown FK	deleted 1974
—	Chocolate Brown FB	
—	20285 Chocolate Brown HT	
Chocolate Brown NS	—	
20220 Thiazine Brown R	—	
28440 Brilliant Black BN	28440 Brilliant Black BN	
35445 Black 5410	removed *c.* 1961	

*Before 1955 some 40 coal-tar dyes were approved as food colours.
†Now called synthetic colouring substances. In 1970 a standard for purity for food colours was adopted by NHMRC.
#Consumer representatives on FSC 1974–5, observer from AFCO since.

APPENDIX 12.4

Rank of countries based on consumption (in litres) of spirits, beer, wine, and total alcohol—year 1975

Total Alcohol			Spirits (pure alcohol)		
1.	France	16.90	1.	Poland	4.0
2.	Portugal	15.15	2.	Hungary	3.3
3.	Italy	14.21	3.	United States	3.2
4.	Spain	13.65	4.	Luxembourg	3.1
5.	Luxembourg	11.72	5.	Canada	3.0
6.	West Germany	11.69	5.	Spain	3.0
7.	Austria	11.16	5.	Yugoslavia	3.0
8.	Hungary	11.11	6.	Sweden	2.9
9.	Switzerland	10.73	6.	Finland	2.9
10.	Australia	10.03	7.	Netherlands	2.8
11.	Belgium	9.77	7.	Czechoslovakia	2.8
12.	Czechoslovakia	9.66	8.	Iceland	2.7
13.	Canada	8.25	8.	West Germany	2.7
14.	Yugoslavia	8.03	9.	Romania	2.4
15.	Denmark	7.95	9.	France	2.4
16.	Romania	7.87	10.	Switzerland	2.2
17.	Netherlands	7.78	11.	Italy	2.0
18.	United States	7.58	11.	Austria	2.0
19.	New Zealand	7.49	11.	Bulgaria	2.0
20.	Ireland	6.66	12.	Belgium	1.9
21.	Poland	6.61	12.	Ireland	1.9
22.	England	6.58	13.	Norway	1.8
23.	Finland	6.57	14.	New Zealand	1.7
24.	Sweden	6.18	15.	Denmark	1.6
25.	Japan	5.91	16.	Japan	1.5
26.	Bulgaria	5.14	16.	England	1.5
27.	Norway	4.23	17.	Australia	1.3
28.	Iceland	3.79	18.	Portugal	1.0
29.	Israel	1.77	19.	Israel	0.7

APPENDIX 12.4 (*Continued*)

	Beer			Wine	
1.	Czechoslovakia	152.7	1.	Italy	110.5
2.	West Germany	147.0	2.	France	103.0
3.	Australia	144.7	3.	Portugal	80.0
4.	Luxembourg	135.0	4.	Spain	75.0
5.	Belgium	132.6	5.	Switzerland	45.0
6.	New Zealand	126.8	6.	Luxembourg	40.3
7.	Denmark	114.9	7.	Hungary	38.0
8.	England	114.3	8.	Austria	36.8
9.	Austria	106.2	9.	Yugoslavia	29.2
10.	Ireland	86.7	10.	Romania	22.8
11.	Canada	85.5	11.	West Germany	20.2
12.	United States	79.8	12.	Bulgaria	20.0
13.	Switzerland	75.7	13.	Belgium	15.8
13.	Netherlands	75.7	14.	Japan	15.5
14.	Hungary	66.0	15.	Czechoslovakia	12.5
15.	Sweden	58.6	16.	Australia	11.3
16.	Finland	56.2	17.	Netherlands	10.4
17.	France	44.2	18.	Denmark	9.7
18.	Norway	43.9	19.	Finland	9.2
19.	Bulgaria	43.6	19.	New Zealand	9.2
20.	Spain	42.0	20.	Sweden	7.7
21.	Yugoslavia	37.2	21.	Poland	6.7
22.	Poland	36.1	21.	England	6.7
23.	Japan	33.0	22.	Canada	6.3
24.	Portugal	27.0	23.	United States	6.1
24.	Romania	27.0	24.	Israel	3.8
25.	Iceland	15.5	25.	Ireland	3.6
26.	Italy	14.4	26.	Norway	3.2
27.	Israel	10.3	27.	Iceland	2.6

Source: Dutch Distillers Association or brewers' associations in the various countries. Australian Associated Brewers—public submission to Senate Standing Committee on Social Welfare, 25, February 1977, Hansard 2599.

APPENDIX 12.5

Ames test

Whilst many toxic substances give a characteristic dose-response relationship with a threshold level below which the test animal does not respond—the no-effect level, in the case of carcinogens the situation is less clear. It has not been established that there is a threshold for carcinogens. On the other hand, there is considerable evidence which shows a variation between species in response to carcinogens, for example in response to aflatoxin B—a toxin formed by a fungus which attacks peanuts in moist conditions and for which the NHMRC recommended maximum level (1977) is 5 micrograms per kilogram.

Because experiments with animals similar to man are expensive, a simple rapid test for mutagenic activity of chemicals has been established using bacteria. *Salmonella typhimerium* (one of the microbes responsible for gastro-enteritis) can be bred in a mutant form which cannot grow in the absence of a particular amino acid histidine. This mutant is used in the Ames test.

A particular type of mutation in this organism—called a frame shift—can be caused by some mutagenic agents and when this occurs, the mutant organism can revert to the original form which doesn't need histidine.

So a standard number of mutant organisms are plated onto an agar medium which is free of histidine. When exposed to the mutagen, the organisms which mutate back can grow on the medium and be counted.

Its relevance to the detection of carcinogenic activity is based on the claim that some carcinogens are frame shift mutagens whilst others are converted to such mutagens in the liver. The test is purely qualitative and not quantitative.

Source: Food and Nutrition Research. Report of the ARC/MRC Committee, London HMSO 1974, p. 158.

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Chapter 13

THE HEAVY METALS[1]

The contamination of our environment by heavy metals is a constant and disturbing problem. Heavy metals are among the most dangerous and least understood of contaminants. Because they exist naturally as part of the earth's crust they occur in all soils, rivers, and oceans. In the right quantities some are essential to life. Elements which have a function in our bodies are H, O, C, N, S, P, K, Na, Cl, Ca, Mg, Fe, Cr, Mn, Zn, Cu, Al, Co, Se, I, F, and Br. Selenium has only recently been shown to be significant. Many we require only in minute (trace) quantities and they are, like selenium and fluorine, very toxic indeed at higher concentration.

The heavy metals are in widespread industrial use and when released into the air or into rivers they distort the naturally occurring distribution of metals with which we have come to terms in evolving in our 'natural' environment. This distribution is very critical because our need for traces of some elements such as selenium is very low. It is the most toxic element known to be essential to mammals. The uptake and need for copper depends on the level of zinc and molybdenum to which we are exposed and *vice versa*. It is also known from laboratory experiments that selenium compounds have a protective effect against the toxic action of mercury. Seals and dolphins from many parts of the world show a one-to-one correlation between the accumulation of mercury and selenium (Hg = 2.53, Se = 10.2, in mg/kg), which is not found in the fish on which they feed. This seems to indicate that the ratio is metabolically established in the marine mammals. We are only just beginning to understand some of these subtle interactions.

Our modern technology is heavily dependent on the use of these materials, but they are by no means indispensable in all their uses. Where there is a known problem and a reasonable alternative solution, consumer groups and environmentalists have good reason to believe that their case for restriction and control is justified. To develop an understanding of the complexity of the argument, a number of factors have to be considered.

HEAVY METAL ANALYSIS OF CONSUMER PRODUCTS

in conjunction with Microanalytical Laboratory, Research School of Chemistry, Australian National University

November 1973 Margarines

Brand X: 38 mg/kg lead (material in contact with container). Same manufacturer, brand Y: 11 mg/kg lead (material in contact with container). Problem due to incorrect plastic used in package—led to setting of standards for plastic packaging materials.

17 September 1974

Margarines X and Y; no lead detected; no cadmium detected.

17 September 1974 Glazes used by schoolchildren in pottery classes

Brand X labelled 'lead free'.

	Pb (mg/kg)	Cd
Type 1	2300	—
Type 2	700	—
Type 3	1000	—
Type 4	49200	—

This matter was soon rectified.

15 April 1975 Baby teething rings (imported)

	Pb (mg/kg)	Cd (mg/kg)
1. Round yellow	1295, 1100	—
2. Animal motif	1060	340
3. Paint from (2)	810	267

Led to setting standards for children's toys. (This investigation was conducted in conjunction with the ACT Consumer Affairs Council.)

1 October 1975 Wrapping paper for Bread

	Cr (mg/kg)	Pb
Brand 1	—	—
Brand 2	540	5186
Brand 3	—	—
Brand 4	—	—
Brand 5		
White colour	—	—
Yellow colour	trace	130
Orange colour	391	2100
mixed	205	1000

Submission made to Department of Health

March 1977 Wrapping paper for Bread

Brand 5—no detectable chromium or lead

What materials are involved?

The term *heavy metals* in this context signifies the metals mercury, cadmium, and lead in the first instance. In a broader sense other toxic elements are included. Some of these also have no part in our personal biochemistry, such as arsenic and barium; while others like copper, zinc, and selenium are essential at the correct level.

In what form are they dangerous?

Depending on the physical and chemical form of the metal, the substance can be very poisonous or harmless. Liquid mercury, as in a thermometer bulb or in a mercury dental amalgam, is harmless, but long exposure to the small amount of gaseous mercury given off by the liquid, but not the amalgam, is readily absorbed into the lungs and can lead to poisoning. The toxicity of inorganic mercury compounds depends on how soluble they are in the body fluids. The use of soluble mercuric nitrate in the felt-making process led to the traditional notions of 'hatters' shakes' and 'mad as a hatter' and also accounts for the use of the term *hatter* for solitary, acutely shy gold miners who recovered their gold by distillation of the gold–mercury amalgam in crude stills. On the other hand, the relatively insoluble mercuric oxide was used in eye ointments.

The most toxic forms of mercury are now recognised to be the organo-mercury compounds—in particular alkyl-mercury which is produced from inorganic mercury by micro-organisms present in the bottom of waterways. These compounds, while not soluble in water, are very soluble in fat and hence are stored in the body with an average residence of about seventy days, in contrast to inorganic mercury where the residence time is of the order of six days. Thus, with continuous exposure of low levels, it is possible to build up concentrations in the body of ten times the amount of organic mercury compared to inorganic mercury at the same level of exposure. A publication of the Australian Department of Health (1973) shows how the calculation of a maximum allowable level of alkyl-mercury in fish of 0.5 mg/kg was arrived at. This level was set with a safety factor of only ten, whereas the normal practice involves a factor of 100. Further details are given later in this chapter.

While soluble barium compounds are very poisonous, barium sulphate, which is used for increasing the contrast of internal organs for X-rays is so very insoluble as to be harmless. Metallic lead is not considered particularly dangerous in itself, although water collected from lead-lined roofs has been a considerable problem. Some forms of lead used in paint are very soluble in body fluids and, hence, are toxic. Copper is an essential metal, but water

passing through copper plumbing in Australian hospitals was found to produce up to 1 ppm of copper compound in dialysis fluid which could add about ten times the dietary intake of copper to the copper stored in the liver.

Cadmium compounds are used as pigments (lemon, yellow, orange, maroon) in ceramic glazes, paints, and plastics. Cadmium is absorbed from food and water slowly so that something like 98 percent of the cadmium in food is excreted within forty-eight hours. However, cadmium that is absorbed remains, so that cadmium levels build up from zero at birth with increasing age. The absorption from the air is much more efficient (10–15 percent). Cigarette smoke contains cadmium—twenty cigarettes contain an average of 30 micrograms of which about 70 percent is extracted into the smoke. There is a good correlation between stored cadmium levels and high blood pressure, and injection of cadmium chloride into animals can apparently cause irreversible damage to the testes. More details on cadmium are given later in this chapter.

At what levels are they dangerous?

Medical tradition divides poisoning into three categories—acute, chronic, and subclinical.

Acute toxicity means that you show a rapid poisoning response and need immediate treatment. Generally, this is the result of an accidental intake.

Chronic toxicity involves the effect of a long-time low-level exposure to a material which causes a slow and steady poisoning process. Again this is less likely to be a common consumer problem than an occupational hazard, although children eating lead paint come into this category.

Subclinical toxicity: this is the region in which the levels are so low that any abnormality cannot easily be detected or associated with the particular substance. The main concern here is the effect of such low levels on children because—

1. the child's immature nervous system, including the brain, appears more susceptible to permanent damage than that of the adult;
2. the absorption rate (for lead) through the gastro-intestinal tract is about 50 percent for a child in comparison with 5–15 percent for an adult; and
3. children consume more food in relation to their body weight than do adults because they have a higher metabolic rate and also chew non-food objects which may contain additional heavy metals.

STANDARDS

Obviously, we should set exposure to these materials as low as is reasonably feasible. In this respect, it is disturbing that glazes used by Canberra primary children which were allegedly lead free were found in September 1974 to

contain, in one instance, almost 5 percent lead. Teething rings have now been analysed and found to contain both lead and cadmium in one instance, while a popular form of plastic building kit commonly chewed by children uses over 1 percent cadmium selenide as a pigment. An Australian Standard for children's toys and playthings (safety standards) AS1647 was published in 1976.

Of course one of the questions that can be raised is to what extent these materials are extractable from the toy. The classic piece of work in this area has been carried out by C.W.A. Fowles.[2] He has examined toys in the United Kingdom and found cadmium levels of up to 1 percent in the plastic (cadmium sulphide/selenide). Extraction of cadmium from shavings of plastic (type ABS) toys taken with a variety of hand tools which do not heat the plastic showed that under conditions likely to be present in the human stomach (namely 37.5°C and 0.1M hydrochloric acid) significant amounts of cadmium can be extracted from plastic shavings.

Practical gnawing experiments by Fowles, his children, and a number of 'guinea pigs' have shown that similar shavings can be obtained quite easily. The risk is not associated with the sucking, because saliva will not favour extraction, but with the gnawing. Toys made from polypropylene or polystyrene type materials are less easily wetted and give lower extraction levels. He is critical of the test methods used by industry in which sawn cubes rather than small shavings are used because any method involving heating can seal over exposed pigment particles and give falsely low results. To give some idea of a consumer chemist's dedication, the following is quoted from his manuscript:

> Toy 47 (red)—samples taken by teeth.
> Bulk sample gnawed by the teeth of the author and gnawings spat out. One gram of sample obtained in 30 minutes. Sample washed by decantation, so loss of very fine particles; remaining sample passed through 1 mm mesh with the exception of a few larger pieces—all used in standard extraction text (4 hr, 25 ml 0.1 M HCl, 37.5°C). Cadmium extracted in HCl (simulates stomach juices): 128 micrograms, cadmium in saliva: 3.5 micrograms.

In the first edition of this book (1975) the story ended at that point. However, since then there have been some chemically interesting developments. . . . The extraction by HCl as a stimulant for stomach juices was taken into account but not adopted in the Australian Standard for toys (AS 1647–1974/6) but Professor Fowles had already found that while this method gave excellent reproducibility for duplicate samples, different sets of identical samples examined on different occasions sometimes showed unacceptable variations. The factors that showed up were:

1. The acid strength should correspond approximately to the *empty* stomach, ≈0.1 M HCl, and should be checked after extraction to guard against loss of strength by neutralisation by a basic filter

2. Raising the temperature from ambient to 37.5°C (body heat) increases the extraction rate by about 2–3 times
3. There are differences between measurements made at different times during the day and at different seasons

Light has a dramatic effect—a photoflood can increase rates of extraction by a factor ≈×10 for selenide (red) and ≈×3 for sulphide (yellow). The effect is perhaps not too surprising since both cadmium sulphide and cadmium selenide are photosensitive (cf. the effect in glazed ceramic tableware).[3] Most human stomachs can be assumed to be dark! Another trap lies in wait for those who don't read labels. Not only does most of our food come pre-packaged these days but so do many standard chemical solutions. The 0.1 M HCl concentrate provided by Volucon is labelled *preservative added 13.5 mg $HgCl_2$ per litre* (even chemicals have to be preserved!). The presence of mercuric chloride in the hydrochloric acid used by Professor Fowles in his original extraction method would inhibit the cadmium extraction presumably by forming a *more* insoluble layer of mercuric sulphide over the grains of cadmium sulphide and so presenting further extraction. The levels of cadmium extracted under these more rigorous conditions were lower.

Fowles has also examined copper enamelling powders for lead and used his gnawing talents to test whether comics contained lead or chromium compounds that could be ingested in the stomach of a child who chewed and swallowed part of a comic. He gives an issue by issue report of the levels of extractable metal in the comic series.

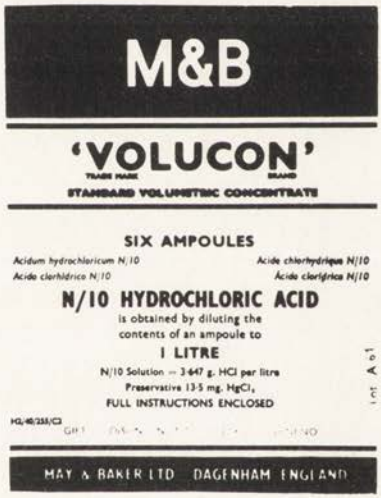


PLATE 13.I *Acid with preservative*

METALS IN FOOD

As well as the avoidable intakes of heavy metals, we ingest a certain amount with our food. Some work done on tea urns in Western Australia highlights this problem.[4] Domestic utensils used for boiling water are of variable quality, in that some of them introduce significant amounts of cadmium into the water for making beverages. The practice of connecting urns to boiling hot water supplies rather than using normal outlets should be avoided. High 'enrichment' (in one case ×197) are generally found in Hydrotherms. These are continuously heated thermostatically controlled sealed units in which a constant water level is maintained. Impurities in the water source concentrate on evaporation, particularly if the device has a low usage.

Food consists of chemical compounds mainly based on the elements carbon, hydrogen, oxygen, and nitrogen, and to a minor extent such elements as sodium, calcium, potassium, and phosphorus. Early investigations found a large number of other elements in quantities too small for accurate determination by available methods. These elements, they said, were present in trace amounts, leading to the term *trace elements*. Modern techniques, such as atomic absorption spectroscopy, square wave polarography, and neutron activation, have permitted the determination with reasonable accuracy of many trace metals at levels of about 10^{-7}–10^{-9} g.

ESSENTIAL, NON-ESSENTIAL, OR TOXIC?[5]

Trace elements were at first generally regarded as undesirable contaminants of food, but later it was realised that some of these elements, notably iron and copper, were essential for the health and well-being of humans. Trace elements were accordingly classified as essential, non-essential, and toxic. Essential elements, like fluorine and selenium, were at first regarded as toxic, but at high intake almost all elements become toxic, and the margin between beneficial and harmful levels may be small. Hence the classification of essential, non-essential, and toxic is unsatisfactory.

