A HISTORY OF THE CHEMISTRY AND INDUSTRIAL PRODUCTION OF POLYVINYL CHLORIDE

by
Morris Kaufman

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SUMMARY

This thesis attempts to trace the history of pvc from the first synthesis of the monomer in 1835 to the stage of its development at the outbreak of the Second World War. It deals with the theoretical and industrial aspects of the chemistry involved in the manufacture of the monomer, polymer and its modifications and with the major aspects of compounding pvc. It also discusses the evolution of the machines used to process the plastic from those which were used in the rubber industry.
The final chapter considers some of the early applications of pvc and the factors which stimulated its widespread use.

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CONTENTS

Chapter 1

Prehistory

The preparation of vinyl chloride was first recorded in 1835 by Regnault in a paper which appeared in almost identical German[1] and French[2] versions. This paper and a second which followed in the same year[3,4] showed that the preparation was essentially a by-product of the great polemic in organic chemistry on the nature of radicals which was then taking place. Their fundamental role in organic chemistry was generally accepted, but which precisely was the radical present in the compounds under examination or what indeed constituted this combination of elements which moved as a body from one compound to another, this was the subject of powerful disputation. The giants among the protagonists were Dumas and Liebig, the former championing the "etherin" (C_2H_4) radical and the latter "ethyl".

Henri Victor Regnault, a young Frenchman, born in Aix-la-Chapelle in 1810, came to work for a short time in the winter of 1834-35 in Liebig's laboratory at Giessen. "Here", said Liebig, in a footnote to one of Regnault's papers,[1] "I set Mr. Regnault, one of the most talented pupils at the Ecole Polytechnique and the Ecole des Mines in Paris, to work on this investigation ['The synthesis of chlorinated hydrocarbon']. Some experiments which I carried out several months ago have provided the basis".* Liebig, incidentally, seemed to be trying to woo Regnault from his mining engineering interest, for in the same note

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* This quotation and others in this thesis, is my own translation from the original language.

he opined that "in the interests of science it is much to be desired that Mr. Regnault should not become estranged from chemistry for which he has a decided talent".

The context of Regnault's original work "On the synthesis of chlorinated hydrocarbon (Oil of olefiant Gas)" is given in the paper itself. "Dumas and with him a number of other chemists regarded the 'oil of the Dutch Chemists' [i.e. dichlorethane] as a simple combination of equal parts of olefiant gas [i.e. ethylene] and chlorine. Liebig on the contrary, believes it is rather more complicated. Certainly it is difficult, at first sight, to account for the formation of such large quantities of hydrogen chloride. Theory on the formation of this compound is inadequate. I have arranged a number of experiments to explain these points..."

Liebig himself explained in a letter to Berzelius the point of the work; "an investigation which is likewise related to the etherin theory was recently completed by a young student of the Ecole des Mines working in my laboratory. ... This clearly leads to the conclusion that in the oil of olefiant gas the chlorine is present in two forms and that Dumas' view, according to which it is the first member of his ether theory, $C_4H_8 + {}_4Cl$ is completely wrong".[5]

The "oil of the Dutch chemists" was first prepared by the four Dutchmen - Diemann, Trotswyck, Bondt and Laurverenburgh - in 1795 by reaction of chlorine and ethylene in diffuse light to give a liquid oily compound of olefiant gas[6]. Liebig had noted that the reaction between this oil and alcoholic potash leads to hydrochloric acid and this combines with the potash. He found the reaction of great interest because it suggested that the two chlorine atoms of the molecule were not equivalent and hence that the oil of the Dutch chemists was not, as Dumas maintained, a compound of "etherin". It was for this reason that Liebig set Regnault to work on a more thorough examination of the reaction.

It is interesting to note in passing that Regnault acknowledged Liebig's prior observation of this reaction in the German version of his first paper. "I would comment further that the reaction of the oil of olefiant gas with potash to produce potassium chloride and a new ether-like compound was first observed by Liebig".[7] But in the French paper[2] there is no such recognition.

Regnault described the preparation of vinyl chloride as follows: "When one mixes an alcoholic solution of caustic potash with oil of the Dutch chemists, one can observe after some time the appearances of a precipitate which continues to increase. When one takes the vessel containing the reaction mixture into one's warm hands, the liquid begins to boil and a large amount of gas with an ether-like smell is evolved. This burns with a yellow flame with a green mantle".

He examined the white precipitate and identified it as potassium chloride. The gas however proved less simple "It could not be hydrochloric ether since if this were so it would be impossible to account for the acid part of the potassium chloride. It is therefore necessary to postulate another product, acetic or a similar compound". But the careful repetition of the experiments made certain the absences of every substance which might have been found. There were grounds for suggesting that the HCl ether-like compound is a new substance of a specific composition.

"Further investigation confirmed this surmise". His work supported Liebig's characterisation of the substance which established that it has a smell rather like that of olefiant gas but with overtones of garlic, that it can be condensed between -15° and -18°C and, he further found, that it is soluble in alcohol and ether in all proportions and to a much lesser degree in water.

Regnault subjected his substance to extensive and repeated elemental analysis and finally arrived at the conclusion: "If one, ... takes the ratio given by the first determination, 4 atoms of carbon to 6 of hydrogen and adds 2 chlorine atoms, in short if one ascribes the formula C_2H_3Cl to the new compounds, its formation is explained in a simple and satisfactory way. If one abstracts from

$$\begin{array}{lcl} \text{2 atoms of olefiant gas + 2 of chlorine} & = & 2C + 4H + 2Cl \\ \text{1 atom of the new substance} & = & \underline{2C + 3H + Cl} \\ & & \quad\ H + Cl \end{array}$$

one atom of HCl is left which combines with the potash to give potassium chloride".

"In this reaction oil of the olefiant gas has given half of its chlorine and a corresponding amount of hydrogen in the formation of HCl. It must follow that in the oil of olefiant gas the chlorine exists in two different ways and therefore the view of Dumas that there is a simple combination of chlorine with olefiant gas cannot be correct."

In his second paper of 1835 Regnault[3] took this matter further by describing the bromine and iodine analogues of vinyl chloride and from the new series of compounds C_2H_3Cl, C_2H_3Br and C_2H_3I he postulated a new radical which he thought would account neatly not only for his own compounds but also for some discovered by Liebig. Thus "regarding the way in which the constitution of these new substances might be considered it would be simplest to regard them as chloro-, bromo- and iodo-compounds of the hydrocarbon C_2H_3-. I name this <u>aldehydene</u> because it likewise appears in a remarkable substance which Liebig recently discovered and called 'aldehyde'. Furthermore I consider this hydrocarbon as a completely hypothetical radical and give it a name only because of the necessity of providing one for the etherlike substance in the description of its properties.

"Aldehyde has the formula $C_4H_8O_2 = C_4H_6O$ plus H_2O. On treating aldehyde with silver oxide, Liebig obtained a new acid which he called aldehyde acid. It has the formula $C_4H_6O_3 + H_2O$.

"One can accordingly construct the following series

C_4H_6 - aldehydene-hypothetical radical
$C_4H_6Cl_2$ - chloroaldehydene
$C_4H_6Br_2$ - bromaldehydene
$C_4H_6Cl_2 + H_2Cl_2$ - chlorohydrocarbon
$C_4H_6Br_2 + H_2Br_2$ - bromhydrocarbon
$C_4H_6O + H_2O$ - aldehyde
$C_4H_6O_2 + H_2O$ - aldehyde acid
$C_4H_6O_3 + H_2O$ - acetic acid

"The decomposition of the chlorinated hydrocarbon compounds with alcoholic caustic potash seems to be far from favouring the view according to which the olefiant gas appears as an unchanged radical in this compound and accordingly the oil of the Dutch chemists must be considered as the hydrochloric acid of chloraldehyde".

In the continued quest for true radicals, Liebig in 1839 decided that Regnault's aldehydene (C_4H_6) should be renamed "acetyl".[8] With this he gave up his earlier theory that "ethyl" was present in these compounds for he stated that "Ether and ammonia compounds assume one form if one regards "Amid" (N_2H_4) as the unchanging radical of the ammonia compounds and "acetyl" as the startingpoint of the ethers". Thus

$Ac = C_4H_6$ acetyl
AcH_2 = olefiant gas
AcH_4 = ethyl
AcH_4O = ether
$AcCl_2$ = acetyl chloride
$AcBr_2$ = acetyl bromide
$AcCl_2 + H_2Cl_2$ = oil of the Dutch chemists

This theory gained currency for a while as the description of vinyl chloride as "chloride of acetyl" in E. Turner's "Elements of Chemistry", which was a standard text[9], shows.