Research work has gradually added to the list of essential trace elements and it is now believed that fourteen trace elements are essential for animal life, namely iron, iodine, copper, zinc, manganese, cobalt, molybdenum, selenium, chromium, nickel, tin, silicon, fluorine, and vanadium. It is probable that other elements will be added to this list as experimental techniques are further refined. Five of the fourteen elements, namely nickel, tin, silicon, fluorine, and vanadium, have emerged as essential nutrients in the diets of laboratory animals only in the last few years following the introduction of ultra-clean environments and the use of pure crystalline amino acids and vitamins. Much remains to be learned about the metabolic functions of the 'newer' trace elements and their practical significance in the health and nutrition of humans.

To state the obvious, all the elements of food come from the environment in which the food is produced. Plants extract elements from the soil in which they grow, and some of these elements are required for the plant's nutrition. We receive our trace elements from our food and air. Processing and packaging may increase the undesirable trace elements while depleting essential trace elements. It should not be surprising that minute quantities of some elements are essential for the health and well being of people for the human race evolved in an environment containing most of the known elements. The environmental relationship is illustrated by the fact that a person's body burden of sodium and potassium follows fairly closely the crustal abundance of these elements.

In the following more detailed discussion of some elements there is no significance in the selection of elements.

Essential elements

Zinc

Until recently, zinc deficiency was regarded as important only in the practical nutrition of pigs and poultry and therefore was only of indirect importance to humans. Zinc deficiency has now been demonstrated to be a public health problem in several countries. Inadequate zinc in the diet results in growth failure, in sexual infantilism in teenage individuals, and generally in impaired wound healing. Zinc-responsive growth failure has been observed in Egypt and Iran where a major constituent of the diet is unleavened bread prepared from high extraction wheat flour. In the United States the same phenomenon has been observed in young children of middle-class homes where the children consume little meat, that is, less than 30 g/day. The average adult requires 15 mg or more of zinc per day and lactating women require about twice this quantity, but the biological availability of zinc is related to the type of food consumed. For example, zinc availability in cereals and vegetables appears to be lowered by the complexing action of some cereal components and this appears to be largely responsible for zinc deficiency in Egypt and Iran. Studies indicate that only about 20–40 percent of the zinc in a mixed western diet is actually available for absorption.

The food which contains the most zinc is oysters, some of which contain more than 1000 mg/kg. Another good source of zinc is yeast, which may contain about 100 mg/kg, but meat is the most important source in a normal diet. Of course, high levels of zinc are undesirable in food, especially if the food is liquid; for example, a large number of Sydney school children were ill when they consumed a cordial which had been stored overnight in a galvanised container and had developed zinc levels of about 500 mg/litre.

Copper

Copper deficiency has not been reported in human adults even in areas where copper deficiency is severe in grazing animals. But copper deficiency is implicated in anaemia in infants from impoverished communities where the diet is based on cow's milk. Infants' diets containing less than 50 micrograms of copper per kilogram body weight per day have resulted in copper depletion and produced clinical lesions. (Copper is a component of several amine oxidases, and it is possible that in some animal species defects in the synthesis of vascular elastin and of collagen in the bones and connective tissues are due to copper depletion causing a decline in amine oxidase activity.) Sulphur in the diet in the form of sulphides can markedly decrease copper absorption, and cadmium concentrations in the order of 3 mg/kg can adversely affect copper utilisation. Infants appear to require 50–100 micrograms/kg per day, and adults about 30 micrograms/kg per day. The condition commonly known as 'kinky hair' in infants is caused by a genetic defect in copper absorption. Liver, oysters, many species of fish, and green vegetables are good sources of copper, but milk and cereal products are poor ones. Indeed, copper is an undesirable constituent of milk, fats, and fatty foods, as it is a catalyst promoting rancidity of fats even at a very low concentration. Polyunsaturated milk produced by special feeding is even more sensitive to traces of copper and fairly high levels of antioxidants must be added.

Copper is frequently implicated in food poisoning and copper in water at a concentration of about 20 mg/litre is often the problem. Under certain conditions, drinks from machines dispensing carbonated beverages may contain high concentrations of copper. Water from a copper water service may contain high copper concentrations (up to about 70 mg/kg) if allowed to stand for some days without flushing. Following illness in children immediately after eating ice blocks, 285 samples mostly of the offending brand were analysed for copper. A small number had levels of 43–80 mg/kg, these levels being sufficient to cause vomiting. This is a recurring problem and arises because some manufacturers used tinned copper moulds. The acidic mixture used to produce ice blocks will dissolve copper from de-tinned areas of the moulds if the mixture is left in the moulds for excessive lengths of time.[6]

Copper bracelets. Is there anything in the myth that copper bracelets have therapeutic value? Well this question has been investigated in Australia by W.R. Walker[7] in the department of Chemistry at the University of Newcastle. Through letters in the newspapers about 300 sufferers from arthritis were contacted (half of whom previously wore 'copper bracelets') and were randomly allocated for a psychological study. This involved wearing copper bracelets and placebo bracelets (anodised aluminium resembling copper) alternatively. Preliminary results have shown that for a statistically significant number of

subjects, the wearing of a copper bracelet appeared to bring some therapeutic benefits. Copper from the bracelet is found to dissolve in sweat and the amount lost was about 13 mg/month. If this were absorbed into the system it would amount (over twelve months) to more than the usual copper level in the body. The level in sweat was about 500 mg/kg from the bracelet but if sweat is left in contact with copper turnings for twenty-four hours the concentration rises by a factor of 100 (turns blue). The skin is permeable to most materials to some degree and copper does move through. The perceived effectiveness of the bracelet was tested with carefully prepared pyschological tests and found to be significant. It was also interesting that respondents to the questionnaire described over 100 different conventional medical treatments of their (arthritic) conditions most of which were accompanied by undesirable side-effects.

Chromium[5]

Chromium deficiency in man appears to reduce tolerance to glucose. (Chromium is a co-factor of insulin, essential to proper glucose metabolism.) Chromium deficiency may result from a grossly deficient diet. The chromium requirement of man is very difficult to estimate, because little is known of its form in food and its biological availability. Meat appears to be the best source of chromium in the diet, as it may contain several mg/kg; *yeast*-leavened bread is an important source of chromium.

"Could I 'ave a copper pair for me arthritis?"

PLATE 13.II *'For me arthritis'* (Newcastle Morning Herald, 18 September 1976)

Selenium[5]

As discussed earlier, selenium may well prove to be one of the most important elements, since it has been shown to be essential in animal diet, although many toxic effects have been described. To date, no pathological conditions in man have been identified resulting from selenium deficiency, but selenium *reduces* the toxicity of methyl mercury and selenium deficiency may reveal heavy-metal toxicity.

Selenium and sulphur can replace each other in certain chemical structures and reactions, but sulphur cannot replace selenium in its essential nutritive role. The selenium intake varies widely throughout the world and blood levels accordingly vary from about 0.8 micrograms/ml in Venezuela (selenium-rich area) to 0.07 microgram/ml in Egypt (selenium-poor area).

Cobalt[5]

Cobalt is thought to be unique in that so far it is the only trace element shown to be physiologically active in one particular form only, namely cyanocobalamin, or Vitamin B_{12}. Cobalt nutrition in humans is thus primarily a question of source and supply of Vitamin B_{12}, whereas ruminants in contrast utilise dietary cobalt since the microflora of the rumen convert cobalt into Vitamin B_{12}. Hence sheep have been given metallic cobalt pellets which remain in their rumen. All ordinary diets contain considerably more cobalt than can be accounted for as Vitamin B_{12}. Cobalt intake is about 0.15–0.6 mg/day. Levels of 25–30 mg/day can be toxic to humans.

Cobalt was implicated as the cause of heart failure leading to a number of deaths in beer drinkers consuming about twelve litres a day. The cobalt had been added to the beer in concentrations of about 1.2–1.5 mg/litre to improve foaming. At this level the heavy drinkers ingested about 6–8 mg cobalt per day. This represents a quantity that can be ingested without ill effects in normal diets, and it appears that the cardiac problem arose from the combination of poor quality diet, high alcohol consumption, and high cobalt intake.

A number of other trace elements have been shown to be essential in animal nutrition, but for manganese, vanadium, tin, molybdenum, and nickel there is no clear evidence that they are essential to humans. Many trace elements have no known beneficial effect and some of them are toxic if their levels in food are high. These elements include mercury, cadmium, arsenic, antimony, and lead. The levels of these elements naturally present in food is only very rarely sufficiently high to produce symptoms of acute toxicity, but chronic toxicity may arise because the intake of a trace element may exceed the body's ability to eliminate the element.

National Health and Medical Research Council, Standard for Metals in Food

Recommended levels presented for approval by Council at the seventy-third session, October 1971.

1. No food shall be in contact with any antimony, arsenic, or lead, nor shall it contain any antimony, arsenic, lead, tin, or other poisonous metal or compound of any of them.
2. It shall not be a contravention of this standard if the food specified in the following two schedules contains not more than the quantities of the metals or their compounds specified in each case; provided that such metals or compounds are unavoidably present in the food.

Schedule 1

*Milligrams per kilogram**

	Arsenic calculated as arsenious oxide		Lead calculated as the metal	
Phosphates for use in food	1.5		10.	
Ales and beer	0.15		0.2	
Baby foods (solid and semi-solid)	—	(0.8)	—	(0.8)
Baby foods (liquid)	—	(0.12)	—	(0.2)
Baking powder	1.5	(1.2)	10.0	(4.0)
Cheese and other foods wrapped in tinfoil	1.5	(1.2)	4.0	(2.0)
Cream of tartar	1.5		20.0	
Food additives not included in the Food Chemicals Codex, British Pharmacopoeia, British Pharmaceutical Codex, or the Standards of the British Standards Institute (relative to 100% dry active additive)	1.5			10.0
Fruit and fruit products other than dried fruit	1.5	(1.2)	4.0	(2.0)
Dried fruit	4.0	(1.5)	15.0	(2.0)
Gelatine	4.0	(3.0)	10.0	(4.0)
Glucose	1.5	(1.0)	10.0	(3.0)
Lactic acid	5.0		10.0	
Meat in tinplate containers	1.5	(1.2)	5.5	(2.5)
Milk	0.15		0.2	
Milk and milk products in tinplate containers	1.5	(1.2)	2.0	(1.0)
Non-excisable fermented drinks	0.15		0.2	
Sauces	1.0	(0.8)	10.0	(2.0)
Summer drinks and aerated waters	0.15		0.2	
Vegetables	1.5	(1.2)	4.0	(2.0)
Vinegar	1.0	(0.8)	10.0	(4.0)

*Milligrams per kilogram**

	Arsenic calculated as arsenious oxide		Lead calculated as the metal	
Fish in tinplate containers	1.5	(1.2)	5.5	(2.5)
Prescribed colourings not included in Standards of the British Standards Institute, Specification for Identity and Purity and Toxicological Evaluation of Food Colours (FAO/WHO) FAO Nutrition Meeting Report No. 38B/1964 or Specifications for Identity and Purity of Food Additives, FAO Vol. 2 (relative to 100% dry active dye)	1.5		10.0	
All other foods	1.5	(0.8)	2.0	(1.5)

Figures not adopted by the NHMRC are shown in parentheses.
*Refers to a representative sample from the total contents of the container.

*Milligrams per kilogram**

	calculated as the metal	
Antimony in beverages	0.15	
Antimony in other foods	1.5	
Cadmium in beverages	—	(0.15)
Cadmium in shellfish	—†	(2.0)
Cadmium in any other food	—	(1.0)
Copper in beverages	5.0	(2.0)
Copper in ghee	0.15	
Copper in shellfish	—*	(30.0)
Copper in other foods	30.0	(10.0)
Heavy metals other than lead in food additives not included in the Food Chemicals Codex, British Pharmacopoeia, British Pharmaceutical Codex or the Standards of the British Standards Institute (relative to 100% dry active additive)	100.00	
Heavy metals other than lead in prescribed colourings not included in Standards of the British Standards Institute, Specifications for the Identity and Purity and Toxicological Evaluation of Food Colours (FAO/WHO) FAO Nutrition Meetings Report No. 38B/1964 or Specifications for Identity and Purity of Food Additives, FAO Vol. 2 (relative to 100% dry active dye)	100.0	

Cont. next page

	*Milligrams per kilogram** calculated as the metal	
Mercury in fish, crustaceans, molluscs, the fish content of fish products and the fish content of canned fish.	0.5	
Mercury in any other food	0.03	
Selenium in any food	2.0	
Tin in any food packed in tinfoil or tinplate containers	250.0	(150.0)
Tin in other foods	40.0	
Zinc in beverages	5.0	
Zinc in gelatine	100.0	
Zinc in shellfish	—*	(500.0)
Zinc in other foods	40.0	

*An *ad hoc* committee was set up by NHMRC to set alternate levels for metals in seafoods. Its findings, e.g. 1000mg/kg Zn in shellfish, were unacceptable to FSC.

Schedule 2

Any metal other than aluminium, arsenic, antimony, calcium, copper, iron, lead, lithium, magnesium, manganese, mercury, potassium, selenium, sodium, tin, or zinc:

(a) 5.5 milligrams per kilogram in any solid food.
(b) 0.15 milligrams per kilogram in any beverage.

Non-essential elements

Tin[8]

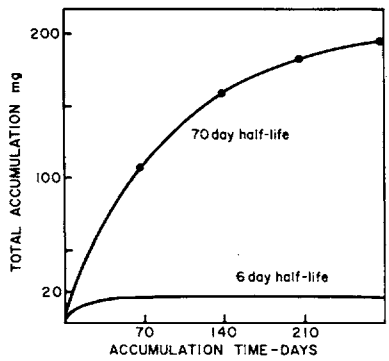
Tin in its inorganic form is generally regarded as non-toxic, but the attachment of one of more organic groups to the tin atom produces a maximum biological activity against most species when the number of attached groups is three—R_3SnX. If the chain length of the *n*-alkyl group is steadily increased the highest toxicity to mammals is attained when R = ethyl. The tributyltin compounds on the other hand show a high activity against fungi and are used as fungicides in wallpaper pastes (see Plate X). They are less dangerous to mammals. A combination of quaternary ammonium salts $R_4N^+X^-$ with tributyltin oxide gives a water-soluble formulation. Organo-tin fungicides have also been incorporated into marine paints where they protect the surface from marine growth. The triphenyltin compounds are also toxic to fungi. Increasing the chain further reduces biological activity and the tri-*n*-octyltin compounds are of low toxicity.

The largest single application for organo-tin compounds (17,000 tonnes p.a.) is as stabilisers for polyvinyl chloride plastic (see Chapter 6) and sulphur-containing organo-tins are unsurpassed in their ability to confer heat resistance to the plastic. Several dioctyltin compounds are allowed in PVC for food contact use.

PLATE 13.III *Can of roast veal*, 1824 (By courtesy of International Tin Research Institute, U.K.)

Mercury, $_{80}$Hg *(hydrargyrum; Latin: liquid silver)*

The first recorded mention of mercury was by Aristotle in the fourth century B.C. when it was used for religious purposes. Earlier still, man is known to have used vermilion (cinnabar, HgS) as a decorative war-paint (cosmetic). Paracelsus (1493–1541) introduced the treatment of syphilis with mercury. In 1799 Howard prepared mercury fulminate, used as a detonator for explosives. Economically mercury often cannot be replaced by any other metal (nor can it replace other metals), so its unique properties have proliferated its uses. With the exception of iron almost all other metals can be *amalgamated* (alloyed) with mercury. Sodium amalgams are formed in electrolysis cells used for producing chlorine and caustic soda. Many mercury compounds are used as industrial *catalysts*. Dental amalgam is prepared with 60 percent mercury plus 40 percent dental alloy (silver 65 percent min.; tin 29 percent max.; copper 6 percent max.; zinc 2 percent max.; and mercury 3 percent max.), and 'squeezed out' to about 50 percent of mercury max. It is unique in its properties. Within ninety seconds of the start of mixing all the alloy and mercury must amalgamate to a smooth plastic mass. Within three to five minutes it should set to a carvable mass and remain so for fifteen minutes. Within two hours it must develop sufficient strength, hardness, and toughness to resist biting and chewing stresses. It must expand enough to maintain a good marginal



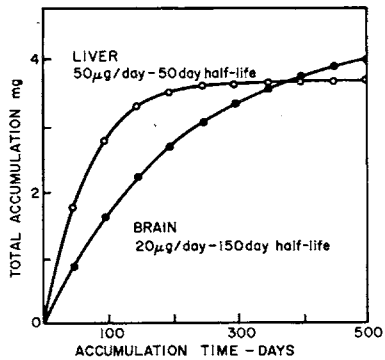
13.1 Half-life accumulation of mercury in the body. The effect of different periods of half-life on accumulation in the body. Organic mercury reaches ten times the level of inorganic mercury in nine months. (At the 2 milligram per day ingestion level shown here symptoms of severe poisoning from organic mercury would in fact appear about the third month.) Source: Tucker.[1]

seal but not so much as to overstress the tooth. It must not produce toxic or soluble salts or tarnish or produce significant amounts of mercury *vapour*.

The *equilibrium* vapour pressure of mercury (20°C—20 mg/m³ of air) is about two hundred times the recommended atmospheric concentration. In an amalgam the equilibrium vapour pressure is greatly reduced and ventilation prevents build up to equilibrium.

Inorganic mercury is swept through the body fairly rapidly by the body's natural detoxification system. This means that it concentrates rapidly in the liver and kidneys, where, if the dose is high enough, massive damage can occur, but the half-life in humans is six days (i.e. half the material ingested is excreted in six days). In contrast the half-life for organic mercurials is about seventy days.

What this means is shown in Figure 13.1. A daily intake of 2 mg of *inorganic* mercury will not reach a steady state level of 20 mg in the body however long the exposure. On the other hand a similar intake of *organic* mercury would top 200 mg within a year—although you would be dead long before that. Even worse is the fact that although the best biologically protected areas such as the brain or foetus have a much slower uptake of organo-mercury, they have a much slower excretion as well.



13.2 Accumulation of organo-mercury in the brain and the liver.
Source: Tucker.[1]

Figure 13.2 shows accumulation in brain and liver assuming a guessed 20 percent and 50 percent absorption respectively of a daily dose of 100

micrograms—and a longer brain half-life. A dose of 100 micrograms would be contained in a normal single meal of fish that contained 0.5 mg/kg mercury wet weight (the permitted maximum in Australia). Brain half-life is not known accurately but is believed to be considerably longer than that of the liver. Half-life in the testes is also long. According to some scientists, symptoms of damage to the brain first appear at concentrations as low as 3 micrograms per gram of brain tissue—which would be reached in fifty days on this half-life basis. Other scientists believe that 20 micrograms per gram of brain tissue is the damage symptom threshold. This explains the devastating effect of organo-mercury poisoning—the cells of the brain, which do not reproduce and have limited repair facilities, are destroyed.