The first reference to Regnault's compound as "vinyl chloride" seems to be Kolbe's Lehrbuch der organischen Chemie dated 1854[10]. I say seems to be because in his discussion of the subject Kolbe, while introducing a distinction between what he called the vinyl and acetyl radicals did not explicitly say that here was the origin of the term. On the contrary it came into the discussion without introduction and without any explanation as to why the word "vinyl" was chosen. Nevertheless it remains the first reference to the word that I can find.

Kolbe was still at that time very much preoccupied with the subject of radicals and presented "vinyl" as a very important example. "It is very apparent", he said, "that ethylene and its homologues are themselves hydrogen compounds of particular radicals and have similar constitutions:

Ethylene C_4H_4* = (C_4H_3) H
Propylene C_6H_6 = (C_6H_5) H
Butylene C_8H_8 = (C_8H_7) H
etc.

"Supporting this assumption is the fact that one of the hydrogen atoms of all these substances can be more easily removed than the rest and can be replaced by Cl, Br, I, etc. while at the same time it is difficult to change one radical into another."

Kolbe noted the similarity between these radicals and those of the "so-called fatty acids", but could not believe them to be identical, since there were such large differences between the two groups of compounds. He therefore suggested that there were two parallel series "In the vinyl radical of ethylene, C_4H_3, all four carbon atoms are presumably equal, while in acetyl $(C_2H_3)C_2$ the radical of acetic acid, two atoms of carbon behave differently from the other two".

He went on to list and describe the preparation and properties of a series of vinyl compounds. The first was vinyl hydride (ethylene)and the second was vinyl chloride. As synonyms of the latter he gave chloroacetyl, acetyl chloride gas, chloroaldehydene and chloroethenide. It is noteworthy that in his description of vinyl chloride and its reactions there is no mention of its polymer, or anything that could be taken for it. Nor for that matter was there any suggestion of the polymer in either of Regnault's papers in spite of later assertions in various books that he had noted the polymerisation of vinyl chloride.

Among other substances Kolbe included in his list of vinyl compounds various chlorinated substitution products of ethylene e.g. chlorinated vinyl chloride $C_4H_2Cl_2$, and

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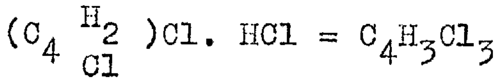
* It will be noted that in his formulae Kolbe was assuming an atomic weight of 6 for carbon

the hydrochlorides of mono-, di-, and tri-chlorvinyl chloride. The first of these he set out thus:



$$(C_4 \genfrac{}{}{0pt}{}{H_2}{Cl})Cl.\ HCl = C_4H_3Cl_3$$

and the second was $C_4H_2Cl_4$, presumably $(C_4 \genfrac{}{}{0pt}{}{H}{Cl_2})\ Cl.HCl$. Bromo- and iodo-compounds were also present in his list.

Thus some time before 1854, when his Lehrbuch was published Kolbe had satisfied himself about the existence of the vinyl radical and had established the nomenclature leading to vinyl chloride. This in turn seems to have been accepted as a few subsequent publications testify. For example Miasnikoff in a preliminary note in Annalen in 1860 spoke of vinyl bromide[11] and A,W. Hofmann in the same volume reported on the same compound[12].

It is a little surprising, then to find that Kolbe later in the same book executed a complete volte face on the subject of the vinyl radical. Among some final "afterthoughts"[13] written in 1859* and even earlier in the book[14] he said "It has already been stated on p.738 that the hypothesis on the constitution of ethylene and its derivatives, described on p.345, according to which they are considered as vinyl compounds, can no longer be taken as correct since Wurtz made his important discovery of the so-called glycols". The earlier reference[14] explained why, "The discovery of the ethylene oxide hydrate and other compounds of ethylene oxide have thrown a new light on the chemical nature of ethylene and its derivatives ... The view expressed there that ethylene and its derivatives contain the radical C_4H_3 ... is not compatible with the composition and behaviour of ethylene oxyhydrate. I have become convinced that the hypothesis

* The form and publication of this work is somewhat complex and the following explanation of the situation is offered to assist in an appreciation of the referencing.

Kolbe's Ausfürliches Lehrbuch der Organischen Chemie was part of Otto's Lehrbuch der Chemie which was based on Graham's English text-book.

Graham-Otto consisted of five volumes; the first two were by Otto on inorganic chemistry. Volumes 3 and 4 of the series were written by Kolbe as the Ausfürliches Lerhbuch der organischen Chemie and, as Kolbe said, had no connection with the organic section of Graham's book. They were intended to be quite self-contained. The organic section was subsequently completed by a 3rd volume (Volume 5 of Graham-Otto) written by E.V. Meyer, A. Weddige and H.V. Fehling. This was in two parts with the second section by Fehling published in 1869 and the first section by Meyer and Weddige in 1876.

When the book first began to be published in 1854 an announcement explained the intended method of publication: "The work will comprise two volumes, and will be issued in parts consisting of six folios, as often as feasible. When these folios follow each other in quick succession double parts of 12 will appear."

Vol. 1 of Kolbe's Lehrbuch (as found in the British Museum Library) has a title page dated Braunschweig 1854 and also final Nachträge and Nachwort dated 1859. It also has bound into the back of it a title page dated 1859 which might well have come from the issue published at that time.

cannot be further developed and I therefore abandon it, since it is just these facts which at first demonstrated its untenability that speak most decisively from the old view propounded by Berzelius, that ethylene (called "elayl" by Berzelius) is an organic radical."

Thus we have arrived at the situation in which the word "vinyl" was coined, in which it was applied amongst others to vinyl chloride in which it achieved a certain degree of currency and in which it was abandoned by its inventor, all within a span of five or six years.

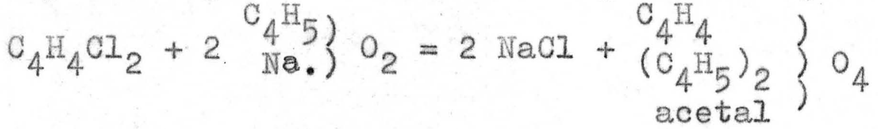
That the name "vinyl chloride" had not achieved general usage within this period is shown by a paper in which Geuther[15] discussed the relationship between aldehyde and elayl (ethylene) chloride. He argued that since the formula of the former is C_4H_4O and of the latter $C_4H_4Cl_2$ $[C = 6]$ one can think of the substitution of oxygen in one by chlorine to give the other. If this is so, the chlorine of elayl chloride should be exchangeable with oxygen as for example from silver oxide.

He carried out this experiment but obtained no aldehyde. In the event he made a liquid in a sealed tube which on opening "seemed to be under powerful pressure within". The liquid disappeared and a leek-like smell was apparent like that of the substance which has the formula C_4H_3Cl, which boils at -15°C. This was vinyl chloride though Geuther did not call it by this name.

Not discouraged, he persisted. "I tried to effect the same change with potash to convert it to the glycol" and thus repeated Regnault's experiment, though not so successfully. Elayl chloride and potash were heated in an oil bath at 130-140°C. This regularly led to an explosion, so it could only be carried out at up to 125°C ... In spite of cooling with ice a considerable explosion occurred on opening ... The same leek-like smell was evident."

Geuther like Regnault noted the abstraction of only one atom of chlorine and concluded "that one cannot consider elayl chloride as an aldehyde in which the oxygen has been replaced by chlorine."

A.Wurtz and Frapolli were also interested in the chemistry of acetal, and in a paper entitled "The Conversion of aldehyde to acetal"[27] described their contact with vinyl chloride through their unsuccessful efforts to make acetal from chlorethylidene (which they thought was an isomer of 'chlorathylen'). "It might be hoped that treatment of chlorethylidene with so-called sodium ether [i.e. alcoholic caustic soda] would give acetal according to the equation.



$$C_4H_4Cl_2 + 2 \left.\begin{matrix}C_4H_5\\ Na.\end{matrix}\right\} O_2 = 2\ NaCl + \left.\begin{matrix}C_4H_4\\ (C_4H_5)_2\\ \text{acetal}\end{matrix}\right\} O_4$$

The results of this experiment did not correspond with this expectation. At least, the main product was not acetal but a chlorine containing gas with the formula C_4H_3Cl, identical in composition and properties with the so-called chloraldehydene or chlorinated ethylene (gechlorte Athylen) derived from chlorethylene (Chlorathlen, i.e. dichlorethane). We verified this identity by determination of the solubities of the products obtained from chlorethylidene and chlorethylene."