It would seem that a sensible precaution would be to restrict severely the use of organo-mercury compounds. However, one of the biggest mercury poisoning disasters, namely at Minamata (Japan) in 1953 was due to the effluent of a polyvinylchloride factory using inorganic mercury which was *converted* in localised areas in the sludge at the bottom of a bay by anaerobic microbes (oxygen depleted conditions) to organic mercury so as to enter food chains in its most deadly form. The preferential methylation of mercury by methane-producing anaerobes results in most aquatic animals containing monomethyl-mercury, the concentration being a rough guide to the species position in the food chain. Thus shrimps, which are low in the chain, generally contain less than 0.05 mg/kg mercury, and sharks which are at the top of the chain, contain levels often in excess of 2 mg/kg, while marlin and swordfish can be around 16 mg/kg.

Limits for metals such as mercury in fish are set as so many ppm wet weight (i.e. the fish weight) or more correctly mg/kg. The original Minamata data were in mg/kg dry weight (i.e. fish without water) and this yields a number about ten times higher (because fish are ~90 percent water). Because this was not appreciated initially, danger levels were set too high! As things stand 15–30 micrograms a day is within the range of the normal daily intake from 'uncontaminated' food (limit 0.03 mg/kg) and this seems to be about the maximum level that the most sensitive section of the population (i.e. children) can tolerate without fear of damage, so that setting 'safe' limits for contaminated foods in the case of mercury may not be realistic. About *150 g* (5 oz) of fish with the maximum of 0.5 mg/kg of mercury eaten by a 25 kilogram child *once a week* alone contributes the maximum allowable daily intake (30 micrograms per day per 75 kilogram body weight). There is also a real danger in dealing with average daily intake. If it takes 40 milligrams of mercury to kill and I get the 40 milligrams while you get none, according to the average we are both safe. But I will be dead. It is the possible repetitive dose taken by an individual that is critical. While the natural quantity of mercury in sea water is about 35×10^6 tonnes only, it takes tens of thousands

of years for metallic marine pollutants to disperse *uniformly*; meanwhile high concentrations build up in discharge areas: estuaries, coastal areas, and shallow continental shelves—i.e. the food productive areas. The other factor that is very important is the ability of marine animals to concentrate heavy metals. An oyster can concentrate mercury by a factor of 100,000. If the *natural* mercury level in water is about 50 parts in 10^{12} (a million million) then an oyster might be able to concentrate this to 5 mg/kg.

Obviously oysters should not become a staple diet item. The concentrating factors of some marine organisms are given in Table 13.1.

TABLE 13.1 *Average abundance of certain trace elements in the earth's crust and sea water, and concentration factors in selected sea organisms*
(all values are in mg/kg)

Element	Earth's crust	Ocean water	Oceanic residence time (years)	*Enrichment Factors* Organism		
				Scallop	Oyster	Mussel
Be	2.80	0.000001	150	—	1,000,000	—
Ag	0.07	0.0001	2×10^6	2,300	18,700	330
Cd	0.20	0.00005*	5×10^5	2,300,000	320,000	100,000
Cr	100.00	0.0006	350	200,000	60,000	320,000
Cu	55.00	0.003	5×10^4	3,000	14,000	3,000
Mn	950.00	0.002	1400	55,500	4,000	13,500
Mo	1.50	0.01	5×10^5	90	30	60
Ni	75.00	0.002	1.8×10^4	12,000	4,000	14,000
Pb	12.50	0.00003	2×10^3	5,300	3,300	4,000
V	135.00	0.002	1×10^4	4,500	1,500	2,500
Zn	70.00	0.005	1.8×10^5	28,000	110,000	9,000
Hg	0.08	0.00005	4.2×10^4	—	100,000	100,000

*0.00002 to 0.0008 ppm in some NSW waters.
Source: Doolan and Smythe.[9]

Oysters grown in unpolluted water may contain as little as 0.05 mg/kg of cadmium, while oysters grown in polluted water may contain cadmium in excess of 5 mg/kg.

Zinc and cadmium are mutually inhibitory in both absorption and retention processes, perhaps due to competition for protein-binding sites. High zinc intake may reduce the toxicity of cadmium and conversely high cadmium intake with marginal zinc deficiency may aggravate the deficiency. Unfortunately, as we saw, the residence time of cadmium in the body is very long.

Table 13.2 gives the results of analyses for trace metal content in a number of Australian seafoods.

TABLE 13.2 *Trace metal content of marine products based on wet weight—New South Wales*

Food	Samples (no.)	Methyl mercury (mg/kg)	Total mercury (mg/kg)	Cadmium (mg/kg)	Copper (mg/kg)	Zinc (mg/kg)	Lead (mg/kg)	Other metals (mg/kg)
Fish		0.12	0.50	1.4(6)	6.54(6)	71.0(6)	0.36(6)	2.0(56)Selenium
organs	62	(0.04–1.06)	(0.05–6.17)	(0.10–3.60)	(1.25–18.0)	(6.8–216)	(<0.02–0.6)	
Snapper		0.17	0.18	0.04(2)	0.02(2)	6.1(2)	0.65(2)	0.3(237)Selenium
(Chrysophrys auratus)	293	(0.01–1.90)	(0.01–2.01)			(1.3–10.8)	(0.5–0.8)	
Marlin		0.31	0.7(54)					0.6(36)Selenium
(Makaira sp.*)*	49	(0.06–0.73)	(0.09–3.25)					
Tuna		0.37	0.38	0.04(18)	0.40(18)	5.1(18)	0.46(18)	0.5(8)Selenium
(Thunnus sp.*)*	20	(0.11–0.94)	(0.11–0.98)	(0.02–0.08)	(0.18–0.46)	(1.8–24.0)	(0.1–0.8)	1.0(8)Arsenic
Tailor		0.16	0.17	0.036	0.33	11.8	0.64	0.5(4)Selenium
(Pomatomous saltatrix)	9	(0.05–0.26)	0.05–.28)	(0.02–0.07)	(0.2–0.5)	(2.5–26.5)	(0.06–1.0)	0.1(4)Arsenic
Bream		0.20	0.21	0.033	0.53	6.9	0.8	
(Acanthopagrus sp.*)*	6	(0.11–0.32)	(0.12–0.34)	(0.03–0.04)	(0.1–1.2)	(1.6–13.0)	(0.5–1.1)	
Jewfish		0.35	0.39	0.085	7.1	69.8	0.68	
(Sciaena antarctica)	4	(0.06–0.48)	(0.14–0.51)	(0.02–0.24)	(0.3–26.3)	(3.3–264)	(0.3–1.6)	
Shark		0.15(4)	0.45	0.01(4)	1.04(4)	2.5(4)	0.22(4)	1.1(4)Arsenic
	5	(0.09–0.26)	(0.09–1.6)	(0.01–0.02)	(0.82–1.26)	(2.3–2.6)	(0.17–0.26)	
Miscellaneous		0.026	0.05	0.03(10)	0.38	5.2	0.56(10)	1.1(7)Arsenic
fish	9	(0.01–0.05)	(0.01–0.11)	(0.01–0.11)	(0.22–0.55)	(2.8–7.7)	(0.1–0.9)	
Canned			0.127				1.33	18.7(30)Tin
fish	30		(0.01–0.50)				(<0.1–4.6)	
Oysters*				0.93	45.2	650(168)	0.72	1.0Arsenic
	165			(0.15–3.62)	(21–86)	(230–1700)	(0.02–2.2)	

Average figures are followed by the range in parentheses. Where less analyses were carried out for individual metals, the number of samples analysed given in parentheses.

*Each oyster sample analysed is a homogenate of the flesh of 20 oysters.

Source: Health Commission of New South Wales[6]

Cadmium

Cadmium is entirely a by-product metal extracted from zinc and lead. It looks like zinc but on bending the coarse-grained cadmium gives a crackling sound similar to that given by tin. It is used for plating, bearing alloys, soldering aluminium (Cd–Zn), orange-red glaze in ceramics, in nuclear reactors as a shield against neutrons and as a control rod. It is used in nickel oxide cadmium accumulators. Organo-cadmium compounds are used as PVC stabilisers and as mould release agents for plastic articles.

Large concentrations of cadmium have bizarre effects. In 1955 the Japanese reported an affliction called 'Itai-Itai Byo'. The name mimics the cries of sufferers and has been translated 'Ouchi-ouchi disease'. The disease takes a long course of increasing painfulness which, beginning with simple symptoms such as 'joint pains', ends with total and agonising immobility as the result of skeletal collapse. Cadmium leads to bone porosity and to the total inhibition of bone repair so that the load-bearing bones of the skeleton suffer deformation, fracture, and collapse. In Japan the disease has been associated with rice and soya (in the range of 0.37–3.36 ppm dry weight) in the local diet. In Japan the disease is also known to occur in workers engaged in the preparation of cadmium-based paints.

PLATE 13.IV *Zinc Point casino*

Cadmium is chemically related to zinc (see Table 13.3—they are in the same column) and it is found together with zinc in nature and in zinc products. The zinc/cadmium group is also related to the magnesium/calcium group (for reasons which can be found in elementary chemistry books) so that is why cadmium (and strontium) can interact so effectively with the calcium in the bones. The mutual replaceability of metals depends both on their *chemical similarity* and *the size of the atomic ion.*

TABLE 13.3 *Ionic radii in picometres (10^{-12} metre)*

Group IIA			Group IIB			Group IV
Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}
99	113	135	74	97	100	121

Arsenic

Arsenic is a component of almost all soils and hence all food contains trace amounts of arsenic. Oysters, which concentrate arsenic, probably contain the highest levels. The arsenic in marine animals is organically combined; it does not appear to be very toxic and is rapidly excreted by man, apparently unchanged.

Organic arsenicals are widely used as additives in stock foods because these compounds appear to stimulate growth and improve food utilisation. Animal diets typically contain 35–40 mg/kg arsenic at which level there is some accumulation in edible tissues, usually less than 0.5 mg/kg in muscle and 2.0 mg/kg in liver. Before the advent of DDT, arsenic was one of the principle pesticides, being used as both insecticide and herbicide; therefore it is likely that arsenic levels in food were then much higher than they are today as very little arsenic is now being used in agricultural practices.

There appears to be a level of arsenic intake above which arsenic accumulates in the system and below which the body appears to be able to excrete all the arsenic ingested. Normal intake is about 0.007–0.6 mg/kg body weight per day and the acceptable load is tentatively set at 0.05 mg/kg body weight per day. It appears unlikely that any problem would arise from this element; arsenic poisoning is only likely in cases of individuals occupationally at risk or who happen to be attempted murder victims.

Lead

Lead was used in prehistoric times for glazing pottery by the early Egyptians. It was used by the Romans in water pipes and storing wines (the latter being a possible source of lead poisoning).

In 1970 the primary producers of lead were, in millions of tonnes: United States, 0.57; Australia, 0.50; USSR, 0.49; Canada, 0.40; Mexico, 0.20; Peru, 0.17; Yugoslavia, 0.14; Bulgaria, 0.13; China, 0.11. In the same year, the United States also reclaimed 0.6 megatonnes of lead from secondary sources and imported an equivalent of 0.35 megatonnes, 20 percent of this from Australia. In fact the total consumption of lead in the United States was 1.36 megatonnes of which 44 percent went on lead-acid storage batteries—but most of which is recycled and about 0.35 megatonnes were salvaged from old batteries. Lead tetra-ethyl additive for petrol took about 10 percent of the world lead consumption in 1970, the United States consuming about 0.26 megatonnes per year for this purpose. The USSR also uses leaded petrol. Most of the *bromine* produced from sea water is used to produce ethylene dibromide which is added along with lead tetra-ethyl in order to exhaust the lead from the cylinder as volatile lead dibromide (for each molecule of lead tetra-ethyl there are 0.5 molecules of ethylene dibromide and 1.0 molecule of ethylene dichloride in the usual antiknock additive).

The toxicology of lead is complicated. Inorganic (Pb^{2+}) lead is a general metabolic poison and is cumulative in man. It inhibits enzyme systems necessary for the formation of haemoglobin (levels of urinary δ-aminolaevulinic acid are monitored to indicate this interference). Children and young people appear specially liable to suffer more or less permanent damage. Lead can replace calcium in bone, so tends to accumulate there; but an unplesant feature is that it may be remobilised long after the initial absorption—e.g. under conditions where calcium is suddenly needed by the body such as feverish illness, during cortisone therapy, and also in old age. It can cross the placental barrier, and thereby enter the foetus.

Lead alkyls (organo-lead) such as lead tetra-ethyl are even more poisonous than Pb^{2+}, and are handled quite differently in the body. Lead tetra-ethyl causes symptoms of mimicking those of conventional psychosis. There is little or no elevation of blood lead, so correct diagnosis is difficult in the absence of suspected exposure. Yet leaded petrol has been almost a 0.1 percent hydrocarbon solution of this compound. The danger of using leaded petrol for degreasing or cleaning is generally not appreciated. Man has evolved in the presence of a certain amount of lead—it averages about 10 ppm in the earth's crust. We know that over 2 megatonnes of lead is mined each year in comparison with about 180 kilotonnes estimated to be naturally mobilised and discharged into the ocean and rivers.

Typically an urban adult breathing air containing, say, 3 micrograms of lead per cubic metre and respiring about 15 m^3 of air per day will absorb 20–25 micrograms of lead per day (about 50 percent efficiency in absorption). A normal daily diet containing about 300 micrograms of lead will lead to about the same amount of absorbed lead (5–10 percent efficiency in absorption). Fallout of airborne lead also adds to the lead present in food and water.

Even the present average blood lead levels of adults in industrial countries are not far below those which can lead to obvious clinical symptoms.

CONSUMER USE OF METALS[10]

Our use of metals has been increasing rapidly over the last decade, as is shown by Table 13.4.

TABLE 13.4 *World consumption of metals 1964–73 (10^3 tonnes)*

	1964	1966	1968	1970	1972	1973
Aluminium	6110	7592	8841	10030	11768	13601
Copper	5980	6421	6506	7284	7985	8786
Lead	3128	3306	3517	3885	4158	4421
Zinc	3968	4221	4668	5056	5709	6283

The effect of resource consumption is illustrated by statistics such as the fact that between 1950 and 1970 we consumed half of all the zinc ever produced in the world up to 1970. Production of lead during 1970–1980 will exceed total production during the whole of the last century.

Zinc is used mainly in galvanising steel, to protect it from corrosion. Die-casting has moved from zinc to aluminium while plastics have taken over roles in low stress and decorative products. Zinc is used in brass. Zinc-coated steel guttering is being replaced by PVC. There has been a demand for zinc oxide as a coating for the papers of a document-copying system as well as its traditional use in rubber reinforcement.

Lead is showing significant change in its usage patterns—Table 13.5.

TABLE 13.5 *Major end-use for lead 1964–74 (10^3 tonnes)*

	United States		Japan		United Kingdom		W. Germany	
	1964	1974	1964	1974	1964	1974	1964	1974
batteries	389	669	64	123	188	80	94	118
tetra-ethyl lead	203	227	—	—	35	56	—	—

In developed countries the storage battery is showing strong growth while the use of lead for sheathing power transmission cables is declining because of replacement by plastics and aluminium. Lead in petrol is a declining use. Lead is easy to recycle because it is relatively inert (over 80 percent of lead in car batteries is recovered). Metal used in petrol is currently completely lost but might be recovered with suitable mufflers.

Recycling

Recovery of metals from consumer durables, such as scrap motor cars, washing machines, refrigerators, involves, as its main cost, the delivery of the items to a processing plant. The rate of recycling has remained static even though quite sophisticated technology exists. Part of this malaise is being overcome through publicity and more efficient collection—particularly for glass, paper, and aluminium. Some products such as the 'tin' can (which is made from steel, tinplate, lead solder, and often an aluminium lid) cannot be recycled. The scrap processors can themselves be a source of pollution—e.g. fume emissions in copper cable-stripping and car component recovery. To some extent these problems have been overcome.

TABLE 13.6 *Recycled metals as a percentage of total consumption—United Kingdom*

	1964	1966	1968	1970	1972	1974
Zinc	23	24	24	25	24	24
Lead	57	57	65	67	64	61
Copper	35	39	42	41	35	38
Aluminium	33	33	33	33	34	28

(The United Kingdom Medical Research Council's dubious assurance on lead had been given in the House of Lords on 10 March 1971.)

A TRAGI-COMEDY IN ONE ACT:

Scene: House of Lords; the time 2.40 P.M.

The Characters: Lord O'Hagan, a young and vigorous peer who takes seriously both social and environmental problems. Lord Mowbray and Stourton, Government spokesman on the environment. And others.

LORD O'HAGAN: My Lords, I beg leave to ask the Question which stands in my name on the order paper. [To ask Her Majesty's Government what they intend to do about lead in petrol.]

LORD M & S: As I told the noble Lord on March 10, H.M. Government are considering whether any action is needed to reduce the lead content of petrol.

LORD O'HAGAN: . . . As the noble Lord is not able to speak again, may I ask him a question so that he can? Does he accept that catalysts in after-burners are poisoned by lead? And even if he is not able to accept that will he publish the evidence on which he based his earlier and rather complacent reply?

LORD M & S: . . . catalysts used in America for the after-burner are poisoned by lead. May I ask the noble Lord to repeat his second question?

LORD O'HAGAN: . . . will the noble Lord publish the evidence on which he based his views?

LORD M & S: . . . The evidence on which I based my information was worked out by the Medical Research Council, as I informed him. I can absolutely vouch for its accuracy.

LORD O'HAGAN: . . . Is the noble Lord saying that what is poisonous in America is not poisonous here?

LORD M & S: No, my Lords. What I said is that the catalyst is destroyed by any presence of lead in petrol. . . .

LORD SHACKLETON: My Lords, is the noble Lord aware that I think the House is nearly as confused as he is by his answer? I wonder whether he would now take advice from the noble Lord, Lord O'Hagan, and choose an opportunity to speak again . . . ?

LORD AMULREE: My Lords, surely the issue is whether the amount of lead in petrol which comes out of exhaust fumes . . . is likely to be deleterious to health?

LORD M & S: . . . We accept that lead in itself is not a good thing to have: we are not going to give ourselves more. What we must also realize, though, is that even the natives in New Guinea have an enormous intake of lead. The amount of extra lead we get from pollution by exhaust gases is comparatively small. I accept that we would be better without it, but if we do without it we have to use a lower octane petrol . . . it is a matter of economics and sense.

LORD HENLEY: My Lords, how will this affect the lead in the noble Lord's pencil?

LORD SHACKLETON: . . . is the noble Lord aware that he has made a very serious statement. I understand that there are cannibals in New Guinea. Is he aware that there is already concern about the edibility of Western people because of the amount of DDT in them? How do DDT and lead mix? Is this not a matter for the Food and Agriculture Office?

LORD M & S: My Lords, I can assure the noble Lord the leader of the Opposition that we are not importing any cannibal meat from New Guinea.

With this, their noble Lordships turned their attention to another matter, that of religious broadcasting.

Source: Tucker,[1] citing *Hansard*, vol. 316, no. 76, 24 March 1971

APPENDIX 13.1

Periodic Table of the Elements

APPENDIX 13.2

SOME FACTS ABOUT LEAD GLAZES FOR WORKSHOP AND STUDIO POTTERS

(a pamphlet issued by the National Health and Medical Research Council, 1975)

Approved by NHMRC at the Seventy-Seventh Session, November 1973

Introduction

For centuries, lead compounds have been included as constituents in pottery glazes because of the many advantages that accrue to both the potter and the consumer from their use. Lead compounds readily dissolve other essential ingredients such as alumina and silica to form a glaze with a high gloss and brilliance. Lead glazes have a relatively low melting point and a wide softening range. The low surface tension and viscosity of the melt allow minor imperfections on the surface of the clay body to be covered and a ready release of trapped air and good healing of the surface. Generally, there is sufficient reaction between the molten glaze and the underlying clay to form an intermediate layer which relieves stresses and offers a high resistance to crazing and devitrification. The affinity of lead glazes for colouring agents permits the development of a wide range of colours, many of which are difficult to attain by other means. It is often claimed that lead cannot be replaced by any other material that will provide comparable aesthetic effects with equivalent ease and effort.

Lead is, however, a toxic metal. When lead glazes are applied to surfaces used in contact with food and beverage, lead may be leached out by acids present in the food and beverage at levels which are toxicologically unsafe for human consumption. This hazard, primarily due to insufficiencies in glaze formulation, application and firing has been recognised for a long time. Research, however, into formulation, application and firing procedures has enabled lead glazes to be produced.

Ceramic Glaze

A ceramic glaze is a thin glossy coating fused onto the clayware body. An analogy rests between a glaze and a mixture of rock components fused together at a high temperature, much the same way as nature produces molten lava in an erupting volcano which then coats the earth with a glossy substance. Volcanic rocks can be pulverised and used as glazes. However, the major difference between a lava and a man-made glaze is that, in the latter, a flux is added.

Glazes are formulated from basic compounds such as alumina and silica with derivatives of barium, boron, calcium, lead, lithium, magnesium, potassium, sodium, strontium and zinc. In addition, the formulations may include colouring agents containing antimony, cadmium, chromium, cobalt, copper, iron, manganese, nickel or selenium, as well as opacifiers such as tin, titanium and zirconium. Consequently, the chemistry of glazes is extremely complex, being further complicated by the reaction between the glaze and the clay body during the firing operation.

Flux

A flux is an additive which permits the basic components of a glaze to fuse together at a lower temperature to form a homogeneous mass. The more commonly used fluxes are compounds of boron, calcium, lead, potassium and sodium.

Frit

A frit is a pre-formulated glaze. Selected raw materials are carefully proportioned, mixed and fused in a high-temperature furnace to form a glass. The glass mass is then milled to a fine powder. The frit is evenly dispersed in water and applied to the surface of the shaped piece. During firing the particles re-melt to form a thin layer of finished glaze. By the use of frits it is possible for the potter to exercise rigid control over the formulation of his glaze.

Frits are generally designed to be either lead-free or to contain a high percentage of lead. In the latter case, lead is chemically bound with the other constituents so that the level of leachable lead from the finished surface is negligible, even under the most stringent conditions. Lead leachability depends on different formulation parameters and is not necessarily related to the actual content of lead in the glaze. Frits are designed to be safe when used by themselves or with compatible on-glaze decorations and other accessories. Their indiscriminate use with incompatible materials can lead to increased lead leachability. Such practices are to be strongly discouraged. Not all manufactured lead frits are safe. In some cases lead frits are merely fluxes. Many commercial glazes are designed exclusively for the decoration of artware such as tiles, sculptures and architectural ceramics. The normal use of such wares does not present a health hazard. Care should, however, be exercised to ensure that such commercial glazes are not used on wares that could contain food and beverage.

Formulation

Instead of purchasing a commercial frit, the potter may elect to prepare glazes from his own basic constituents. A multitude of published recipes are available for this purpose. In the selection of a glaze recipe only those proven reliable by laboratory examination of the finished article should be considered.

It is frequent practice to reduce the melting point of a glaze by the addition of a greater amount of flux. In so doing, the potter should realise that he may present serious health hazards both to himself and the consumer. Some potters also, for economic reasons, pool excess glazes and then use the haphazard mixture. This practice is to be strongly discouraged because of the uncontrolled imbalance of formulation that inevitably results.

With a full understanding of the physical chemistry of glazes and proper care to formulation, safe glazes can be obtained. A very wide freedom of choice is permissible when glazes are intended for ornamental ware alone.

Colouring Agents

Problems sometimes occur when colouring agents are introduced. Although a lead frit or a balanced formulation may be safe, the incorporation of oxides or carbonates of copper or cobalt, and to a lesser extent those of nickel and of other metals, can cause a release of lead from the silicate matrix. Regardless of the care taken in firing, research has shown that the association of copper or cobalt with a lead glaze triggers off chemical interactions which predispose to a marked increase in lead leachability. In general, any glaze which finishes with a blue or green colour should not be applied to a surface of a utensil intended to contain food or beverage. In some instances, black surfaces can also be unacceptable.

Leadless Glazes

A wide range of leadless glazes with well-balanced formulations are available. When doubt prevails on the reliability of a lead glaze intended for domestic ware, preference should be given to the use of a leadless glaze from a reliable source. Both leadless frits and many leadless formulations have been developed which provide excellent results

with an attractive and serviceable finish. Leadless glazes are available which mature at temperatures above 1200°C and below 1200°C respectively for stoneware and ceramicware. In some instances where a high percentage of alkali is present, advanced knowledge and skill are required to avoid subsequent deterioration of the surface. Some formulations are intended entirely for art glazes on ornamental ware.

Kiln Operation

Adequate glaze maturation requires due care to firing conditions, particularly kiln temperature, firing time and the kiln atmosphere. At temperatures below 1080°C glaze constituents may not react sufficiently with each other or with the clay body to provide adequate maturation. Sufficient time is also required to allow the products of reaction between the glaze and clay body to migrate through the glaze network, thereby strengthening and making the glaze more impervious. For adequate maturation, a heavy glaze application (2mm or more) requires considerably longer firing time than that of a thin layer. The correct firing schedule for temperature and time can be conveniently achieved by the use of pyrometric cones.

Oxidising conditions in the kiln atmosphere are essential. Without proper controls, products of combustion in gas, oil and wood fired kilns may result in reducing conditions. These conditions favour the reduction of metallic compounds to a form in which they can no longer be securely bound to silica, alumina and other adjuncts.

An improperly fired glaze cannot be made safe by refiring, washing with acids or baking in an oven.

Occupational Hygiene

Unless handled with due care and with the use of proper equipment, lead glazes are hazardous to the health of the potter. Good housekeeping is important. The workshop should be vacuumed and mopped regularly. Any spill of material should be immediately damp sponged and, if dust appears, the workshop vacuumed thoroughly. Dust of any kind is to be avoided. All operations which disperse dust and fumes should be controlled by forced exhaust ventilation. A dust respirator complying with the specification of Australian standard AS Z18 should be used when dry glazes are mixed or ground. The spraying of glazes should only be done in a well-ventilated booth exhausted to the exterior.

As lead volatilises during the firing procedure, the atmosphere around the kiln may, under certain circumstances constitute a health hazard. The kiln should therefore be located in an area where children or adults are not unwittingly exposed to lead fumes. The kiln should also be carefully fitted with a hood exhausting to the exterior.

Personal Hygiene

Extreme care should be taken to avoid transferring lead from the hands to mouth. If gloves are not worn when handling glazes, hands and fingernails should be thoroughly scrubbed upon finishing work. Food, drink and tobacco should not be brought into the workshop area. Changes of protective clothing should be provided for use in the workshop; but never worn elsewhere. Children should not be allowed to enter a workshop unless supervised by a responsible person.

Recommendations of the National Health and Medical Research Council 73rd Session, October 1971

Lead Hazards from Pottery Glazes

Council noted that, following cases of poisoning by lead leached from pottery glazes, Australian and overseas investigations have shown that a number of pottery food and

drink utensils are available from which lead may be leached by acid foods such as fruit juice, soft drinks, wines, cider, vinegar, sauerkraut and tomatoes and the use of such utensils may therefore constitute a threat to human health. Council also noted that the implications inherent in the results of these investigations have led to a strengthening of overseas regulations concerned with pottery glazes on food and drink utensils.

Council considered that pottery utensils with glazes which release 7 ppm or more of lead, as determined by the ASTM method, C-555-71, 'Estimation of Lead Extracted from Glazed Ceramic Surfaces', are unsafe for use as human food or drink containers. Council therefore recommended that:

(i) legislation be enacted by the Commonwealth and the States to prohibit the sale of pottery food and drink utensils which may, by the release of lead, be hazardous to human health;
(ii) glazing formulations containing lead which are available in Australia should be labelled "WARNING this glazing material contains lead';
(iii) amateur or handicraft potters should not apply glazes bearing lead to the insides of food and drink utensils unless they are able to ensure that the techniques they employ preclude the subsequent release of unsafe amounts of lead from the glaze; and
(iv) acidic foods and beverages should not be stored in pottery containers unless the containers are known not to release significant amounts of lead

75th Session, May 1973

Teaching of Pottery Crafts in Schools

Council recommended that in the teaching of pottery crafts in primary and secondary schools lead compounds should not be used in the making of utensils that could be used as containers for food and beverages.

77th Session, November 1973

Uniform Poisons Schedule of the Uniform Poisons Standard

Schedule 6

New entry: Lead, compounds of, except in preparations for therapeutic or cosmetic use.

**Appendix A*

New entry (q) 'unless adequately fired, utensils glazed with this preparation must not be used as containers for food or beverages; to do so may cause lead poisoning'. Glazing preparations containing lead compounds.

List of Exemptions

Amend entry for glazes to read: glazed pottery.

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*Required to be labelled with a warning statement.

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Chapter 14

EXPERIMENTS IN CONSUMER CHEMISTRY

INTRODUCTION

In April 1937 Consumers' Research Inc. Washington NJ produced a 40-page booklet *Consumers' Test Manual*, 'Comprising simple and readily-applied tests of common household articles and supplies suitable for use by students of chemistry, physics, general science, household arts, and by consumers generally.'

The introductory note starts off with the following statement:

> It was expected that the task of compiling this *Test Manual* would be a fairly easy one and that it would be completed within a few months after work upon it was begun, but the amount of material available was so great and the necessity of careful selection and checking of diverse and conflicting methods so obvious as the work proceeded, that a far more ambitious job was done than was originally intended.

The price charged was a nominal 25 cents in order to make it generally available. Unfortunately the foreshadowed additional sections

> on the efficiency and safety of electrical appliances, performance of radio sets, strength and wear resistance of textiles and paper, accuracy of time pieces, efficiency of flashlights, cutlery, can openers, kerosene, gas and electric stoves

never appeared.

The Manual gives a method for determining the water content of butter by distillation with xylene on which the Dean Starke experiment described in this chapter is based. It gives the wool test for coal tar dyes, the turmeric test for borax (and *vice versa*), starch in face powders, sulphides in depilatories, lead in petrol, lead in paints, water in oil paints(!), gas efficiency of baking powder, ammonia in household ammonia, lead in drinking water (dithizone test). There is a strong section on the analysis of soap starting with the water content, followed by carbonates, silicates, rosin, free alkali, sugar, and starch.

The quality of eggs is checked in detail. An interesting and simple test (the Preece test) for the *uniformity* of coating of zinc on galvanised sheet metal and wire fencing is given. One of the tests for bleached flour unfortunately involves a dangerous reagent but this could be modified. There is an appendix on methods for producing standard solutions.

In 1939 Professor Römpp produced his *Chemie des Alltags* (*Chemistry of Everyday*), which has gone through twenty-two editions and 127,000 copies (1975) and is now edited by Professor Raaf. Its 300 pages make little allowance for dilettantes and although occasionally lighthearted (by German standards) it is a serious textbook organised in an alphabetical format ('Von Alkohol bis Zündholz'). It had an accompanying volume *Chemische Experimente die gelingen* (*Chemical experiments which work*) expressing the same sentiment as Consumer Research on the accuracy of the literature.

PRACTICAL SESSION —HOW TO TEST FOR WHAT'S IN IT AND HOW MUCH

The aim of this chapter is to introduce you to the ways chemical analyses are carried out. Modern analytical techniques involve sophisticated machines as well as the traditional boiling flasks and test tubes. A tremendous amount of care and skill and patience is required to obtain accurate and precise measurements of low concentrations of materials. Often the search for one substance will be inhibited by interference due to the presence of another. I have chosen a number of (atypical) examples. They are chosen to be relevant and interesting as well as *safe* and *simple* to perform.

Safety

A chemical laboratory has certain hazards which chemists learn to assess and deal with almost by instinct after years of contact and it is difficult to condense these in a few lines. What follows is thus rather sketchy.

1. You must wear adequate protective clothing—preferably a laboratory coat but otherwise clothes for which a localised change of appearance does not represent a catastrophe—and 'sensible' shoes which cover the top of the feet.
2. You must never eat or smoke in the laboratory and make sure you wash your hands thoroughly after the lab.
3. Heat solutions only electrically or via a hot water bath except for aqueous (water) solutions where a bunsen burner (flame) can be used. Practically all solvents are flammable (will burn).
4. Chemicals are manipulated with spatulas (nickel spoon-like objects) and fingers are *never* allowed to come in direct contact with chemicals. Any spillage should be washed off immediately.
5. Carefully label all containers used for holding chemicals and solutions.

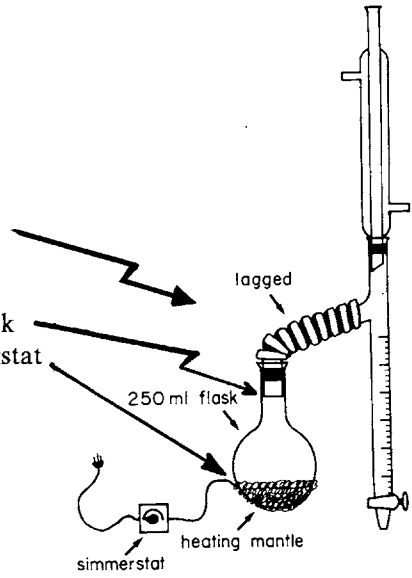
Reports

You should make notes of what you are doing and then write a short report on the conclusion of your experiment which is useful to you and others attempting to repeat similar work.

EXPERIMENT A
DETERMINATION OF WATER (AND FAT) CONTENT USING A DEAN AND STARKE APPARATUS

Equipment needed

1. Dean and Starke apparatus
2. fume hood
3. water bath
4. 250 ml round bottomed flask
5. heating mantel with simmerstat
6. toluene or cyclohexane
7. weighed vials and beakers



14.1 Dean and Starke apparatus

Principle involved

The Dean and Starke apparatus is shown in Figure 14.1. It is used to determine the amount of water present in such materials as detergents, oils, meat, cheese, etc.[1] We can also use it to determine the amount of fat or fat-like material present in a product.

The principle of the experiment is that in a mixture of toluene and water, boiling occurs at 85°C and both water and toluene are in the vapour. On condensing, two layers of liquid are formed: a bottom layer of water (with 0.06 percent toluene dissolved) and a top layer of toluene (with 0.05 percent water dissolved). The relative volumes are 18 percent water and 82 percent toluene. The excess toluene flows back into the flask and distils back over with more water. (The sample size should be such as to provide no more water than will fit into the calibrated arm.)

The experiment should be carried out in a fume hood because toluene vapour can be harmful over a period of time. If a hood is not available, cyclohexane should be used. It is less efficient (carrying over only 8.5 percent water) but less harmful.

TABLE 14.1 *Fat and water analyses of ground meat*

Description	*Analyses*	*% fat*	*% water*
Topside mince	(2)	16.0	66.5
	(2)	16.4	64.9
	(2)	19.1	63.1
Hamburger mince	(4)	8.0	71.8
	(4)	12.6	66.6
	(2)	13.2	67.7
	(2)	13.3	69.7
	(2)	13.5	67.4
	(2)	14.5	68.2
	(2)	20.2	63.9
Sausage mince	(2)	16.1	54.1
	(2)	17.5	50.9
	(2)	19.3	51.7
	(4)	23.7	55.1
	(2)	24.2	53.3
	(2)	26.6	47.6
	(3)	27.6	50.5
	(2)	28.5	47.8
	(4)	33.3	50.0

The prices paid in October and November 1974 were as follows:
Topside mince, 67–69 c/lb
Hamburger mince 49–86c/lb,
Sausage mince 30–38c/lb

Source: Canberra Consumer No. 50, 1975, 9

However, if ethyl alcohol is present (as in some of the recent concentrated detergents), use hexane so that the bottom layer contains mainly water and ethyl alcohol and only a little of the carrier hydrocarbon. The efficiency of

hexane is low (3.8 percent water) and so the process is much slower. In any event the concentrates are hygroscopic and should be measured immediately on opening or stored in sealed containers.

If in doubt as to the suitability of the method for a product, it is best to make up a standard sample of known composition.

Method

(i) Detergents

10.0 g of liquid dishwashing detergent is distilled with 90 ml of toluene in a Dean and Starke apparatus for about twenty minutes or until no more water is seen to be distilling over. The heating should initially be slow to avoid excessive frothing and carry-over of detergent. The amount of water distilled over (as the bottom layer) is measured approximately as the volume in the calibrated arm but is best collected in a pre-weighed vial and weighed.

After the toluene has been poured out of the flask any solid residue remaining should be noted. A white precipitate suggests a salt—either common salt, NaCl, or Na_2SO_4, etc. A hard white compound formed around the joints in the condenser suggests the presence of urea in the detergent.

(ii) Minced sausage meat (or cheese)

20.0 g of meat (or cheese) is distilled with 80 ml of toluene as in (i). The toluene solution remaining in the flask is carefully poured into a weighed beaker and several additions of toluene are made to the meat, the flask shaken up and the toluene also poured into the beaker. The toluene is evaporated off in a fume hood over a water bath and the beaker reweighed to determine the weight of fat. (The approved method of analysis of fat content involves the use of diethyl ether which is very volatile and flammable.)