Although Kolbe had abandoned his concept of the vinyl radical by 1859 it was nevertheless to be found in another text-book, by F.A. Kekulé, dated 1861[16], in which there is a reference to the vinyl group C_2H_3, in the formation of vinyl bromide from a brominated amine. Later in 1866, in Kekulé's <u>Lehrbuch</u>[17], the vinyl radical C_2H_3-, is described without any reservations. "The chloro-, bromo- and iodo substitution products of ethylene can, from their constitution be recognised as the chloride, bromide and iodide of the monatomic [einatomig] vinyl radical." Kekulé described some reactions leading to vinyl compounds and quoted an interesting example from Berthelot[18] in which vinyl sulphate was formed by the addition of sulphuric acid to acetylene. The addition of various compounds to the triple bond of acetylene e.g. hydrochloric acid, hydrogen cyanide, acetic acid and alcohols is a reaction currently employed today in the manufacture of many important vinyl compounds.

What is somewhat puzzling is Kekulé's categoric statement taken from Berthelot that the hydrolysis in boiling water of the addition product of sulphuric acid and acetylene gives vinyl alcohol. "The vinyl alcohol after systematic rectification is a colourless liquid. It has a characteristic smell, similar to acetone, boils at something less than 100°C, and is soluble in water." This is an interesting characterisation of a substance which does not exist. Vinyl alcohol is a tautomer of acetaldehyde and whenever it is produced by the hydrolysis of a vinyl ester immediately goes over to the aldehyde form. It might be understandable, though perhaps surprising, if Kekulé had described the aldehyde and called it vinyl alcohol but in the final sentence of his section on vinyl compounds he pointed out that "vinyl alcohol is isomeric with aldehyde".

Semenoff in 1864 was also preoccupied with attempts to prepare vinyl alcohol from vinyl halides[19]. In his explanation of the preparative method which he chose he also characterised the latter as "derivatives of the monatomic radical, vinyl, C_2H_3" and went on to say "in a manner analgous to the behaviour of Cl, Br and I compounds of other monatomic alcohol radicals they must be capable, by double decomposition, of replacing hydrogen in another compound by C_2H_3 and finally be able to produce a compound of the composition

$$\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O \text{ i.e. vinyl alcohol"}$$

He tried to do this with vinyl iodide but was unsuccessful.

Thus there seems no doubt that by the middle of the 1860's the name of vinyl chloride was quite unequivocally established and it was recognised as a substitution product of ethylene. This link with ethylene inevitably brought it into the field of enquiry concerned with the nature of the carbon-carbon bond and in particular the question of unsaturation.

As early as 1853 Rochleder in a paper concerned with basic questions of organic chemistry[20], was feeling his way to the concept of unsaturation. In deriving various compounds from the methyl radicals which he represented thus $C2\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$ he came to ethyl $C_2\left\{\begin{matrix}C_2H_3\\H\\H\end{matrix}\right.$ by substituting C_2H_3 for a hydrogen atom. This hydrogen atom could be replaced by other radicals as could the other two and so more complex compounds would result. It also happened, he said, that in some compounds the hydrogen atoms could be taken away without replacement thus leaving *lücke* or gaps. In the paper Rochleder produced some tables showing the derivation of many such compounds and in his Table 1 he included $C_2\begin{matrix}(C_2H_3)\\\square\\\square\end{matrix}$ wherein $\square$ was equivalent to a gap.

For some reason, although he named the othermembers of his table he did not attach a name to this one. It is clear however that this is the first suggestion of unsaturation in vinyl chloride.

Kekulé took the concept of unsaturation further in his Lehrbuch with his formulation of "carbon rich compounds"[21]. These stood in contrast to the paraffins in which all four valencies of each carbon were satisfied according to the general formula C_nH_{2n+2}. Ethylene was one of the olefins named in which "one must assume a more dense disposition of the carbon atoms."

Vinyl chloride was considered more explicitly by Lothar Meyer in 1866[22]. He was stimulated to investigate various isomers by Kekulé's "discovery of the four fold saturation capacity of the carbon atom" and felt in particular that "it is necessary to explain the isomerism of the two compounds with the formula C_2H_3Cl, one of which was obtained by Regnault from elayl chloride and the other by Harnitz-Harnitzky from phosgene and aldehyde".[23]

He had, he thought, to assume "unsaturated affinities" in both compounds, otherwise they would be identical. On this assumption he postulated three forms:

.HHCCHCl.   ..HCCHHCl   ..CICCHHH

"in which univalent atoms are placed next to the carbon atom to which they are bound and the unsaturated affinities are indicated by dots". He speculated that "of these three chemical constitutions the first may be an as yet unprepared substance, the second is Regnault's compound, and the third is that of Harnitz-Harnitzky".

Meyer thinking along these lines, tentatively suggested the possibility of an isomer of ethylene, "one which has been encountered up to now only in compounds with the ethylidene radical".

.HHCCHH.	..HCCHHH
ethylene	ethylidene

On this basis he proposed that vinyl chloride has the composition ..HCCHHCl and not HHCCHCl "because on decomposition of oil of the Dutch chemists with alcoholic potash only one chlorine atom, rather than both, is eliminated with one atom of hydrogen. It seems that the affinity thus freed is different from the unsaturation in ethylene.

This edifice of speculation was unceremoniously demolished by Kekulé and Zincke in their paper entitled "On the so-called Chloraceten".[24] In it they demonstrated that the compound C_2H_3Cl which Harnitz-Harnitzky had prepared from phosgene and aldehyde, chloraceten, was not a pure compound and indeed did not exist.

Kekulé and Zincke considered this work of great importance from a theoretical point of view. "The constitution of chloraceten and its isomerism with monochlorethylene (vinyl chloride) appeared remarkable from the beginning. When later we tried to explain this from the standpoint of valency (<u>Wertigkeit</u>) we came to the view that in any event vinyl chloride contained doubly bound carbon. It followed that chloraceten could not be constituted in this way and that it must therefore contain a four-valent carbon next to a two-valent carbon or, putting it another way, one carbon with two unsaturated affinities:

$H_2C = CHCl$	$H_3C - -CCl$
vinyl chloride	chloraceten

assuming of course that one cannot accept a three-point carbon".

"... The existence of an isomer of vinyl chloride has a considerable theoretical significance because if the assumption of a two valent carbon is necessary in such a simple case then it is at least permissible in complex examples. It did not seem to me, from the standpoint which we currently assume that the existence of a compound constituted in this way was probable."

"In this situation we believed we ought to make the personal acquaintance of chloroacetene."

Four explanations of this situation seemed possible and the fourth suggested quite baldly that "possibly all the statements about chloroaceten are wrong and some may even be deceitful. ("... und manche davon sogar auf Schwindel").

"When we began our investigation .... we believed that it was possible that both compounds were polymers and that chloraceten was a gas produced by decomposition. Now that we have completed our work we hardly doubt that the fourth view is correct."

Thus with this paper the constitution of vinyl chloride was established unequivocally.

It will be noted that so far in this account there has been no mention of any polymer of vinyl chloride. This in spite of frequent assertions in the chemical literature that Regnault observed polyvinyl chloride in his early investigations. The first mention of a vinyl polymerisation occurred in a batch of "Miscellaneous Reports" in 1860, wherein Hofmann described the "metamorphis of a simple brominated ethylene".[12] On leaving a "monobrominated ethylene" in a glass tube overnight "the colourless mobile liquid changed into a white porcelain-like mass. On opening the tube no pressure was evident and the white amorphous odourless substance was insoluble in alcohol, ether and water. On heating it carbonised with a vigorous evolution of hydrogen bromide".

"Analysis showed, as might have been anticipated, that the vinyl bromide had merely been subject to rearrangement".

The figures quoted for carbon and hydrogen analysis, and bromine by difference, corresponded fairly closely with the formula C_2H_3Br.

Although Hofmann managed to effect this change from time to time, he had to say that "the conditions for this conversion are quite unknown. In vain did I try to bring about the modification at will". It seemed to him almost capricious. "The liquid vinyl bromide was stored for weeks without the observation of a trace of change and then suddenly I found the liquid changed to a solid mass." At one time he suspected that the presence of water favoured the conversion but "I convinced myself through special experiments that this was a deception. The conversion occurs in the presence or absence of water in quite the same way".

Hofmann had seen the polymerisation of vinyl bromide but had little idea about the nature of the change. This is quite clear from his use of the word "metamorphosis" to describe the event. The subject was taken further, however, by a more intensive investigation by Baumann which he reported in 1872 under the title "Some Vinyl Compounds".[25] Initially his purpose was to examine the reaction of vinyl bromide and alcoholates, in particular sodium methylate, and in this connection a comparison of the behaviour of vinyl bromide with the other vinyl halogens was of interest but "the work itself led to interesting isomers of vinyl bromide and chloride" whose preparation and properties were described in the second part of that work.

Baumann conducted his first experiments with vinyl bromide. He confirmed Hofmann's observations both in respect of the conversion to the polymer and the inconsequence of the presence of water and then went on to investigate the influence of light on the reaction. But since he repeated this work for vinyl chloride there is no need to elaborate on this part of his paper.

Baumann could find no reference to the analogous behaviour of vinyl chloride and iodide and he therefore "undertook to investigate whether or not both these compounds undergo the same change and in what conditions."

"In order to find out whether sunlight in the presence of small ammounts of water bring about a similar change as with vinyl bromide, three tubes were filled with dry vinyl chloride. To one of them several drops of water were added. This one and that with dry vinyl chloride were placed in direct sunlight. The third tube was left in the dark. The first two became turbid almost simultaneously after 6 - 7 hours and a white milky precipitate settled out after shaking". This was the insoluble polymer precipitating from the monomer. "After 8 days the contents of both tubes had changed to a bright white opaque mass. The third tube showed no change after four weeks. When the latter was exposed to diffuse light for three weeks, it underwent the same conversion as the other two but more slowly". In his experiment with vinyl bromide Baumann had shown that diffuse daylight had the same effect as direct sunlight but that it acted more slowly and less reproducibly.

"On opening the tube there was hardly any residual pressure and only a trace of vinyl chloride escaped. The solid compound ... was without smell". Analysis showed that it had the same empirical formula as vinyl chloride. On examination he found that "the converted vinyl chloride possessed almost the same properties as the converted vinyl bromide. It is hardly attacked by solvents and acids, (unlike the bromide) it is not dissolved by liquid bromine.

On heating with alcoholic caustic potash it is decomposed like the bromo-compound but with greater difficulty. On rubbing with silk it becomes even stronger electrically, it is more elastic and can be comminuted with scissors only. Its specific gravity is 1.406 as determined in the pyknometer with alcohol (because the compound is not wetted at all by water). It can be heated to 130°C without decomposition and at higher temperatures it melts to a black-brown mass and produces considerable amounts of acid vapours as well as a brown distillation product which dissolves in alcohol with a brown fluorescence".

In this description Baumann in 1872 set out what might be regarded as a specification for polyvinyl chloride (pvc) which is instantly recognisable to the modern plastics technologist.

He then went on to repeat experiments on conversions effected by light which had earlier been carried out by Regnault "on twice-chlorinated ethylene".[26] He prepared it by the chlorination of vinyl chloride and subsequent treatment with alcoholic potash. He confirmed that on exposure to sunlight a white solid was produced.

Baumann experienced some difficulty in preparing vinyl iodide and when eventually he made some he could not polymerise it. He did find however that vinyl iodide inhibited the polymerisation of vinyl bromide. This must be one of the earliest references to a polymerisation inhibitor.

Throughout his paper the author spoke of polymerisation as "conversion" and the polymer as the "converted product" or "isomer". From such terms it is difficult to decide whether he had any idea that the product was a polymer. It is not impossible that he thought this was so because judging from contemporary literature the concept of the isomer, originally propounded by Berzelius, seems sometimes to have included the polymer. It is more likely however that when Baumann spoke of isomers he meant what we now mean by this term. This conclusion is supported by the relationship which he and Hofmann before him[12] saw between vinyl compounds and acetaldehyde. They regarded the compounds as derivatives of vinyl alcohol, which is isomeric with acetaldehyde.

Whether or not Baumann was aware of the polymeric nature of his product may well be open to doubt. What is certain is that by 1872 vinyl chloride and its polymer were known and had been described in some detail. They had emerged during the formative period of organic chemistry, as part of the process by which its inner laws and conventions were established. There is no hint in the literature that any of the investigations that have been discussed were stimulated or inspired by thoughts of possible applications of the products. This was to come later and in this sense the phase which concluded with Baumann's preparation and description of polyvinyl chloride might be described as the prehistorical period of modern pvc technology.

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Chapter 2

The Industrial Origins of Polyvinyl Chloride

The work described in the last chapter was essentially academic. Nowhere in the papers referred to was there any suggestion that the authors entertained any thoughts about practical applications of vinyl chloride or its polymers. Signs of industrial interest began to appear alongside theoretical curiosity only after the turn of the century, particularly in the form of patents and in this connection the name of Fritz Klatte is outstanding.

However between Baumann's work on the polymerisation of vinyl chloride reported in 1872[1] and Klatte's historic patents in 1912 further theoretical developments in this field were recorded in the chemical literature. For example H. Biltz refined the method for making vinyl chloride from ethylidene chloride[2], described earlier by Wurtz and Frapolli[61]. Biltz thought that the Wurtz-Frapolli method was quicker than Regnault's from dichloroethane and he modified the former so that the vapour of ethylidene chloride or ethylene chloride was led through a combustion tube filled with small pieces of pumice heated to dark-red heat. J.B. Senderens in a study of catalytic dehydration of organic compounds used alumina and with dichloroethane found that at 370° the loss of HCl gave vinyl chloride[3].

Sabaneef in 1873 gave the first hint of a method based on acetylene, for the preparation of vinyl chloride[4]. He did not actually prepare this substance but reacted acetylene and hydrochloric acid unintentionally. In view of subsequent events this is of some interest. In decomposing copper acetylide with concentrated hydrochloric acid he purified the resulting acetylene by passing it through bottles of water and potash solution. "On boiling the last residues of copper acetylide with hydrochloric acid, oil drops which sank collected in the water purification bottle. They were assumed by Berthelot to be acetylene hydrochloride $C_2H_2 2HCl$, but without convincing himself of this by analysis or by boiling point determinations. "The liquid which I obtained distils completely between 56° and 58°. Ethylene chloride boils, according to Bunte, at 57.5° so that these two substances are identical".

Berthelot's erroneous belief that he had prepared vinyl alcohol by the hydrolysis of vinyl sulphate[5], led to further experiments by workers who were doubtful about his conclusions. Lagermark and Eltekoff suggested that the vinyl alcohol was in fact crotonaldehyde[6] but S. Ziesal in discussing his own investigation into "The reaction of acetylene and sulphuric acid" thought both they and Berthelot were wrong[7]. "The result of my work is largely negative in that I have proved that Lagermark and Eltekoff were in error when they believed that acetylene was itself converted to crotonaldehyde. Pure acetylene produces no crotonaldehyde with successive treatment of sulphuric acid and water. This is much more a reaction product of the vinyl halide ether [vinylhalogenäther] formed in the work of Lagermark and Eltekoff, through the action of HCl on the acetylene from copper acetylide, vinyl chloride".

This was, I believe, the first, albeit oblique, reference to the synthesis from acetylene and HCl, the route which has until very recently dominated in the manufacture of the monomer. The equimolar addition of these two reactants was unequivocally described for the first time in a patent dated October 11th 1912[8]. The "inventor" was Fritz Klatte and the patentee was the Chemische Farbik Griesheim Elektron of Frankfurt-am-Main. As a matter of fact this patent was one of a group emanating from Griesheim Elektron, which we shall discuss later, and they were concerned with the products of acetylene reactions. The mainspring of this interest is of considerable historical significance and was closely related to the fluctuating prospects of acetylene in the first days of its commercial exploitation. In particular it seems that the high hopes that were rested on acetylene as an illuminant and which were subsequently disappointed led, among other things, to an industrial interest in its chemistry.

The story began with the discovery of the electrothermal process for making calcium carbide. The originator of this process is the subject of some dispute but, Partington notwithstanding[9], it appears that the claim of T.L. Willson in the United States to be the first inventor of the process must be recognised. He was indeed the man who developed it on an industrial scale. I do not propose to discuss the matter in any detail here since it is not really germane to our central theme and because it has been adequately ventilated elsewhere[10,11,12]. It is enough to say that the discovery of 1892 and the simultaneous observation of the reaction of calcium carbide and water to give acetylene which burned with a brilliant white light, aroused interest in various parts of the world.