If powdered laundry detergents are being examined then there will be water of hydration tied up in some of the components, e.g. tripolyphosphate. A higher boiling solvent is needed to ensure the hydrate is broken down (xylene or petroleum ether, bp 140°C).

Urea is often used as a solubilising agent to keep fairly insoluble material in solution—this is true for some of the detergent concentrates; in dilute detergents it can be used as a thickening agent. Because it is alcohol-soluble, *initial* tests on a detergent would add it to the fraction of material classed as 'active' whereas it is not a surfactant.

EXPERIMENT B

SEPARATION OF FOOD AND DRUG COMPONENTS USING CHROMATOGRAPHY

Chromatography is a term used for a variety of separation techniques. The components of the mixture to be separated are distributed between two phases, one of which remains stationary while the other phase—the *mobile phase*—percolates through the interstices or over the surface of the *stationary phase*. The mobile phase can be a liquid or a gas and the stationary phase can be a solid or a liquid—several combinations (types of chromatography) are thus possible.

(i) Separation of amino acids by paper chromatography

Equipment needed

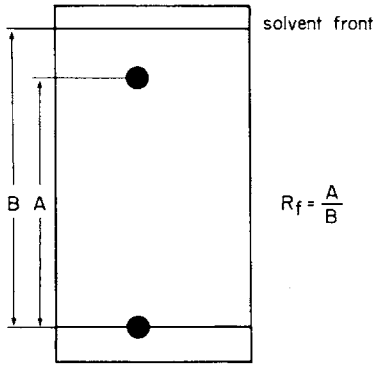
1. 1000 ml beaker cover with aluminium foil containing solvent (see item 9)
2. capillary tubes or spotters
3. five 8 × 1.2 mm test tubes
4. oven set at 100°C
5. paper—Whatman No. 1 filter paper—sheets 12 cm × 22 cm
6. 2 percent ninhydrin in ethyl alcohol
7. protective gloves
8. samples of glycine, tyrosine, leucine, aspartic acid
9. solvent: a solution of 10 ml of 2 percent ammonium hydroxide in 20 ml of propan-2-ol(isopropyl alcohol)

Principle involved

In paper chromatography, one liquid phase is allowed to move along a strip or sheet of cellulose (filter) paper. The paper and a second liquid phase, which is strongly adsorbed on the paper, constitute the stationary phase. The liquid phases are referred to as the *solvent system*.

> One of the earliest applications of chromatography was the separation of a mixture of pigments from leaves into components of different *colours*; hence the name which comes from the Greek words *chroma* = colour, *graphein* = to write.

In the present experiment, a mixture of amino acids is to be separated using aqueous isopropanol as the solvent system. The components can be identified by comparison with pure samples of amino acids chromatographed in the same way. The sample solutions are applied to the paper as spots with any device that will transfer a very small amount of material, such as a capillary tube (spotter). The paper is then placed in a vessel containing a small volume of the chosen solvent system (development, see Figure 14.5). The experimental procedure will be described in detail below. The vessel must be covered to maintain an atmosphere saturated with solvent vapour. The solvent mixture ascends the paper by capillary action and solutes will move at a rate which depends on their partition between the stationary and mobile phases and hence on their structure. The ratio of the distance travelled by a compound to that travelled by the solvent front is called the R_f value (or retardation factor) of that compound (see Figure 14.2). For a given solvent mixture and paper, the R_f value is characteristic of the solute. The R_f values of the amino acids in the solvent system given above vary from 0.1 to 0.8. In any homologous series among the amino acids (such as glycine, alanine, α-amino-butyric acid, etc.) the R_f value increases with the size of the molecule, indicating a successively smaller tendency to absorb, as the molecule gets bigger.



14.2 Chromatography plate

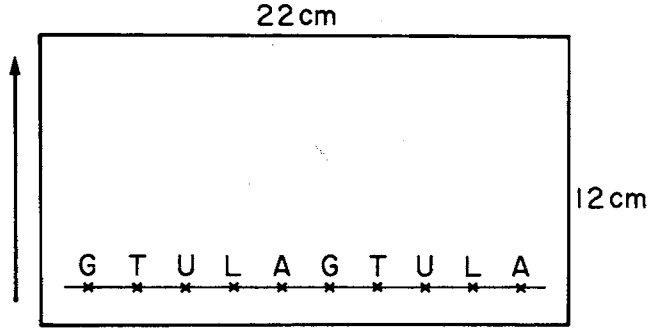
Common methods of detecting the position of compounds on the paper after development are (1) inherent visible colours when possible, (2) reactions with colour-producing reagents, (3) fluorescence, and (4) prevention of fluorescence of the stationary phase by absorption of ultraviolet light.

The amino acids (colourless) are detected using a ninhydrin spray. Ninhydrin reacts with α-amino acids to yield highly coloured products. Ninhydrin should be kept off the body because it reacts with proteins in the skin to form a rather long-lasting purple discolouration. The spray reagent is prepared as a 2 percent solution of ninhydrin in ethyl alcohol. Fingerprints also yield ninhydrin reactive material. Therefore, to protect chromatograms as well as skins, you should wear protective gloves when handling chromatographic paper and also when spraying.

Method

Place the labels on five clean 8 × 1.2 mm test tubes and place one spotter into each tube. From the stock solutions on the shelves (containing about 0.05 M solutions of the amino acids in 1.5 percent hydrochloric acid), transfer a few drops of the appropriate material to each of the first four test tubes. Obtain a few drops of an unknown from the instructor for the fifth tube. (The unknown will contain from one to four of these same amino acids at a concentration of about 0.05 M each in 1.5 percent hydrochloric acid.)

Stationary phase. Obtain a clean sheet of Whatman No. 1 filter paper, about 12 cm by 22 cm, and make a light pencil line parallel to the bottom (Figure 14.3) and about 1.5 cm away. Along this line, at intervals of about 2 cm, place ten light crosses. Under each cross place identifying marks, two for each known and two for the unknown.



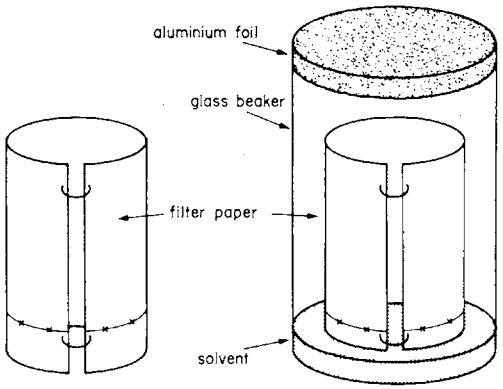
14.3 Amino acids spotted on plate

Using the capillary tubes, place a small amount of each appropriate solution on its two positions along the line on the filter paper. Avoid getting the spot on the paper larger than about 2 mm in diameter. (Although your paper gives you two chances to make a proper addition, it is advisable first to practice transferring solution to an ordinary piece of filter paper.) Let the paper dry for a few minutes in air. Add a second portion of the unknown to one of its two positions, to make certain that sufficient quantities of each component of the unknown will be present for good visual observation when the paper is developed.

Roll the paper into a cylindrical form (avoid putting fingerprints on paper), and staple the ends together about a third of the way in from the edge (Figure 14.4). Staple the paper in such a fashion that the ends of the paper do not touch each other—otherwise the solvent will flow more rapidly at that point and form an uneven front.

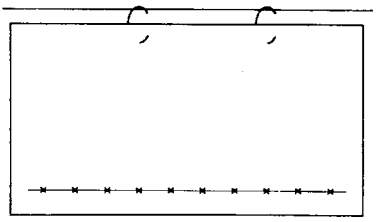
When the spots on the cylindrical paper are dry (it may be necessary to place the paper in an oven at about 100°C for a short time), place it carefully

in the beaker of solvent, and cover carefully and tightly with the aluminium foil (Figure 14.4). Make certain that the paper does not touch the sides of the beaker, and use care in keeping solvent from splashing onto the paper.



14.4 Paper chromatography in process

Let the solvent rise up the paper for *at least* 1½ hours. If the time is shorter, the components may not be sufficiently separated for easy identification. Remove the paper and place it upside down in the fume cupboard to dry. When most of the solvent has evaporated open the cylinder by tearing it apart where it was stapled and hang it in a fume hood (Figure 14.5). Spray the paper lightly but completely with a solution of ninhydrin, and leave the paper in the hood until the spray solution is dry. Place the paper in an oven at 100–110°C for about 10 minutes or until all the spots have developed.



14.5 Paper hanging to dry

Circle each spot with a pencil and measure the distance each spot has travelled. (Use the *centre* of the spot for measurement.) Measure the distance the solvent has travelled at each position and calculate R_f values for each amino acid (Figure 14.2). Determine the composition of the unknown by visual comparison of spot colours and by the relationships of R_f values.

(ii) Food colours in jelly beans[2]

Equipment needed

1. White wool (3 m—for 3 samples)
2. chromatography paper + melting point capillaries
3. five chromatography tanks 20 cm by 4 cm diameter
4. twenty 100 ml beakers
5. stapler and ruler
6. hot plate
7. water bath
8. five 100 ml graduated cylinders
9. five glass rods
10. solvents:
    acetic acid (0.1M)
    ammonia 2 percent solution
    developing solution:
    butanol, ethanol, 2 percent ammonia } 3:1:1

Method

White wool is used in the extraction of food colours. It is prepared beforehand by boiling for 10 minutes in 1 percent ammonia solution, then rinsing well under the tap to remove the fluorescing dyes, and then drying.

Warm water —20–25 ml—is added to about 3–6 jelly beans of each colour. The number of beans used depends on the depth of colour. They are allowed to stand for about 10 minutes or until they look white. If they are allowed to remain too long in solution, or if it is too hot, too much sugar is extracted. The solutions now contain both dye and sugar which must be separated. This is done by dyeing wool.

A length—about a metre—of prepared white wool is placed in each 100 ml beaker and a dye extract added and the whole acidified by adding a few drops of dilute acetic acid (CH_3COOH in water). The mixture is brought to the boil and simmered for 5 minutes, at which stage the wool can be seen to be dyed. The wool is now removed and washed well under the tap until no stickiness or jelliness remains.

The dye is now re-extracted from the wool in a beaker containing about 20 ml of 1 percent ammonia solution (NH_3 in water) simmering for about 5 minutes. When complete the wool is removed from the beaker and the extract is evaporated to dryness on a hot plate in a fume cupboard (ammonia has a nasty smell). The residue is stirred with the minimum number of drops of water (to maintain a high concentration) to mix completely.

Each solution is spotted on chromatography paper as in Experiment B (i) —the labels on the paper are now the colours of the beans used. The solvent system is butan-1-ol:ethanol:2 percent ammonia, 3:1:1.

For more details see British Standard BS 3210 (1960): Analysis of Water-Soluble Coal-Tar Dyes Permitted for Use in Foods.

This method has been criticised as being more complex than necessary and an alternative method is suggested for Smarties.[3] Because the intense colour of Smarties is on the outside layer only, it is sufficient to lick the tablet and rub it directly onto chromatography paper. (The wool method however ensures that only *acid* dyes are extracted.) The separation can also be simplified. If the paper is dipped in 1 percent aqueous sodium chloride solution, the dyestuff separates within 10–20 minutes. The separations are not affected by pH in the range 4–9. The salt is necessary. This now makes a nice lecture demonstration.

(iii) Separation of drugs by thin layer chromatography[4]

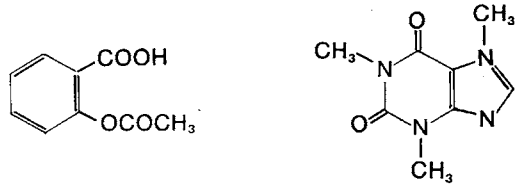
Method

Analgesics contain a number of standard drugs in various formulations. It was common, until the early 1960s, for analgesics to contain phenacetin, until it was withdrawn from the market due to its adverse effect on the liver (see Chapter 10—the metabolism of phenacetin). It was replaced in many proprietary lines by the structurally related product paracetamol (see Figure 14.6) and many products still retain this drug. Codeine is also a common

phenacetin paracetamol

14.6 APC

ingredient (present as the phosphate) in pain-relieving preparations available 'over the counter' in Australia provided the amount of codeine is less than 1 percent (see Chapter 9). In the United States the alkaloid caffeine (Figure 14.7) replaces codeine in analgesic preparations. Indeed many products in Australia also contain this drug. However, the most common and well accepted pain-relieving ingredient is aspirin, acetylsalicylic acid (Figure 14.7).



aspirin caffeine

14.7 APC

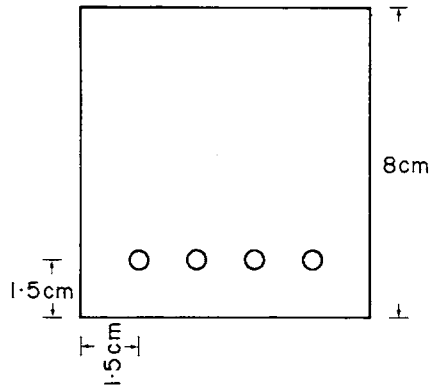
The chromatographic technique used in this experiment is thin-layer chromatography (TLC) which is similar to paper chromatography. Instead of paper, a thin layer of finely divided adsorbent (e.g. silica gel, alumina, powdered cellulose) supported on a glass plate is used. Commercial TLC plates, prepared by coating a plastic film with the adsorbent, are also suitable.

(a) Separation of caffeine, aspirin, phenacetin, and paracetamol[4]

Label five tubes: A, B, C, D, M

Collect a few drops of a stock solution of authentic aspirin in chloroform (10g/100 ml) in tube A, caffeine in chloroform in B, phenacetin in chloroform in C, paracetamol in chloroform in D and a mixture consisting of equal volumes of all four in M.

Solvent: butyl acetate:chloroform:85 percent formic acid (6:4:1 by volume).



14.8 Drug separation by plate chromatography

Spot samples of A, B and M near the bottom of the chromatographic plate (as shown in Figure 14.8). Prepare a similar plate with C, D and M. (The chromatographic plates comprise a layer of silica gel as adsorbent, calcium sulphate as binder, together with a fluorescing agent to aid location of sample by ultraviolet illumination.) Develop the plates using the solvent system designated above. When the solvent front has reached almost to the top of the plates, remove, dry, and examine the plates under ultraviolet light (short wavelength, 254 nm; e.g. a germicidal lamp). Mark the position of the samples and of the solvent fronts. Record the R_f values. Repeat the experiment and compare duplicate R_f values. (Remember to clean spotter between samples.)

When satisfied that the reference samples can be detected clearly, continue with the next stage of the experiment. If R_f values are not consistent, check procedure with your instructor. (Common errors include: spotting too close to edge of plate; spot too large in diameter; too much sample—this leads to streaking; spot not dry prior to commencing chromatography.)

(b) Investigation of a selection of analgesic drugs

The same procedure is used for chromatography and detection in this section of the experiment. Samples are prepared from a tablet (or powder) of each product by grinding the tablet with chloroform (15 ml) and using this as the text sample. Fill in Table 14.2 with the manufacturers' specifications for their analgesic preparations.

TABLE 14.2 *Analysis of analgesics*

Product name	Sample	Manufacturer's specification: Aspirin	Caffeine	Phenacetin	Paracetamol	Other
Blue Codral	E					
Codiphen	F					
Aspirin	G					
Veganin	H					
Panadeine	I					
Vincents	J					
Bex	K					
A P C	L					

It is best to use the mixture M prepared previously as a reference sample.

(iv) Chromatographic examination of fats and oils (adapted from Unilever)

Equipment needed

1. $AgNO_3$ coated chromatography plates and capillary droppers (made up 3 days in advance)
2. five chromatography developing tanks (14 × 18 × 25 cm)
3. samples of fats and oils
4. chloroform / ethyl benzene } 95:5
5. 4,5-dibromofluoroscein
6. pasteur pipettes
7. sample tube and stoppers
8. spoon spatulas
9. chromatography spray
10. source of air pressure
11. oven at 100°C
13. tissues to line tanks
14. ultraviolet viewing box

Method

Plates 20 × 5 cm are coated with a slurry of 25 g silica gel and 55 ml 2 percent silver nitrate with a thickness of 0.25 mm. The coated plates are stored in the dark because silver salts are light sensitive—compare photography—and dried at room temperature. Before use they are activated to 110°C for 30 minutes.

Dripping, maize and safflower oils, margarines, and butter are to be examined as 5 percent solutions in chloroform. Rough measurements can be used, such as for the solids half a spatula-spoonful of fat in 10 spoonsful of chloroform and for the oils 1 drop of oil in 20 drops of chloroform.

Applications of the solutions are done with glass capillaries and each spot should be 2–3 mm in diameter for good separation. Each solution is single and triple spotted (a spot is allowed to dry and then another added on top allowed to dry, etc.) along a base line 2.5 cm from the edge of the plate, as the solution concentrations vary. After spotting the plate is allowed to dry and then developed in tanks lined with tissue soaked in solvent to provide a saturated atmosphere inside the tank. The solvent used is chloroform:ethyl benzene (95:5 v/v) and is poured to a depth of 1.5 cm in the tank.

After the plate is developed (about 40 minutes) it is dried and sprayed with 0.2 percent ethanolic solution of 4, 5-dichlorofluorescein. After drying examine the plates under ultraviolet light and observe separated triglycerides with different levels of unsaturation. (This is preferable to the use of 50 percent sulphuric acid followed by heating in an oven at 130°C for 10 minutes.) The plates can then be compared to others run with standard known fats.

EXPERIMENT C
EXTRACTION OF CAFFEINE AND BENZOIC ACID FROM SOFT DRINKS

Introduction

An American study was undertaken in 1970 on the effect of food acids on human teeth.[5] The teeth were soaked in acidic solutions of equivalent strength to those found in foods, as well as cola drinks and orange juice. Colas turned the teeth brown but did not damage the enamel, but the enamel of the teeth soaked in orange juice could be flaked off with a fingernail. Experiments conducted with ANU classes also confirmed that cola drinks do not dissolve baby teeth (supplied by a class member in large numbers!). It is important to remember that the contact time for drinks with teeth in real life is in fact quite short. Of far more concern is the sugar content of these drinks which can vary between 6 and 9 teaspoons per 340 ml can.

Coca Cola started off as French wine coca—the Ideal Nerve and Tonic Stimulant—registered by John Smyth Prembreton in 1895. A year later it was modified by removing the wine, adding a pinch of caffeine and extract of the kola nut and other oils to produce Coke, the registered trade mark of the Coca Cola Company.

PLATE 14.1 *Experiment on caffeine in Coke*

Equipment needed

1. ten 1 litre conical flasks
2. five 250 ml separating funnels
3. ten 100 ml beakers
4. five watch glasses
5. five 100 ml graduated cylinders
6. ten funnels
7. five spatulas
8. ten glass rods
9. water bath + distillation apparatus
10. pasteur pipettes
11. infra-red spectrometer, Nujol, ethanol, soda plates, mull plates and razor
12. sodium carbonate
13. dichloromethane
14. conc. HCl
15. potassium chlorate
16. 2 M ammonia
17. benzoic acid (standard)
18. caffeine (standard)

Method

(i) Isolation of caffeine[6]

Each student will take a sample of kola (record brand name) and carefully measure 150 ml of this sample into a conical flask (1 litre). To this is added 2.0 g of sodium carbonate (the amount is not critical provided the resultant solution is basic—test with pH paper), which is added to stop contamination of the extract with benzoic acid, a commonly added preservative. The benzoic acid, being acid, reacts with the basic sodium carbonate to form sodium benzoate which is water-soluble and so not extracted into organic solvents.

Then 50 ml of methylene chloride (1,1-dichloromethane) is added to the conical flask and the flask swirled gently for at least 5 minutes. (*Do not* shake vigorously; this often causes an emulsion to form which hinders separation.)

The combined liquids are then transferred into a separating funnel and allowed to settle (5–10 minutes). The lower methylene chloride layer is drained through the tap into a clean 250 ml conical flask. A fresh sample of methylene chloride (50 ml) is added to the separating funnel and the flask stoppered. *Gently* invert the funnel a few times to allow the remaining caffeine to be extracted into the methylene chloride layer. The lower layer is separated and combined with the first extract.

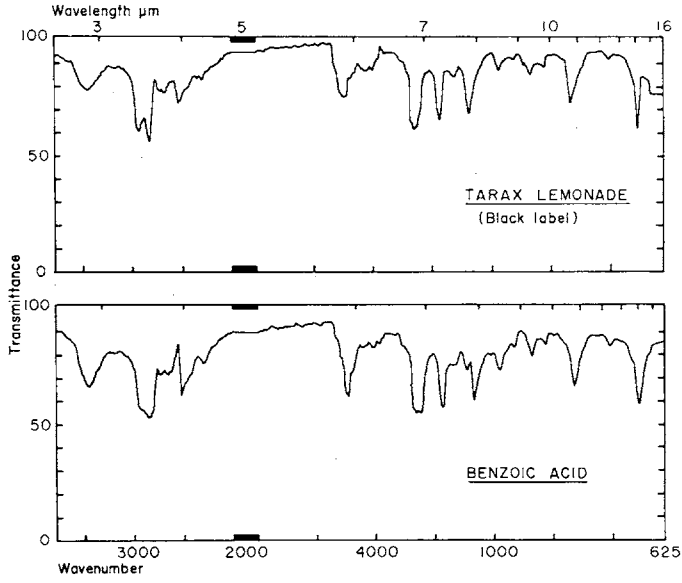
The total extract is treated with anhydrous magnesium sulphate (~5 g) to remove the water (it forms an insoluble hydrated magnesium sulphate salt) and the methylene chloride (it should be clear) is filtered through a cotton wool pad into a 250 ml beaker. Evaporate the methylene chloride on a water bath in a fume cupboard (better is to distil it off and recover the solvent). The product should be weighed and then tested as follows:

1. Place a small amount of precipitate on watch glass and mix with 2–3 drops of concentrated hydrochloric acid (care!). Add a *few* small crystals of potassium chlorate—mix well with glass rod and evaporate to dryness on water bath (boiling) in a fume cupboard with the front protector down. Cool glass and moisten with a drop or two of 2M ammonia solution (NH_4OH). Residue turns purple.
2. A sample should be prepared for analysis by infra-red spectroscopy by formation of a Nujol mull (if an instrument is available) and the spectrum run using sodium chloride plates on the spectrometer.

(ii) Isolation of benzoic acid

Half a can of lemonade is poured into a 2 litre conical flask and acidified with 2 drops of dilute hydrochloric acid. 50 ml dichloromethane (methylene chloride) is now added and the flask swirled gently for at least 5 minutes and

then poured into a separating funnel and allowed to settle (5 minutes). The solvent layer only is drained into a 100 ml beaker and allowed to evaporate, leaving a residue of benzoic acid. Confirm by running an infra-red spectrum of a mull of residue and compare with a standard sample (if an instrument is available).



14.9 An infra-red fingerprint

EXPERIMENT D
ESTIMATION OF VITAMIN C IN TABLETS, FRUIT JUICES, ETC.[7]

Two methods are described. The first is applicable to samples with a high vitamin C content, such as tablets; the second is more appropriate for fruit juices.

(i) Tablets

Powder a tablet finely in a mortar. Add a little water and grind into a slurry. Rinse the slurry into a flask using in all about 80 ml of water. Add about 10 drops of concentrated hydrochloric acid and shake vigorously.

Add a few drops of 1 percent starch indicator. Finally add 0.05M iodine solution from a burette until the solution acquires a permanent blue colour. Each ml of the iodine solution is equivalent to 8.81 mg of vitamin C, so that a 250 mg tablet should require about 250/8.81 = 28.5 ml of iodine solution.

Repeat the sample preparation as described in the first paragraph, but before adding the starch, boil the suspension gently for some time. Cool the mixture, add starch and titrate with iodine solution as before. This procedure should demonstrate the destruction of vitamin C by cooking (which is speeded up in alkaline solution—try adding sodium bicarbonate before boiling).

(ii) Fruit juice

The sample to be titrated should contain not more than 1.0 mg of vitamin C; 3.0 ml of a juice stated to contain vitamin C should be about the right amount. It is best to use an orange or lemon rather than a can.

Note the method given here for the determination of vitamin C is unsuitable for some other products because of complications. These include interferences from ferrous salts (iron dissolving from a can), sulphite (preservative) and compounds formed during extensive heat treatment or long storage. The key to success with the 2,6-dichlorophenolindophenol method is freshness of reagents, rapid titration, and short time to end-point, because other reducing substances react more slowly with the blue dye than vitamin C.[8]

Pipette 3.0 ml of the juice into a flask. Add a few grains of oxalic acid (*poison*) and shake. If the juice is not too strongly coloured it can now be titrated directly with dichlorophenolindophenol solution until the solution becomes pale pink in colour; 1 ml of this solution is equivalent to 0.1 mg of vitamin C.

If the juice is strongly coloured, titrate with the test solution until you think you can detect a pinkish colour or until you have added 10 ml. Now add 10 ml of ether from a measuring cylinder, and shake. If the ether is coloured violet-pink you have gone too far. Take a new 20 ml sample of the juice and repeat the titration, adding say 8 ml of the test solution. Test with ether again. In this way you can bracket the volume of test solution required and quickly arrive at a good estimate of the vitamin C content.

There are alternative methods of measuring vitamin C.

1. *Amphometric Titration*—Unilever Laboratory Experiment Number 12 (1973)

This method requires a sensitive moving spot galvanometer, some platinum electrodes, and 1.5 volt battery. It is also recommended that a 5 percent v/v solution of metaphosphoric acid in water is used for extracting vitamin C from vegetables.

Vegetables—15 g dehydrated or 50 g fresh, are cut and pulverised with 350 ml of metaphosphoric acid solution in a mortar or macerator. Next 1 ml of 50 percent v/v solution of sulphuric acid is added to each 25 ml of extract and then 3 ml of formaldehyde solution is added to condense with sulphites (preservatives), sulphides, and thiols.

2. *Titration using N-bromosuccinimide*—This method is described by M.Z. Barakat, M.F.A. El-Wahab, and M.M. El-Sadr in volume 27 (1955) of *Analytical Chemistry*, page 536. It works well.

3. Chemical firms supply test strips for a variety of spot analyses such as for ascorbic acid, nitrate, nitrite and sulphite (e.g. Merck). The strips should be calibrated against standard solutions before use.

SHORT EXPERIMENTS

EXPERIMENT E—TEST FOR LEAD IN PETROL

Equipment needed

1. ultraviolet lamp
2. dilute acetic acid
3. dithizone solution (2–5 mg in 100 ml chloroform, freshly prepared)

A piece of filter paper is saturated with petrol and exposed to strong sunlight for several hours or more quickly under ultraviolet light. It is then moistened with dilute acetic acid and a few drops of freshly prepared potassium iodide solution (16.5 g/100 ml). The appearance of a yellow colouration after several minutes indicates the presence of lead as lead iodide. Alternatively an even more sensitive test involves dithizone (diphenylthiocarbazone) reagent (2–5 mg of dithizone in 100 ml of carbon tetrachloride or chloroform—use freshly prepared). The reagent changes from green to red if placed on a filter paper containing lead salts (concentration limit 1 mg/kg). See Chapter 11.

EXPERIMENT F—TEST FOR LEAD IN GLAZED POTTERY

Equipment needed

1. detergent
2. distilled water
3. 4 percent v/v acetic acid
4. dithizone solution (as for Experiment E)

The surface of the sample must be clean and free from grease. It should be washed in water containing detergent, then rinsed with distilled water. The

utensil should be filled with acetic acid (4 percent v/v) left covered at room temperature for 24 hours. The acid should be stirred thoroughly and tested for lead as in Experiment E.

(The British Standard allows 2 ppm lead and 0.2 ppm cadmium for large casseroles (holloware), 7 ppm lead and 0.7 ppm cadmium for small casseroles and 20 ppm lead and 2.0 ppm cadmium for plates. This standard has been adopted by NSW. However the NHMRC has recommended a flat 7 ppm lead and 0.7 ppm cadmium for all utensils.)

EXPERIMENT G—PERMANENT PRESS FOR WOOL

Equipment needed

1. Permanent crease solution (3 percent sodium bisulphite or sodium metabisulphite solution containing a little detergent)
2. two wool samples
3. small sponge
4. watch glass
5. detergent
6. steam iron

Pour some of the permanent crease solution into a flat dish and sponge a line of solution down the centre of one of the wool samples. Then crease the sample along the sponged line and press the crease in with the steam iron for about 30 seconds. Using the steam iron again, press a similar crease in the untreated sample.

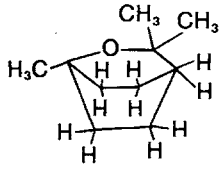
Immerse both samples in warm water (about 70°C) containing a small amount of detergent. Then check to see if the treatment has produced a 'permanent crease'.

Wool is a protein polymer. And human hair is a protein polymer very similar to wool. A 'permanent wave' in human hair is much the same as a permanent crease in a skirt or a pair of trousers.

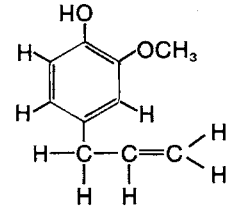
EXPERIMENT H—STEAM DISTILLATION OF EUCALYPTUS LEAVES

The oil produced from eucalyptus leaves contains eucalyptol (1,8-cineole) in many cases as the main component in an oil yield of about 1–3 percent. The oil is useful in cough drops, mouthwashes, gargles, dental preparations, inhalants, room sprays and medicated soaps. It is an important disinfectant. See Figure 14.10.

Because the oil decomposes when boiled (bp 176°C), the method used to extract it from the leaves and purify it is to distil the leaves with steam. The amount of oil carried over with the steam depends on how volatile the oil is. (You might also like to produce oil of cloves, eugenol, bp 164°C, from cloves.) Using this method of steam distillation the temperature of the oil never



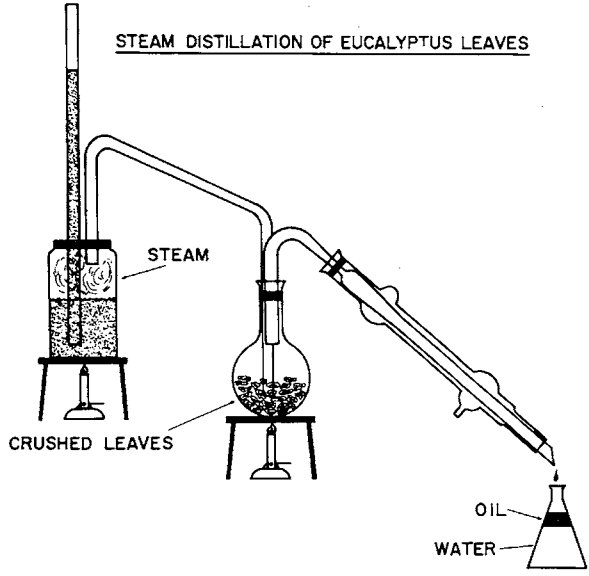
eucalyptol



eugenol

14.10 Essential oils

exceeds 100°C and the oil is not destroyed. In fact this technique is identical to the one used in the Dean and Starke experiment, except in this case we are interested in the oil phase rather than the water phase. See Figure 14.11.



14.11 Steam distillation of eucalyptus leaves. The oil settles out as a separate phase (layer) on top of the water.

An interesting consumer aspect of steam distillation involves the use of the antioxidant BHA in vegetable oils used for frying (see Chapter 3). The frying of wet foods involves the evolution of steam, which helps to distil out these (phenolic) antioxidants. They come off with the steam just as in Experiment H. It is interesting to note that the natural antioxidant α-tocopherol, because of its long chain, is less volatile and thus more useful. Actually the chemical effects of frying are quite complex. Most of the products of oxidation at room temperature are not found. Peroxides are decomposed rapidly and volatile rancid compounds distil off. On the other hand polymers form (which causes high viscosity), the colour darkens (oxy-compounds), and excessive foaming occurs (the polar oxygenated compounds formed act as surfactants).

EXPERIMENT I—TESTS ON PLASTICS

When burning plastics

1. *Use very small pieces of your samples and hold them with tongs or a wooden peg*
2. *Experiment in a well ventilated place because of fumes produced*
3. *Hold the burner or candle at an angle so that any drops of molten plastic fall onto an asbestos or other non-flammable mat.*

(i) Copper wire test

Heat a copper wire (stuck into a cork as a holder) in a gas flame until any yellow or green colour disappears. Press the heated wire into the plastic sample and then put the wire with a little molten plastic on it back into the flame. A green colour indicates that the plastic contains halogen—probably chlorine in polyvinyl chloride (PVC) or polyvinylidene chloride (PVDC). Before repeating the test with another plastic, again heat the copper wire until the green colour disappears.

It should be noted that an additive may contain a halogen (chlorine, bromine, or iodine) that gives rise to a positive result. Also cyanide (from, say, Orlon) may give a positive result.

(ii) Density

Some polymers are less dense than water and hence will float; these are polyethylene, polypropylene, styrene-butadiene, nitrile (some types). It is essential that the sample is properly wetted and pushed below the surface and then released. The presence of large amounts of additives can change the density.

(iii) Feel

Polyethylene and polytetrafluoroethylene have a waxy feel which is not possessed by other polymers.

(iv) Heating tests (in a laboratory)

A small piece (0.1 g) of the material is placed on a clean spatula (nickel spoon-like object), previously heated to remove traces of combustible material. It is then gently warmed without ignition, over a small colourless gas flame until it begins to fume. The sample is removed from the flame and the odour of the fumes and whether they are acid, alkaline, or neutral (damp litmus paper) is ascertained. The sample is now moved to the hottest zone of the small gas flame and the following points noted:

1. Whether or not the material burns and if so, how easily
2. The nature and colour of any flame (very sooty flame generally indicates an aromatic polymer, but may be due to carbon black filler)
3. Whether or not the material continues to burn after removal from the flame
4. The nature of any residue

TABLE 14.3 *Burning test on plastic*

(i) The material burns but extinguishes itself on removal from the flame

Plastic	Flame colour	Odour	Other features
casein	yellow	resembles burnt milk	
melamine-formaldehyde	pale yellow with light blue-green edge	formaldehyde and fish like	very difficult to ignite—alkaline fumes
nylon	blue with yellow tip	resembles burning vegetation	melts sharply to clear liquid which can be drawn into fibre
phenol-formaldehyde	yellow	phenol and formaldehyde	very difficult to ignite
polytetrafluor-ethylene	yellow	none	burns with extreme difficulty chars very slowly acidic fumes
polyvinyl chloride polyvinylidene chloride	yellow with green base	acrid	acidic fumes
urea-formaldehyde	pale yellow with light blue- green edge	formaldehyde and fish like	very difficult to ignite—alkaline fumes

(ii) The material burns and continues to burn on removal from the flame

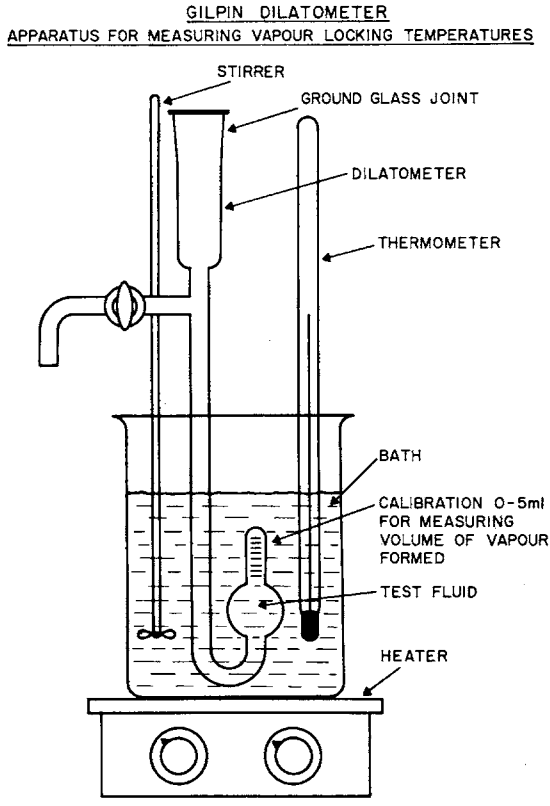
Plastic	Flame colour	Odour	Other features
acrylonitrile-butadiene-styrene	yellow with blue base, smoky	styrene	
alkyd	yellow smoky	pungent, unpleasant	
cellulose acetate	yellow	acetic acid (vinegar)	acidic fumes
cellulose nitrate	yellow	possibly camphor on gentle warming	burns at a very fast rate —may explode
epoxide	orange-yellow smoky	acrid	
ethyl cellulose	pale yellow with blue-green base	resembles burning wood	drips on ignition
polyacrylonitrile	yellow	*cyanide* initially; and then resembles burning wood	
polycarbonate	yellow, smoky	phenolic	difficult to ignite initially
polyethylene polypropylene	yellow with blue base	resembles burning candle wax	becomes clear when molten
polymethyl-methacrylate	yellow with blue base	methyl-methacrylate	
polystyrene	yellow with blue base, very smoky	styrene	
polyurethane	yellow with blue base	acrid	
polyvinylacetate	yellow, smoky	vinylacetate	black residue
polyvinylalcohol	yellow, smoky	unpleasant sweet	black residue

Table 14.3 considers some of the possibilities. It was compiled using *uncompounded* polymers. Thus highly plasticised PVC may *not* be self-extinguishing etc.