The situation was elegantly summarised by Dr. Frederick Rose, Her Majesty's Consul at Stuttgart in Germany, who as a chemist and an authority on acetylene was well placed to observe the scene in the country that was in the van of progress in the application of acetylene lighting. He said, in the introduction to a review in 1899[13], "Since the time when civilised man, discontented with the distribution of light imposed on him by nature, first had recourse to artificial sources of light, immense strides have been made both with regard to the quantity produced and the quality of the various illuminants which have been successfully adopted.

"The present century opened its eyes upon the reign of the pine torch, the animal oils and candles, all of which for serious practical purposes have been relegated to the past - and is now passing away, leaving the palm of victory to be contested for by petroleum, coal gas, electricity and the newest and in some respects, most perfect artificial light, acetylene gas ... What the ultimate result of this struggle will be no man can at present predict with certainty. The probability is that petroleum will suffer most, that coal gas will be superseded in some respects - especially with regard to the lighting of small towns - and that electricity will not be appreciably affected. It is not the intention of the acetylene industry to enter into competition with high class, but rather with inferior illuminants, as petroleum and coal gas undoubtedly are".

We can, in passing, admire the basic shrewdness of Dr. Rose's judgement, even though he guessed wrongly in one respect. However the purpose of the rather lengthy quotation is to convey something of the optimistic feeling which some people entertained about the future of acetylene lighting. But Dr. Rose was writing seven years after the discovery of the process for the manufacture of carbide and by that time a carbide industry was already well established. Enthusiasm for acetylene lighting was kindled much earlier. In 1894 F. Wyatt described the great industrial future of carbide as a source of acetylene[14] and in the next year Professor Vivian Lewes gave the first public demonstration of the acetylene flame during a lecture at the Royal Society of Arts[15].

In December 1897 the new industry gave further evidence of its vigour by launching the Journal of Acetylene Gas Lighting which in its first issue reviewed "The calcium carbide industry : its present position and prospects". Therein it quite baldly and confidently asserted that "the future of carbide of calcium is of course almost wholly associated with acetylene gas ... it burns with a flame of intense brilliancy and ever since its first public demonstration in this country ... it has as an illuminating power attracted the most absorbing and widespread attention"[16]. As if to prove the point the second issue carried the following notice "owing to demand for the first number of this journal we shall be pleased to forward copies of the second number in exchange for the first, paying postage both ways"[17].

The industry went from strength to strength. After an exhibition of acetylene gas lighting in Berlin in 1897, the English followed with another at the Imperial Institute in London and this led the Journal of Acetylene Gas Lighting to the thought that "It may now be accepted as a fact that acetylene lighting is fully established as one of the staple industries of this country. Its progress has already been rapid but sure"[18]. The Journal of Gas Lighting confirmed this conclusion in 1900 with the estimate that "at least 100,000 h.p. are now being used throughout the world for making carbide whereas there were not 100 h.p. employed in 1894"[19].

Growth was not uniform in various parts of the world and the most rapid strides were made in Germany. In the review to which we have already referred[13] Dr. Rose gave some account of the extraordinary vigour of the spread and interest in acetylene lighting. For example in July 1898 there were 62,000 jets of acetylene installed in Germany, by the beginning of the following year this had risen to 170,000 and by the end was assumed to be 220,000. As for the development, in 1897, 617 patents had been applied for and in 1898 the number had risen to 937. The corresponding number of applications in other forms of illumination were 288 in 1897 and 209 in 1898.

In France, though the rate of progress was not as great as that of her neighbour, acetylene illumination was making its mark. Some years later, in 1907, <u>Gas World</u> reported that 104 towns with populations of between 1000 and 6000 were lit by acetylene[20].

In England, the relevant authorities seemed to require more persuasion, perhaps because competition from the other sources of illumination were fiercer. In any event acetylene lighting made little impact on the community. Production of carbide in the U.K. at the turn of the century was chiefly in the hands of one company, the Acetylene Illumination Co., who manufactured their product under licence from Willson, at Foyers in Scotland. At that site they combined with the British Aluminium Co., to exploit the hydroelectric power available there. Total production in 1900 was only 1200 tons and all sales for the same period amounted to no more than 2000-2500 tons. The corresponding German consumption was 17,000 tons[21].

This general picture is confirmed by an undated pamphlet (but published after 1905 judging from internal evidence) found in the British Museum library, on "Acetylene : Its uses and advantages as an illuminant"[22] . It was advertising matter probably published by Messrs. Thorne and Hoddle of Victoria St., London, S.W.1., a company that was outstanding in this business, and what is so striking about it is the modesty of its claim. It listed complete installation "carried out by us" in stately homes and other important buildings, such as the residences of the Dowager Countess Grenville of Surrey, the Rt. Hon. Viscount Gage of Sussex (100 lights), the Inebriates Reformatory, Norfolk, and the Quorn Hunt Kennels, Leicestershire, but it made no mention of any major applications. In fact it explicitly if tentatively, claimed "Great advantages lie perhaps in lighting small areas, e.g. private houses ..." The lack of solid progress in the U.K. is reflected in the total absence of official statistics on acetylene as an illuminant.

However, expectations ran high in England as they did elsewhere and in Europe particularly forecasts were so sanguine that the acetylene industry from its earliest days was plagued with crises of overproduction. A bare six years after the initial discovery of carbide the first forebodings were being voiced. "The field of utility of acetylene is however restricted and as company after company is formed to exploit some form or other of acetylene carbide generator, those who are best able to judge cannot but see that the field of operation is so limited and the numbers of forms of generators so large, that at best only a very moderate return on the capital invested can be expected"[23].

A review of the carbide industry in the Europe of 1901 showed how earlier fears had materialised[21]. "The calcium carbide industry in Europe is still under the cloud created by over-capitalisation and over-production of the years 1899-1900. In every European country factories for carbide production had been built without any reference to the probable demand for the commodity and the natural results followed when the price of carbide fell over 50% in a few months".

The next crisis came in 1905 and this caused prices to drop from £28 per ton in 1898 to £8 in 1909. There were subsequent difficulties which persisted until well after the first world war but it is clear that the problem of over-production in the period up to the end of the first decade of this century stemmed directly from the failure of acetylene to establish itself as an important illuminant. In cost it could not compete with coal gas which at this time began to exhibit, on a large scale, the improvements which could be achieved with the Welsbach gas mantle. (A breath of the intensity of this battle is conveyed by a latter sent to the Gas World in 1908 which began "Dear Sir, As I had the pleasure whilst at Magherafelt, Co. Derry, of ousting an acetylene installation on purely cost lines.... [24]). In its competititon with electricity, although initially electric lighting was more expensive, the direct conversion of electric current to light was eventually bound to be cheaper than the multistage process via carbide and acetylene.

Perhaps the rise and decline of acetylene as an illuminant can be epitomised by the entries under acetylene in the 10th and 11th editions of the Encyclopedia Britannica published in 1902 and 1910 respectively. The first one discussed generation and burners at length and concluded hopefully that "This class of burner [Naphey and Doxlan] has been very successful and its introduction together with the realisation of the importance of purifying the gas before combustion has removed perhaps the most important obstacle to the use of this beautiful illuminant"[25]. The 1910 article devoted almost all of its four pages to carbide production and acetylene generation and purification and dismissed lighting application with a reference to the "use of dissolved acetylene for lighting omnibuses, motor cars, railway carriages, lighthouses, buoys, yachts, etc., for which it is particularly adapted"[26].

In such a way were buried the bright hopes of an earlier decade.

But buried hopes or not, the availability of so much unused carbide capacity and the consequent fall in prices inevitably stimulated the search for alternative outlets. Of course interest in other than illuminant possibilities of carbide and acetylene did not arise solely from the failure of acetylene to make the grade in lighting. A number of workers were active in these other fields before this fact became evident but it was only afterwards that their work attracted greater interest and support.

Thus Le Chatelier had drawn attention to the high temperature flame from a mixture of oxygen and acetylene and in 1902 Messieurs Fouche and Picard described the capabilities of their oxyacetylene blowpipe. "The most interesting application of this blowpipe is for welding iron or steel. Sheet iron 1-5 mm thick is welded together edge to edge with the greatest ease ... The process we have described is really new so that we could only mention a few applications, but we consider it certain, on account of the remarkable qualities of the oxy-acetylene flame that varied applications, at present unthought of, will appear from day to day"[27].

These developments with the concurrent growth of oxygen as an industrial product, opened the way for the subsequent massive use of acetylene in engineering.

As a chemical, Frank and Caro discovered in 1895 that calcium carbide could be used to fix the nitrogen of the air in the form of calcium cyanamide, which could then be used as a fertiliser. In 1901 Frank and Freudenberg tried to turn this knowledge to commercial advantage by patenting a process for the manufacture of cyanamide. The rewards were slow in coming, for in 1907 world production was only 1700 tons. But by 1910 this had risen to 20,000 and in 1914, 222,000 tons were made.

The basic chemistry of acetylene had been investigated from Berthelot's pioneering work onwards and has been reviewed.[28] None of this work had made any industrial impact however and only slowly did the chemical aspects of acetylene find their way into the non-academic literature. In 1899 G.F. Thompson was impressed by the chemical potentialities of acetylene[29] and with a directness and simplicity that overcomes slight problems of detail, noted that "when it is considered that alcohol is merely a compound of carbon hydrogen and oxygen in certain proportions and that acetylene contains the first two, it only remains to add the third, together with an additional quantity of hydrogen and the synthesis of this compound is effected".

With its feet more firmly planted on the ground the same journal a year later commented on a route to alcohol based on Berthelot's hydrogenation of acetylene to ethylene and thence by treatment with sulphuric acid to ethanol. It concluded that "the process although apparently practical is rather complicated. It does not appear so far to have been used on an industrial scale".[30]

Another hopeful approach to the exploitation of acetylene came from L. Horwitz who protected a process for "the preparation of elastic plastics masses" from it.[31] He found that he obtained these substances by passing acetylene, in the presence of oxygen, over metals such as copper or nickel or their oxides or salts. In 1911 W. Karo patented a new catalytic process for the hydrogenation of acetylene.[32]

In 1905 Jouas and others patented a process for making alcohol from acetylene by passing the gas into a solution of a mercury salt causing precipitation of mercury acetylide. This liquid decomposes on boiling into acetaldehyde and the regenerated mercury salt. The aldehyde was then reduced with sodium amalgam.[33] These workers took matters a stage further by oxidising instead of reducing the aldehyde, to produce acetic acid.[34]

But the most important and sustained attempts to exploit the chemical reactivity of acetylene occurred in Germany, in the laboratories of three companies : Farbenfabrik Hoechst, the Consortium für electrochemische Industrie at Nuremberg and at Chemische Fabrik Griesheim-Elektron, which subsequently (1925) fused with Farbenfabrik Hoechst.

Professor Paul Duden led a team which continued work on this preparation of acetaldehyde and acetic acid from acetylene for many years. Its progress is recorded in many patents in the first and second decades of the century.

The Consortium was an organisation which resulted from the amalgamation of electrical and carbide producing companies to exploit the future possibilities of carbide and acetylene in the chemical industry. The electrical firm of Schukert decided in 1896 to enter the carbide business and set up a number of subsidiaries in various parts of Europe for this purpose. Somewhat later it set up a research laboratory to investigate chemical outlets for acetylene and possibly as a result the Consortium was established. Its early contribution lay in the working out of processes for the technical production of a series of chlorine derivatives of acetylene and in particular the solvents, tetrachlorethane and trichlorethylene made from it[35,36].

Emil Zacharias led the research at the Mainthalwerke of Griesheim-Elektron and he has described how he began work in this field in 1904 on chlorination products of acetylene[37,38]. However it was in 1910 that he "became extremely interested in the possibilities of the technical application of acetylene through laboratory experimental work" and the direction of his work was much influenced by the mention of the use of mercury salts as catalysts in a "very quickly withdrawn patent application of Ludwigshafen (BASF)".

Zacharias went on to say that "In 1912 there followed the isolation of organic vinyl esters ... together with Klatte. The rather more difficult working out of vinyl chloride and its polymers from acetylene and HCl was done together with Rollett ... At Griesheim in 1916, with the collaboration of Klatte, the larger scale manufacture of monochloracetic acid vinyl ester (so-called Mowilith) was established".

Fritz Klatte gave his version of these events in a paper read in 1929 in which he surveyed "The work on Vinyl Esters at Griesheim".[39] He opened by saying "The hitherto quite unknown vinyl esters were first prepared in the Mainthalwerke in 1912. The initial attempts to react acetylene and organic acids in the presence of mercury salts, an objective set me by Dr. Zacharias, were carried out with acetic acid".

It is interesting to speculate on the reason for this choice of acid. Perhaps it was because it was a product of the acetylene chemistry that they were then investigating, one which they were to produce commercially at a rate of 500 kgs per day in the following year, 1913. On the other hand it might have been selected simply because it was one of the commonest of the organic acids available.

Be that as it may Klatte did not restrict himself to this acid but in the following years prepared a large number of vinyl esters including the formate, propionate, butyrate, iso-valerate, mono and tri-chloracetates, benzoate, chlorbenzoate salicylate, cinnamate, phenyl acetate and phenoxyacetate[40].

Klatte looking back from 1929 went on to say "We were interested not only in the reaction of acetylene and organic acids but also of inorganic acids, in particular the hydrogen halides. We came thus to the technical preparation of vinyl chloride and bromides"[40]. Two patents, applied for in 1912 were a direct outcome of this remit.

The first was entitled "A process for the preparation of esters and ethers of ethylidene glycol and vinyl alcohol"[45] and the second, "A process for the preparation of hydrogen halide addition products of acetylene"[8].

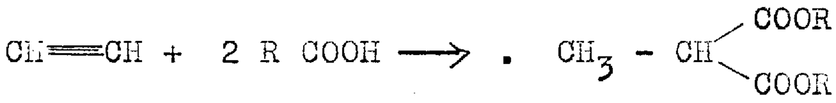
In the first patent attention was drawn to "the surprising observation that compounds with hydroxyl or carboxyl groups absorb acetylene astonishingly quickly in the presence of mercury salts e.g. mercury sulphate or phosphate, in moderately warmed acid or alcohol, when the reactants are stirred vigourously. In this way quantitative yields are mostly obtained of ethylidene esters or ethers in a very smooth reaction".

NOTE:

In the series of patents which I am presently discussing, the name of the assignee i.e. the patent owner, only is given, not the inventor. Enquiries from the German Patent Office in Munich have established the fact that at that time the name of the inventor was not given in the patent (as it is now), nor is it available in the records. It is abundantly clear however from his own writing and from the testimony of his colleagues that Klatte was the "inventor". A particularly valuable source of evidence in this respect are the contemporary records which have been published by Farbenfabrik Hoechst under the general title "Dokumente aus Hoechster Archiven". These have been made available in a number of volumes, consisting, amongst other things, of reproductions of various documents, letters etc. of the time. Volume 10 is of special relevance dealing as it does with "Klatte's Pioneering Patents". In it his wife described his work[42] and his erstwhile colleagues Dr. W. Gersbach[43] and Dr. Willy Herrmann[44] refer to his discoveries. Indeed Dr. Herrmann begins his contribution thus "Dr. Fritz Klatte, chemist at Chemische Fabrik Griesheim-Elektron in Frankfurt am Main, came on to the scene in the years 1912 to 1914 with a whole series of fundamental discoveries".

Of course Klatte was not alone in his work and in his original investigations on vinyl chloride and its polymers Dr. Rollett was an important collaborator.

The patent was largely concerned with ethylidene diesters obtained by the reaction of two molecules of acid with one of acetylene:



$$CH{\equiv}CH + 2\ R\,COOH \longrightarrow .\ CH_3 - CH\begin{matrix} COOR \\ COOR \end{matrix}$$

but did mention in passing "in a number of cases vinyl esters are formed by the reaction of acetylene and acid, in which unlike the earlier example, one molecule of acid reacts with one molecule of acetylene". This was illustrated by the following equation:

$$CCl_3COOH + CH{\equiv}CH \longrightarrow .\ CCl_3COO - CH = CH_2$$

[There is an error in the patent which represents vinyl trichloracetate with a triple bond, $CCl_3COO - CH{\equiv}CH_2$] .

The trichloracetate was manufactured from 1916 as a commercial product, and 40,000 Kgs were made during the first World War. Vinyl acetate, the monomer which subsequently turned out to be very much more important and which can be made in the same way by adjusting the molecular proportions of the reagents, among other things , was mentioned merely as an impurity in the ethylidene diacetate. In Example 1 there occurs the only reference to vinyl acetate. "The unconverted acetic acid which comes over first in vacuum fractional distillation contains small amounts of vinyl acetate; thereafter pure ethylidene diacetate distils over".