EXPERIMENT J—MEASUREMENT OF VAPOUR LOCKING TEMPERATURES[9]

Any hydraulically operated braking system must use a non-compressible fluid in the master and wheel cylinders. The formation of vapour (which is compressible) in the wheel cylinder due to boil off from the brake fluid leads to 'vapour locking' and brake failure. The boiling point of fluid mixtures is seldom 'ideal' and so is not a good parameter for describing what will happen in real circumstances. (*Ideal* is an expression used in physical chemistry to describe systems which obey predictable simple mathematical expressions. Real systems vary from almost ideal to completely non-ideal—just like people!)

A Gilpin dilatometer (see Figure 14.12) consists essentially of a U-tube, one arm of which has a calibrated tube having a volume of 5 ml. Enough brake cylinder fluid is placed in the dilatometer so as to fill completely the calibrated side-arm and the other side of the U-tube is filled to the same height. The filled portion of the U-tube is completely immersed in a bath containing a high boiling silicon oil (which remains transparent at high temperatures). A boiling chip should be added to reduce the temperature range—use silicon carbide. A metal shield surrounding the apparatus helps reduce temperature fluctuations.



14.12 Gilpin dilatometer

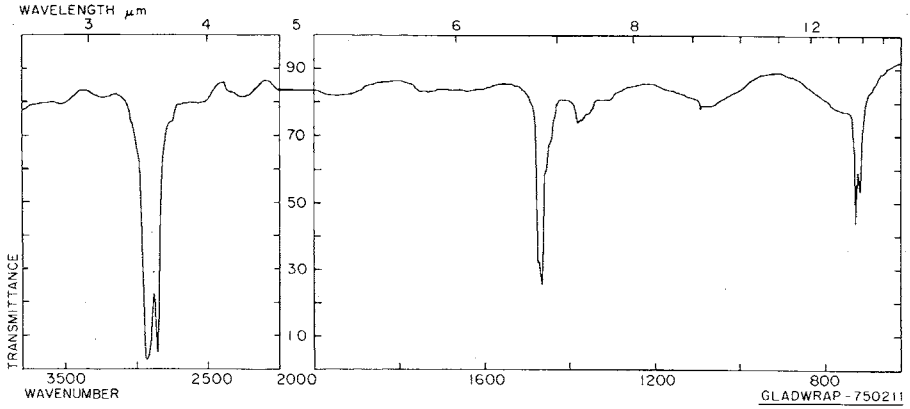
The temperature of the stirred bath is raised slowly near the vapour formation temperature, and a plot of bath temperature versus volume of vapour produced is recorded. Once vapour begins to form there is a rapid increase in vapour volume for only a few degrees rise in temperature.

The experiment should be carried out on brake fluid from a sealed container and then on fluid with 1 percent, 2 percent, 3 percent, and 4 percent added water. A plot of vapour formation temperature versus added water should be plotted (see Figure 11.5). An 'unknown' sample from your car can then be measured. Alternatively, different brands of brake fluid can be compared.

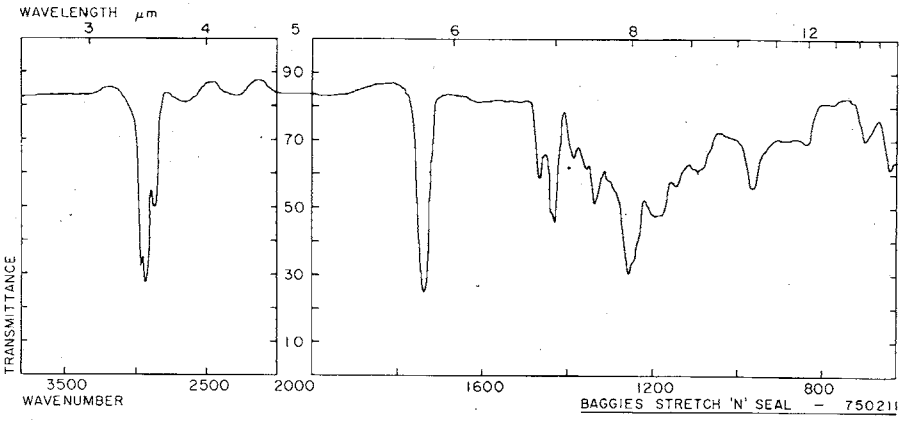
When measuring used brake fluid from a car, a black precipitate is often formed on heating and this remains when the fluid is cooled. This could be due to the heat causing flocculation of carbon black which is leached out of the rubber caps during service. Another possibility is that if the brake fluid has been in the braking system for more than about 12–18 months, the inhibitor system then becomes exhausted (depending on use, moisture uptake, etc.) and corrosion may occur in which case the colloidal ferric hydroxide etc. would similarly flocculate on heating. If this precipitate does occur, filter it off (after cooling) and test it.

EXPERIMENT K—INFRA-RED SPECTROSCOPY

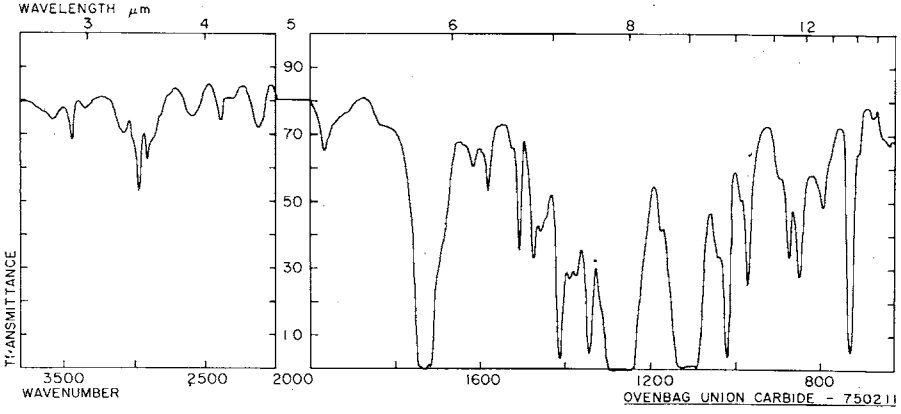
If an infra-red spectrometer is available there are a number of quick experiments that are possible. Plastic film has just the right thickness for an infra-red spectrum to be taken *au naturel*. A number of these are shown in Figures 14.13–15. The compositions can be obtained from authenticated standards, which also allow the other major additives to be assessed, e.g. plasticisers. In addition, the interpretation of the particular spectral bands can be discussed.



14.13 Gladwrap—shows the infra-red spectrum of polyethylene



14.14 Baggies Stretch'n'Seal—shows the infra-red spectrum of polyvinyl chloride



14.15 Oven bag—shows the infra-red spectrum of polyterephthalate (polyester)

A more complex example is provided by something like the plastic linings in wine cellar packs. Lindemans' have the following composition: the outer two layers (films 1 and 2) are identical in composition and are a film of polyvinylidene chloride sandwiched between films of polyethylene; the inner layer (film 3) is a laminate of polyethylene and polyethylene (85 percent) –vinylacetate (15 percent)–copolymer (EVA).

For further details, and for the use of a 'frustrated multiple internal reflectance' (FMIR) accessory, see Perkin Elmer.[10]

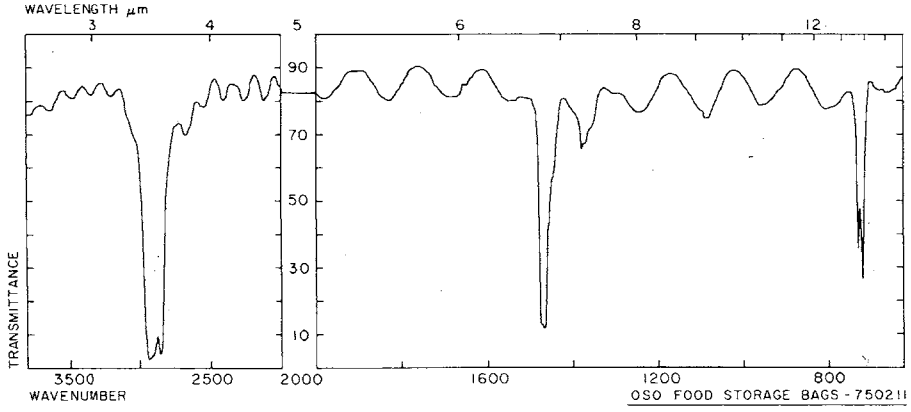
Whenever a beam of radiation transverses a boundary in which there is a change in refractive index, part of the radiation is reflected and interference effects occur which show up in the spectrum as *fringes* (see Figure 14.16). Interference fringes can usually be recognised because of their uniform evenly spaced (frequency scale) appearance. The thickness of the film d is given by

$$d = \frac{\Delta m}{2n(\tilde{\nu}_1 - \tilde{\nu}_2)}$$

where Δm is the number of fringes (complete cycles) in the region $\tilde{\nu}_1$ to $\tilde{\nu}_2$, and n is the refractive index. For example, for polyethylene $n = 1.51$, and using Figure 14.16 we can calculate

$$d = \frac{1}{2(1.51)(2760 - 1985)} = 2 \times 10^{-3} \text{ cm} = 0.8 \text{ mil (thousandths of an inch)}$$

When making the calculation, choose an area free from absorption bands.



14.16 Interferences fringes. Oso food storage bags—superimposed on the polyethylene spectrum are interference fringes from which the thickness of the film can be calculated.

EXPERIMENT L—AN EXPERIMENT IN DYEING

The dyeing of textiles with modern dyes involves immersing the fabrics at a suitable temperature for a period of time. The process is not quite so simple, however. During the process of dyeing the dye molecules sometimes leave the solution entirely. The dye molecules owe their properties of attraction to fibres partly as a result of their large size and partly to the presence of specific molecular groups attached to the molecule which interact with those on the fibre.

In this experiment five fabrics, differing chemically from each other, are dyed in a coloured solution made up by diluting 10 ml of a given stock solution (of Dye X) to 100 ml of water. Dye X is a mixture of three dyes (0.5 g/100 ml of each, in water):

1. a direct dye, e.g. C.I. Direct Red 23;
2. a disperse dye, e.g. C.I. Disperse Yellow 1; and
3. an acid dye, e.g. C.I. Acid Blue 9 (food colour 42090—Brilliant Blue FCF).

The temperature of the dye bath is brought to boiling and small pieces, about 2 cm × 2 cm, of cotton (cellulose), Dicel (cellulose diacetate), Terylene (polyester), nylon (polyamide) and wool (protein) are added.

After 10–25 minutes, the hot liquid is poured off and the murky coloured fabrics are rinsed in a large volume of cold water and then allowed to dry. Each fabric should be a different colour:

Wool—blue	cellulose diacetate—yellow
cotton—red	nylon—green
polyester—very pale yellow	

Note that wool attracts only the acid dye which is the reason that wool is used to extract (legal) food colours in Experiment B (ii). Cotton does not dye with the disperse (non-ionic) dye or with the acid dye. The direct dye is the largest molecule and also forms strong hydrogen bonds which attract it to cellulose. White polyester will dye with disperse dyes—it generally requires superheated temperatures (120°C–130°C) for rapid dyeing. Cellulose diacetate has a stronger attraction for the yellow non-ionic dye and it swells more readily in water and dyes more rapidly.

Wool and nylon become positively-charged in water and so attract the negatively-charged sulphonate groups. The blue dye is smaller than the red dye and in a short time only the blue dye is taken up by wool and nylon. For longer dyeing time, and particularly if the pH of the solution is lowered with acetic acid to about 3, the red dye will be taken up rapidly. (If you want to show this—dilute the bath further to reduce the overall uptake of dye.) Nylon is more hydrophobic than wool so it takes up the yellow (less polar) dye as well and so becomes green.

Supplies of dyes are as follows:
The acid dye—CI 42090—can be obtained as a food colour.
The other dyes (or similar ones) are available from ICI (Australia).

Various fabrics are available from:

Standard Material Supply Service,
Australian Wool Testing Authority,
P.O. Box 77, North Melbourne, Victoria, 3051.

EXPERIMENT M—DEPOLYMERISATION OF METHYL METHACRYLATE RESIN[12]

Place 25g of methyl methacrylate polymer (known in the United Kingdom as Diakon—powder—and Perspex—sheet, and in the United States as Lucite and Plexiglass) in a 100 ml Claisen flask, attach an efficient condenser (e.g. of the double surface type) and distil with a small luminous flame; move the flame to and fro around the sides of the flask. At about 300°C the polymer softens and undergoes rapid depolymerisation to the monomer, methyl methacrylate, which distils over into the receiver.

Continue the distillation until only a small black residue (3–4 g) remains. Redistil the liquid; it passes over at 100–110°C mainly at 100–102°C. The yield of methyl methacrylate monomer is 20 g. If the monomer is to be kept for any period, add 0.1 g of hydroquinone to act as a stabiliser or inhibitor of polymerisation.

EXPERIMENT N—POLYMERISATION OF METHYL METHACRYLATE[12]

Place 10 g of liquid methyl methacrylate in a test tube, add 10–20 mg of benzoyl peroxide, stopper the test tube loosely and heat in a boiling water bath. After 20–25 minutes, the liquid suddenly becomes very viscous and soon sets to a hard colourless mass of the polymer.

APPENDIX 14.1

Sources of consumer information

1. (a) Consumer Organistion publications.
   (b) Government Consumer Protection Bureaux.

(a) *Consumer journals*

AFCO Quarterly No. 1, June 1975, *et seq.*; Report on Australian *Consumer Protection Laws*, Adelaide, 1975. Submission for a White Paper on *Manufacturing Industry*, 17 pp. May 1976. *Australian Federation of Consumer Organisations*, P.O. Box 75, Manuka, A.C.T. 2603.

Choice (monthly, annual index December + cumulative index) *Australian Consumers' Association*, 28–30 Queens Street, Chippendale, N.S.W. 2008.

Consumer Comment (quarterly, index March 1974) *Consumers' Association of Victoria*, G.P.O. Box 1121J, Melbourne, Vic. 3001.

Canberra Consumer (quarterly, annual index December) *Canberra Consumers Inc.*, P.O. Box 591, Canberra City, A.C.T. 2601.

Consumer (monthly, 11 issues p.a., annual index December) *Consumers' Institute of New Zealand*, Private Bag, Te Aro, Wellington 1, N.Z.

Consumer Reports (monthly, includes Buying Guide issue, December) *Consumers Union*, 256 Washington Street, Mount Vernon, N.Y., U.S.A. 10550.

Consumers' Research Magazine (monthly + annual Handbook of Buying Issue) *Consumers' Research Inc.*, Washington, N.J., U.S.A. 07882.

International Consumer (quarterly): *Consumer Review* (alternative monthly) *I.O.C.U.* 9 Emmastraat, The Hague, Netherlands.

Price and Value (quarterly) *Hobart Consumers Group*, P.O. Box 1223M, Hobart, Tas. 7000.

Which? (monthly, annual index December + cumulative index) *Consumers' Association*, Caxton Hill, Hertford, England, SC13 7LZ.

Medical Consumers' Association of NSW, P.O. Box 81, Broadway N.S.W., 2007.

(b) *Annual reports and personal approach (A selection of free consumer information bulletins is available on request).*

Consumer Affairs Council/Bureau, A.C.T., P.O. Box 158, Canberra City, A.C.T. 2601.

Commissioner for Prices and Consumer Affairs, G.P.O. Box 374, Adelaide, S.A. 5002.

Consumers Protection Council, Tasmania, Box 1320N G.P.O. Hobart, Tas. 7001.

Consumer Affairs Council, Victoria, 35 Spring Street, Melbourne, Vic. 3000.

Consumer Affairs Council/Bureau, W.A., P.O. Box 294, Perth, W.A. 6001.

Commissioner for Consumer Affairs, Q'ld. P.O. Box 227, North Quay, Brisbane, Q'ld., 4000.

Consumers' Protection Council, P.O. Box 4344, Darwin, N.T. 5794.

Department of Consumer Affairs, N.S.W., Box 468 P.O., Darlinghurst, N.S.W. 2010.

(c) Consumer Product Safety Commission of the U.S.A. *Annual Reports.*

2. *Popular consumer publications*

Advertising		
Advertising and the Public	R. Harris & A. Seldon	Deutsch
Advertising in Australia	T. Hewat ed.	Ure Smith
Communicators	R. Walker	Lansdowne Press
Confessions of an Advertising Man	D. Ogilvy	Longmans
The Hidden Persuaders	V. Packard	Pelican
The Price of Beauty	R. Simon	Longmans
The Shocking History of Advertising	E.S. Turner	Michael Joseph
The Wordsmiths	G.E. Wood	Consumer Council N.Z.
Understanding Advertising	K.A. Fowles ed.	N.S.W.U. Press Ltd.
Buying		
At your Service	E. Gundrey	Penguin
Buyer Beware	J.T. Graham	Wheaton
How to Read Faster Under Water	G. Reed	Wolfe
The Dark Side of the Market Place	W. Magnuson	Prentice-Hall
The Intelligent Buyer's Guide to Sellers	D. Masters	Consumers Union
The Waste Makers	V. Packard	Pelican
Your Money's Worth	E. Gundrey	Penguin
Design		
Australian Design Index	Industrial Design Council*	
Design for the Real World	V. Papanek	Paladin

*Not a book. Index in Public Library.

Environment		
Defending the Environment	J.L. Sax	Knopf
The Closing Circle	B. Commoner	Knopf
The Problem of Noise	Australian Academy of Science	
Since Silent Spring	F. Graham	Houghton
Vanishing Air—the Report on Air Pollution	J.C. Esposito (Ralph Nader Study Group)	Grossman
Food		
Food for Nought	R.H. Hall	Harper & Row
Processing and Specifications of Milk and Milk Products	Dairy Farmers Co-op. Milk Co. Ltd.	
The Chemical Analysis of Foods	D. Pearson	Churchill
The Chemical Feast	J.S. Turner	Grossman
Australian Food Standards	NHMRC	AGPS

General

Consumers and the Nationalised Industries	Nat.Cons.Council (U.K.)	
Consumers in Action	G.E. Wood	Consumer Council N.Z.
Educating the Consumer	A. Williams	Longmans
How to Complain	C. Ward	Pan
Study Guide on Consumer Protection		ILO., Geneva.

Medicine

Ailments and Remedies		Consumer Association, U.K.
Magic Myth and Medicine	J. Camp	Priority Press
The Drugs you Take	S. Bradshaw	Hutchinson
Documenta Geigy Scientific Tables 7th edition 1970. 900 pp.		Geigy Australia
The Magic Bullet	M. Diesendorf (ed.)	SSRS (A.C.T.)
The Medical Messiahs	J.H. Young	Princeton
The Medicine Show	Consumer Reports (ed.)	Consumers Union (U.S.A.)

Specialist

Contraceptives	Canberra Consumers Inc.	
Unsafe at any Speed	R. Nader	Pocket Books
Vehicle Inspection Results 1975		AAA

Corporations

Multinationals and the Consumer Interest	P. Goldman	IOCU
Safety, Hysteria and the Regulatory Process	J.L. Kanig	PRACI, March 1977, 83.
The Corporate Oligarch	D. Finn	Simon & Schuster
The Social Responsibility of Corporations	P.J. Dunstan	CEDA*

3. *Chemical publications*

Safety

Dangerous Properties of Industrial Materials	N.I. Sax	Reinhold 1968.
Lead Glazes for Workshop and Studio Potters		NHMRC 1975
The Analytical Toxicology of Industrial Inorganic Poisons	M.B. Jacobs	Interscience 1967
The Clinical Toxicology of Commercial Compounds	M.N. Gleason *et al.*	Williams & Wilkins 1969
The Merck Index, 8th ed.	P.G. Stecher, ed.	Merck & Co. 1968

*Seventh position paper in the major CEDA project 'The role of the private sector', Committee for Economic Development in Australia, Dec. 1976.

Toxic and Hazardous: Industrial Chemical Safety Manual	International Technical Information Institute 1975/6, Japan.	

Recipes and trade names

Chemical Synonyms and Trade Names	W. Gardiner	Technical Press, London 1971
The Chemical Formulary (17 volumes in 1973, 300 pp./volume)	H. Bennett	Chemical Publ. Co.
The Condensed Chemical Dictionary 8th ed.	G.G. Hawley	Van Nostrand Reinhold Co. NY. 1971

General

Australian Chemicals Guide Industry Study, 3rd ed.	Dept. Manufacturing Industry, Canberra, 1975	

Lists chemicals manufactured in Australia and their manufacturer

Chemistry for Changing Times, 2nd ed.	J.W. Hill	Burgess Publ. Co., Minneapolis 1975
Chemistry in the Economy	American Chem. Society 1973, 600 pp.	

The place of chemistry in the U.S. economy—no formulae or pictures, just chemical industry facts

Chemistry: Its Role in Society	J.S. Chickos, D.L. Garin & R.A. Rouse	D.C. Heath & Co. 1973
Chemistry, Man and Society	M.M. Jones, J.T. Netterville, D.O. Johnston, J.L. Wood & J.R. Blackburn	Saunders 1972
Chemistry of the Earth	K.K. Turekian	Holt, Rinehart & Winston, 1972
Chemistry and the Technological Backlash	T.L. Pyle	Prentice Hall 1974
Dictionary of Drugs	R.B. Fisher & G.A. Christie	Paladin 1971
Environmental Chemistry	S.E. Manahan	Willard Grant 1972

Environmental Chemistry—an Introduction	L.T. Pryde	Cummings Publ. Co. Calif. 1973
Man, Health & Environment	B.Q. Hafen, ed.	Burgess 1972
Nature in the Balance	W.F. Hartman *et al.*	Heinemann Educ.
Organic Molecules in Action	M. Goodman & F. Moorehouse	Gordon & Breach 1973
Science, Man and Society	R.B. Fischer	Saunders 1971
Taking Things Apart, Putting Things Together	Amer.Chem.Soc., 1976, 120 pp.	
Wednesday Night at the Lab: Antibiotics, bioengineering, contraceptives, drugs and ethics	K.L. Rinehart, W.O. McClure & T.L. Brown, eds.	Harper & Row 1973
Chemistry and the Needs of Society	Chemical Society	U.K.
Chemical Cycles and the Global Environment	R.M. Garrel and F.T. Mackenzie	Kaufmann (Cal.) 1975
Oxford Chemical Series		
The Chemist in Industry	E.S. Stern, ed.	1973, 1974
(1) Fine chemicals for polymers		
(2) Human Health and Plant Protection		
Air pollution	D.J. Spedding	1976

Science in a social context

Siscon editor: Director of Combined Studies, University of Leeds, LS2 9JT. U.K. Siscon units are not designed to be used by students in independent study. Their design assumes both direction from a teacher and the opportunity for frequent tutorial and seminar discussion. About 50 units available at present—*circa* 30 pp./unit. Siscon project: Siscon Project coordinator, Dept. of Liberal Studies in Science, University of Manchester M13 9PL, U.K.

4. *Standards*

(a) *Consumer Report* (Quarterly) No. 1, May 1975

(b) *Monthly Information Sheet*

(c) Annual Reports and Supplements to Annual Reports.

Standards Association of Australia, P.O. Box 458, North Sydney, N.S.W. 2060, free on application. Standards and draft standards are listed in the *Monthly Information Sheet* and the draft standards are issued for public review.

e.g. (i) DR77029 Code for Selection and Care of Buoyancy Aids

(ii) DR77042 Concentrated Liquid Detergents for Household Hand Dishwashing.

Three months is generally allowed for comment after which the committee considers the comment and issues the final standard using a postal ballot for establishing consensus. The standard is then published and sold and manufacturers can apply for the SAA kitemark if their products comply and are subjected to inspection procedures. For example:

Frozen Food Retail Cabinets—B220–1966
revised AS1731–1975

Children's Toys and Playthings (Safety Requirements) AS1647–1974 plus amendments (No. 4 Feb. 1977)

Moulded Plastic Household Garbage Cans—AS1535-1975

Children's Night Clothes having Reduced Fire Hazard—AS1249–1976

Methods for test for Combustion Characteristics of Textile Materials 1. Ease of ignition; 2. Burning time and heat output; 3. Surface burning properties —AS1176–1976

Fabrics for Domestic Apparel of the Low Fire Hazard Type—AS1248–1976

School Wear for Boys and Girls, Part 1—Manufacturing Requirements—AS1994–1977.

Consumer Standards Published during 1977 in which Consumers were Represented Through the AFCO

AS Z42—1967	Non-returnable metal aerosol containers, Amendment No. 2
AS 1176—1976 Parts 1–3	Combustion characteristics of textile materials
AS 1248—1976	Fabrics for domestic apparel
AS 1249—1976 Parts 1–3	Children's night clothes
AS 1430—1976	Household refrigerators and freezers
AS 1647—1974	Children's toys and playthings (safety requirements), Amendments 3,4
AS 154—1975	Child restraints for passenger cars, Amendment 1
AS 1872—1976	Safety chains for trailers and caravans
AS 1876—1976	Petrol for motor vehicles
AS 1877—1976	Toilet soap
AS 1878—1976	Laundry tablet or bar soap
AS 1900—1976	Children's swimming aids
AS 1907—1976	Electric toasters
AS 1919—1976	Rubber condoms
AS 1924—1976 Part 1	Playground equipment
AS 1926—1976	Fences and gates for private swimming pools
AS 1927—1976	Pedal bicycles
AS 1957—1976 Parts 1–3	Care labelling for laundering and drycleaning + Supplement No. 1
AS 1960—1977	Brake fluids + Amendments
AS 1962—1976	Cleansing (scouring) powder
AS 1989—1976	Labelling of children's night clothes + Amendment No. 1
AS 1994—1977 Part 1	Schoolwear for boys and girls
AS 1999—1977	Liquid detergents for household hand washing
AS 2007—1977	Household electric dishwashers*
AS 2020—1977	Safety covers for private swimming pools.
AS 2040—1977	Household electric clothes washing machines*
AS 2071—1977	Electric circulating fans—for household and similar use
AS 2100—1977	Child-resistant medicine and poison cupboards—for domestic use

Source: AFCO Report, 30 June 1977, P.O.B. 75 Manuka, ACT, 2603.

* Test procedure only—no pass or fail level set.

Consumer Standards Committees of the Standards Association of Australia (1977)

CSAC	Consumer Standards Advisory Committee
CS/1	Anchors for small boats
CS/2	Household detergents*
CS/4	Care labelling of textiles
CS/5	Playground equipment
CS/7	Fire guards
CS/8	Performance testing of domestic furniture
CS/9	Contraceptive devices
CS/10	Bicycles
CS/11	Swimming pool covers
CS/12	Household soaps*
CS/13	Plastics for food contact*
CS/14	Safety helmets for sport
CS/15	Petrol for motor vehicles
CS/16	Quality of school wear
CS/17	Fencing of swimming pools
CS/18	Safety of children's toys
CS/19	Child-resistant medicine cabinets
CS/20	Prams and strollers
CS/21	Swimming aids
CS/22	Consumer contracts
CS/23	Car jacks
CS/24	Paint brushes
CS/25	Mattresses
CS/26	Labelling of household chemicals
CS/27	Fuel consumption for motor vehicles
CS/28	Solar water heaters
CS/29	Walking track signs
CS/30	Precious metals for jewellery
CS/31	Chemical carpet cleaners
CS/32	Sanitisers
CS/33	Power lawn mowers
CS/34	Safety of private swimming pools
CS/35	Continental quilts
CS/36	Termite protection
CS/37	Garden soils
CS/38	Shoe sizing
CS/39	Slide fasteners (zip)
CS/40	Babies' dummies
CS/41	Ladders for swimming pools
CS/42	Sunscreens*
CS/43	Car ramps and axle stands
CS/44	Labelling of clothing and other textiles
CS/45	Size colour coding of clothing
CS/46	Infants' and children's wear
AU/8	Adult seat belts

AU/16 Passenger car tyres
AU/22 Child restraints
BD/58 Thermal insulation of houses
CH/3 Paints*
CH/17 Adhesives
DS/10 Wrapping of dairy products
EL/5 Accumulators
EL/5/3 Domestic battery chargers
EL/15/4 Automotive batteries
EL/15 Household electrical appliances
EL/22 Dry cells and batteries
ME/23 Household refrigerators
TX/9 Carpets
TX/13 Flammability of textiles
TX/18 Textile furnishings
PK/13 Aerosols
PL/13 PVC garden hose
PL/36 Flexible foam for furniture and bedding

5. *National Health and Medical Research Council (Australian Department of Health)*
(a) Approved Food Standards
(b) Approved Food Additives
(c) Reports of the sessions of NHMRC
These were once free—now available from AGPS at great cost
6. *Reports from the Australian Government Joint Parliamentary Committee on Prices* (now dissolved)
(a) Price of Meatmeal, Canberra 1973
(b) Price of Carpet Tiles, Canberra 1973
(c) Prices of Household Soaps and Detergents, Canberra 1974
(d) The Prices of Frozen and Canned Vegetables, Canberra 1975

Prices Justification Tribunal
Annual Reports
7. *Trade Practices Commission—Information Circulars* (free on application) some examples only.
No. 4 Consumer Protection—Representations that Goods have Accessories they do not have
No. 5 Consumer Protection—Conditions and Warranties in Consumer Contracts
No. 6 Consumer Protection—Exclusion clauses in consumer contracts, warranties and guarantees
No. 8 Consumer Protection—Television Receiver Screen Sizes
No.10 Consumer Protection—Advertising Guidelines, 33pp.
No.11 Consumer Protection—Misleading Descriptions of Art Reproductions
No.12 Consumer Protection—Motor Vehicle Fuel Consumption Claims
No.13 Consumer Protection—Advertising and Metric Conversion
No.16 Advertising and Promotion of Fruit Juices and Fruit Juice Products
No.17 Refusal to Supply
No.18 Consumer Protection—Real Estate Advertising Guidelines
No.19 Consumer Protection—Travel Advertising Guidelines

*Author has served, or is serving, on these committees.

The Trade Practices *Act* is quite readable—particularly Part V on Consumer Protection

The *Decisions* of the Commission are filed and are available in the Commission offices in each capital city

Consumer Education Report, October 1976, 96 pp. Excellent source of reference to other sources of information. Packaging and Labelling Laws in Australia 1977.

8. *Industries Assistance Commission*

The Commission carries out enquiries in Australian industry. For this it

(a) *prepares* a statistical background (available);
(b) *produces transcripts* of evidence heard at its enquiry (kept at the National Library and I.A.C. Library). Copies are extortionately priced but the National Library will provide photocopies for private study;
(c) *publishes* reports on its enquiries, e.g. 'Soaps, Detergents, Etc.' 1976 (contains the consumer case).

There are also *indexes* to these reports and for more up to date references the annual report should be consulted.

9. *Patent Office Services*

As well as receiving and examining applications for patents, the Patent Office provides a number of services for inventors, manufacturers and other members of the public who are interested in patents and the information contained in them.

These services include—

(1) Libraries in which are collected patent documents filed in such a way that a searcher can find either the document relating to a particular patent or all the documents relating to a particular kind of invention.
(2) A weekly publication: *The Australian Official Journal of Patents, Trade Marks and Designs* contains particulars of new applications for patents, and of patents granted.
(3) Annual indexes of proceedings in the Patent Office.
(4) The sale of copies of patent documents.

All documents and publications may be consulted, and copies purchased, at the library of the Patent Office, Canberra and at the sub-offices in Sydney, Melbourne, Adelaide, Perth and Brisbane.

These offices are open from 10 a.m. to 4 p.m. (Monday to Friday). Some offices are also open one night a week for reference purposes.

The main Patent Office library at Canberra also contains technical and legal books, periodicals, catalogues and trade literature which may be consulted by the public.

Solutions to technical problems are often contained in patent documents. It is not widely known that these are a special, and frequently the only, source of certain information:

—they publish information earlier than conventional forms of publication, and
—they often describe inventions which are free for anybody to use because the corresponding patents were not granted or are no longer in force.

Assistance for searchers

Since 1904, when the Australian Patent Office was established, more than half a million documents have been published.

As it would be a time-consuming task to make a search through the whole of this material, the documents have been subdivided into smaller collections, or 'classes' of invention.

Documents filed before 1975 have been classified into some 900 groups which are defined in the manual: *Classification of Manufactures*.

From 1975, documents have been classified and filed according to the *International Classification of Patents*—a very detailed and modern classification. For each classification there is an alphabetical index indicating the class or classes to be searched for any particular type of invention.

All indexes and classification tables are available for reference.

At each office there is an officer whose help is freely available to searchers wishing to consult classifications and indexes and to locate the search files. Officers are not, however, authorised to conduct searches on behalf of the public or to give technical or legal advice about patents.

Search documents

'Patents' as such, do not form part of the search files. The 'Letters Patent', to give it the full title, is an official document of grant bearing the Seal of the Patent Office. It is generally understood that a phrase such as 'a copy of patent no. . . . ' refers to the corresponding complete specification mentioned in the 'Letters Patent'. A complete specification is a full description of the invention, generally referring to drawings and ending with 'claims' which are definitions of the scope of the patent protection.

The complete specification is normally not available for inspection until eighteen months after it has been lodged in the Patent Office. At that time a microfilm copy is placed in the Patent Office library and in each sub-office, where equipment is supplied for viewing and preparing a paper copy if required. Simultaneously a summary of the invention is filed in the form of a single-page 'abstract'.

When an application has been examined and accepted for the grant of a patent, another single-page summary is published, known as the 'abridgement'. Finally, the complete specification is printed. Copies of an abstract, abridgement or printed specification may be purchased at the main office or at a sub-office.

Foreign patents

Copies of the printed specifications and abridgements issued by most foreign patents offices are also available for reference at the Patent Office Library, Canberra.

10. *Australian Government Green Papers*

These are documents providing background information for public discussion to assist in the formation of policy—e.g., Green Paper on Rural Research. This contrasts with *white papers* which are statements of government policy.

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[11] University of Manchester, Institute of Science and Technology, via Dr David Ward, Department of Organic Chemistry, University of Adelaide; The Textile Institute. *Identification of Textile Materials.* 6th ed. Manchester, 1970.

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Further ideas for infra-red experiments

Perkin Elmer Infrared Applications Study: *Polymer Plastics Industry*. 3 pp. 1968; *Paints and Coatings*. 3 pp. (reflectance methods) 1968; *Packaging and Containers*. 3 pp. plastic films 1968; *Waxes*. 3 pp. 1968; *Analysis of diesel and petroleum base lubricants*. 3 pp; *Drugs*. 34 pp. 1972 (a very well prepared publication with a flow diagram system of identification of about 60 drugs).

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Spectrometric Analysis of Used Oils. Society of Automotive Engineers. 20 pp. 1969.

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Deley, J.P. Gigi, R.J. Liotti, A.J. Identification of Coatings on Paper by Attenuated Total Reflection (IR), *Tappi* **46**, 1963, 188A.

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AND PRICE 1976/40

This book is an expanded version of the first edition of *Chemistry in the Market Place*. It is a work of high seriousness but its 'flavour' is perhaps best captured in the words of its author as he describes the circumstances of its beginnings: 'over three glasses of cool, artificially coloured, artificially foam stabilised, enzyme clarified, preserved, gassed, amber fluid' two colleagues and he came to realise that consumers needed some 'real' chemistry, chemistry that would help them to make sense of the arguments that rage about various aspects of consumer products, particularly those of safety and efficacy.

The thrust of the book is towards the product and the chemistry needed to understand it, rather than towards chemistry illustrated by the product. Its scope is wide and includes chemistry in the laundry, the kitchen, the garden, the boudoir, the medicine chest. It also deals with motor cars, the accidental poisoning of children, and carcinogens. It is extensively illustrated with plates, figures, and tables, and contains practical experiments for its users.

The book will be welcomed by high school, college and adult education lecturers who are interested in creating courses in consumer chemistry. Concerned consumers will also benefit greatly from the information the work contains, regardless of their knowledge of chemistry. Home economics teachers will find that it forms a perfect complement to their existing texts. It is, in short, an important, practical, book on a highly significant subject.

Awarded the 1979 Archibald D. Olle Prize for a scientific work by the Royal Australian Chemical Institute.

Dr Ben Selinger is a graduate of Sydney University and took his doctorate at the Technical University of Stuttgart, West Germany.

He has taught at Sydney University and is at present Senior Lecturer in the Chemistry Department of The Australian National University.

Dr Selinger has worked in surface chemistry, electron spin resonance and single vibronic fluorescence. In 1973–4, as a Leverhulme Fellow, he developed some consumer chemistry applications for the Institute for the Promotion of Teaching Science and Technology in Bangkok.

He is co-author of *A Chemistry Manual for First Year University*, and author of *Simulation of Chemical Systems with the E.A.I.–180 Analogue/Logic Computer* and of over sixty scientific papers on fluorescence spectroscopy and photophysics.