The work described in the patent clearly led to the one which provided the foundation of the pvc industry.[8] It was disclosed some five months later and claimed "a process for the preparation of an hydrogen halide addition product of acetylene in which one leads a mixture of acetylene and hydrogen chloride over a catalyst at elevated temperature". It is a short patent and in a few introductory sentences reviews the limited prior art. Reference is made to the very slow preparation of ethylidene bromide by the reaction of hydrobromic acid on acetylene, as described by Reboul[46] and the fact that HCl, in any event does not add to acetylene in an analagous way. The work of Sabaneef[34] is also dismissed as being of no technical consequence.

It then proceeds in typical patent language to explain that "we have now discovered that one can in a most convenient fashion and with most excellent yields produce the addition product of a hydrogen halide and acetylene ... Mercury compounds have an outstanding catalytic influence but there are many other materials e.g. metals, acids, basic oxides, salts and similar compounds which have a greater or lesser catalytic effect".

The process is illustrated by two examples which in translation reads thus:

"<u>Example 1</u>

Porous material (pumice, coke, etc.) impregnated with mercury chloride is heated to 180° in a tube. Equal volumes of acetylene and dry hydrogen chloride are conducted through the tube and the vinyl chloride produced quantitatively is condensed in cooled vessels. Cooling can, of course, be partially or completely replaced by compression.

"<u>Example 2</u>

Mercury chloride impregnated porous material is maintained in a tube at 200°. A mixture of hydrogen bromide and acetylene is conducted through the tube. According to the ratio of these two gases one obtains a reaction product which is predominantly vinyl bromide or ethylidene bromide. If one uses excess of hydrogen bromide, this can be stripped from the product simply by passage through water. Excess acetylene, after condensation of the product, is either reacted in a second apparatus or is recycled. Excess of acetylene can have advantages, in certain circumstances, in the preparation of vinyl chloride and it can be treated in the same way".

Here then, quite free of any extraneous discussion, was the basis of the process which has since been used to synthesise millions of tons of vinyl chloride. But it is interesting to note that in 1912 the inventors had no inkling that the chloride was any more important than the bromide. Both were described in exactly the same way.

An extension of the process for preparing vinyl halides came in an application dated September 1913.[47] It was, as it turned out, only of historical interest since it never achieved industrial status, but it claimed a process "characterised by the fact that the reagents are brought into contact with dissolved or suspended catalyst, so that there is a considerable concentration of hydrogen halide, at least five per cent, in the aqueous catalyst solution".

This patent therefore protected a liquid phase reaction as distinct from the main one which stipulated addition in the gaseous phase. As a result of carrying out the reaction with the catalyst (which was always referred to as a mercury salt) in solution or suspension Klatte found that with the great solubility of the hydrogen halides large amounts were taken up and acetylene could thereafter be passed into the reaction mixture until nearly all the halide had reacted. At this point the flow of acetylene was stopped and that of the halide resumed. Thus an alternating feed of the reactants could be used instead of a simultaneous flow."

The patent also noted that acetylene can be converted into acetaldehyde in similar conditions, when leading acetylene through a boiling aqueous solution of a mercury salt in the presence of small amounts of hydrochloric acid. In this instance "small amounts" means a concentration of less than 0.1%. In contrast the vinyl chloride reaction requires "concentrations whose lower limits are at about 5%",

The three patents protecting the synthesis of vinyl compounds from acetylene were accompanied and followed by a series emanating from the same source, on the polymerisation of these monomers and methods whereby these products could be put to good use. Within a few months of the original vinyl halide application came "Processes for the preparation of technically useful materials from organic vinyl esters".[48] Claim 1 concerned with polymerisation read as follows: "a process for the preparation of technically useful products from vinyl esters characterised by the polymerisation by heating or exposure to light vinyl esters, with or without additives".

The body of the patent disclosed that vinyl acetate or vinyl monochloracetate can be polymersied in this way to colourless transparent solids whose properties can be varied by changing the polymerisation conditions. It also stated, but did no more, the possibility of copolymerisation, in the phrase: "It has been found that by polymerisation of organic vinyl esters on their own or mixed with one another, useful products can be made ..."

Thus far the patent marked an advance on previous knowledge in that it proposed polymerisation by heating as well as by light. It further suggests that in the year or so between this and the patent on esters of vinyl alcohols[45], the workers at Griesheim began to appreciate the possibilities of vinyl acetate. The patent under discussion however specifically excluded polymers of vinyl halides from the category of "useful products" with the observation that "vinyl halide polymers are porous and chalk-like and easily break up into a white powder which cannot be used technically".

There was an addendum to DRP281,687[49] which is of outstanding interest in the development of polymer chemistry, and it claimed a modification of the polymerisation process wherein it occurred in the presence of a catalyst. This it said resulted in an extraordinary acceleration. Substances exhibiting such catalytic effect included organic peroxides, ozonides, organic acid anhydrides in combination with oxygen or oxygen producing compounds such as perborates and percarbonates. Thus there were listed in 1914 the major free-radical polymerisation initiators in use today.

Klatte elaborated on his discovery of this effect in the 1929 paper on his work at Griesheim[50]. "We first studied polymerisation phenomena with vinyl chloracetate and noted that it was those samples which had been stored for some time which could be polymerised by heat alone without added catalyst. A thick syrup was formed in this way which hardened to a solid in the light. We then found the ideal catalyst, benzoyl peroxide, by a systematic search for such a compound". A little later he explained why they bent their search in this direction "... it appeared that stored esters slowly form traces of a peroxide, probably acetyl or chloracetyl peroxide, and this facilitates polymerisation in the same way as benzoyl peroxide. If the peroxide is removed by reduction the easy polymerisability is lost. For these reasons we are now working to stabilise stored vinyl esters against premature polymerisation by treatment with non-volatile reducing agents. Copper and copper compounds have proved themselves particularly useful in this respect".

In one programme then did Klatte contrive to establish the peroxy initiation of vinyl polymerisation and also its antithesis, inhibition.

The rest of DRP 281,687 was concerned with the means for converting polymerised vinyl esters into useful products as defined in Claim 2: "The further development of the process outlined in Claim 1 according to which the polymer is softened and dissolved, mixed with additives and then returned to its solid form."

This was what we would now term plastics technology and it reflected the all-pervading influence in this field which was exercised by celluloid at that time, in both a negative and positive sense. In the first place although celluloid was a very attractive material the constant threat presented by its dangerous flammability provided a powerful incentive to look for alternatives. The point emerges several times in the patent. At the outset it claimed that polymers of vinyl esters have outstanding properties which can be exploited "particularly as substitutes for celluloid". Then again in describing articles that can be made from them reference was made to films, buttons, combs, etc., all things made in celluloid at that time. In another passage favourable comparisons were made with celluloid, "Another advantage lies in the extraordinary high safety from fire as well as the lack of smell of these products as compared with celluloid".

In a positive way, celluloid technology, developed in the previous forty or fifty years, served as a guide in exploiting the properties of these new materials. Example 1 of the patent said "One can make the solid polymers plastic by immersion in boiling water and then shape them in this condition". This was a technique used for celluloid. The example went on to say "To achieve particular effects corresponding materials can be added ... for example camphor etc.". Camphor was added as a plasticiser and was not particularly good in this respect, but it was the plasticiser that was, and is, uniquely suitable for plastics made from celluloid.

The second example referred to a process for making celluloid-like films by a casting process which was identical with that used in the manufacture of celluloid films and to a method used for making lacquers which was similarly an adaption of a celluloid technique.

The debt owed by vinyl polymer technology to celluloid was not limited to these very early days. Traces,and more than traces, can be detected in work on pvc right up to the 1930's.

The view expressed in this patent that polyvinyl halides were technically useless was quickly modified. In an application which was patented on the same date as DRP 281,687, the authors were at pains to show how these very materials could be used to make "substitutes for horn, films, artificial fibres, lacquers, etc.".[52] It said, by way of introduction, that the polymer obtained by exposing vinyl chloride and vinyl bromide to light "is an opaque porous chalk-like mass which easily breaks up into a powder. To date only one suggestion has been made to exploit these materials, namely to eliminate the halogen and thus to make a rubber-like product". This was an un-named reference to the work of Ivan Ostromislensky to which I shall return.

It continued "In contrast with this the discovery herein described touches on the surprising fact that one can convert the so-far worthless materials, without modification of their chemical structure, into technically valuable products".

These were described as products which "have the advantage of an extraordinary fire-proofness and colourlessness. By the addition of suitable additives, the strength and hardness of the materials can be varied within wide limits, so that the same polymer can become horny and hard or soft and flexible. The method of polymerisation, i.e. the wavelength of the light, also influences the properties of the product".

Processing was summarised thus: "The raw material can be worked-up by dissolving it and then evaporating the solvent or precipitating the polymer. In many cases however it is advantageous to use a volume of solvent which is insufficient for complete solution and in that event one obtains a plastic mass which can be compressed, kneaded, milled, drawn into fibres, formed into blocks and rolled into sheets and films. Of the many processing and application possibilities we give a few examples ..."

The first one dealt with the preparation of non-flammable films by casting from solution polymer made by means of sun-, ultraviolet or arc-light. It noted the influence of polymerising conditions on the properties, particularly solubility and flexibility and mentioned the usefulness of additives "Those substances which are well known in the celluloid industry, as for example camphor, cresol, naphthol, phenol phosphate and carbonate have turned out as particularly effective".

The solution in chlorobenzene, or other solvent, which gave rise to films, could also be used as a lacquer or for impregnation and by precipitation in a non-solvent one could make artificial fibres.

The second of the two examples illustrated the manufacture of films of pvc by a process which was taken lock, stock and barrel from celluloid manufacture. It involved the classical process of block-making, cutting of sheets and so on.

This patent is of great significance because it showed for the first time that pvc could be processed and made into the sort of articles that were the niche of synthetic and semi-synthetic materials. With hindsight we can see that the processes proposed were quite inappropriate but that did not become clear until much later. Their unsuitability however, was, from a historical point of view, quite unimportant as compared with the discovery of the potential usefulness of the polymer. Another interesting aspect of this patent emerges from the choice of examples. Up to this point in the chemical literature vinyl chloride was always described and discussed in close conjunction with vinyl bromide. Indeed of the two, the bromide was regarded as the more interesting; the papers of Hofmann and Baumann provide examples of this. The claim entered by this application also speaks of a process involving "the polymerisation products of vinyl halides" but it is clear from the examples that unlike earlier workers, the inventors regarded pvc as more interesting than the bromide. This is probably because by this time they were aware that "polyvinyl bromide appears to be much inferior to pvc in its stability".[53]

Although they did not directly advance pvc technology, the patents DRP 290,544 and its addendum 291,299[55] should be noted because with their description of the use of polyvinyl esters as lacquers, they complete the series of the eight pioneering patents which form the foundation of vinyl polymer technology.

At this point we should interpolate contemporary work on pvc that was going on a long way from Griesheim and for rather different reasons. In Moscow, Ivan Ostromislensky was one of a school of chemists concerned with problems of rubbers, especially its synthesis. The Russians had long been interested in providing themselves with an indigenous supply and even before the turn of the century some of their outstanding scientists were attracted to this field. I.L. Kondakov's name is well known to rubber chemists, as is S,V. Lebedev's, whose main contributions camesomewhat later. Ostromislensky's interests are described in the Great Soviet Encyclopedia[56] and they involved, amongst other things, the synthesis of raw materials for artificial rubbers. It was in this connection that his name has become associated with polyvinyl halides and for the same reason the direction of his work at this stage was tangential to the main development of pvc.

The results of his researches were published in two forms. The first was a patent[57] and the second a paper which was published in the Journal of the Russian Physical and Chemical Society[58]. The practical, as well as theoretical interest of this work is shown by the initial sentence of the patent which reads "We Ivan Ostromislensky, Doctor of Philosophy, Chemist and the Society for the Production of and Trade in Rubber Goods ..." Its purpose was to protect "A Process for obtaining Rubber or similar substances from polymerised Vinyl-bromide or Polymerised Vinyl-chloride or their Methyl Homologues".

In this process pvc, the bromide and their methyl homologues were intermediates. "The manufacture of rubber or rubber-like substances" as stated in the main claim was "characterised by the polymerisation products of vinyl chloride or vinyl bromide ... being exposed to the action of metals, water, alcoholic or aqueous potash or aromatic amines or simply subjected to a high temperature in solution". Dehydrohalogenation resulted with the production of a polybutadiene or a polyisoprene in the case of the methyl homologues.

Ostromislensky's patent added little to the knowledge available on polymerisation. It merely said "polymerisation of vinyl bromide or chloride takes place completely under the action of sunlight. The speed of the process is perceptibly increased by the action of ultraviolet rays when air is excluded". The inhibiting action of air [oxygen] on the polymerisation of vinyl halides is here mentioned for the first time and the fact that polymerisation "can easily be effected in solution, for instance in bromobenzene, benzene, toluene, xylene or carbon disulphide" is also the earliest reference to solution polymerisation of these monomers. But when this has been said the main concern of the patent, and indeed the work which inspired it, was with a process for making rubbers or rubberlike substances.

The paper published in the <u>Journal</u>[58] was devoted to theoretical aspects of "The structure of polymerised vinyl bromide and Rubber" and although it was restricted to a consideration of the bromide, many of its comments were equally applicable to the chloride.

Ostromislensky's main conclusion was that the polymer of vinyl bromide for which he proposed the name "Kauprenbromide", exists in 3 forms or modifications viz. α , β and γ , which can be distinguished by their appearance, solubility, fluorescence and behaviour at elevated temperatures. The differences in properties arise from their methods of polymerisation and he observed that the "ordinary", α modification is produced by the Hofmann-Baumann method using daylight, the others arise from irradiation with ultraviolet light.

He gave some experimental data. Thus for the formation of Kauprenbromide he exposed 100-300g. of vinyl bromide in a sealed tube 2 metres in length and 2cm in diameter to sunlight. After a variable period, depending on the intensity of the light, the monomer was converted. Thus after 18 hrs, on one occasion,120g of 200g was polymerised. He observed that additives can accelerate, retard or completely inhibit the reaction. The polymer separated out as a white opaque elastic mass, which developed an electric charge when rubbed with silk. It was soluble in a large number of solvents including carbon disulphide, epichlorhydrin, chlorobenzene. On heating it darkened at 120-130° and began to evolve hydrobromic acid at 220°.

β and γ polymers were formed in the rays of a mercury lamp, at a distance of 40-60 cms and after only a few minutes the polymer began to precipitate. These two forms could be distinguished by the solubility of the β modification in carbon disulphide and the insolubility of the γ. The β polymer began to darken at lower temperature than the α, at 90-94°C and at 150°C was completely carbonised.

The γ polymer was apparently insoluble in any solvent, at room temperature, while at elevated temperature its solubility was indistinguishable from the other forms. On heating it behaved rather like α Kauprenbromide

With our present knowledge it seems clear that these three forms differed from one another in their molecular weight and these variations were due to somewhat different methods of polymerisation. The diversity in molecular weight was reflected for example in their solubilities and possibily their behaviour on heating. The view is supported by Ostromislensky's statement that the polymerised vinyl bromide which he obtained from Schuchardt [Schuckert?] contained all three forms. Perhaps he himself had some inkling of this when he suggested that the reasons for the differences might best be sought in the structure of these molecules.

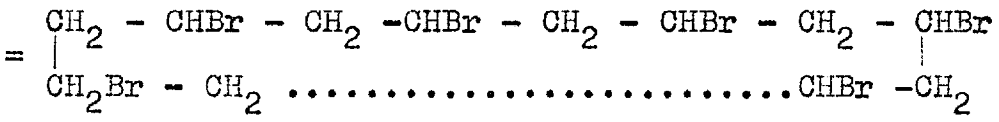
His ideas on the subject of polymer structure were in conformity with the concepts extant at that time. He thought there was a very close affinity between polyvinyl bromide and brominated butadiene rubber, and summarised his conclusions thus[59]:

"1) Polyvinyl bromide exists in three forms

2) Kauprenbromide is an even numbered cyclical compound in whose nucleus there are not less than 12 carbon atoms. In general the number of carbon atoms is a multiple of four

3) Kauprenbromide is a substance which is identical with the bromide of butadiene rubber or an isomer as far as the distribution of halogens in the molecule is concerned. The most probable structure for Kauprenbromide (and also probably for the bromide of butadiene rubber) is as follows:

$$-(CH_2-CHBr-)_n$$



The dots represent the uncertainty regarding the number of carbon atoms".

Ostromislensky's efforts to make synthetic rubber through polyvinyl halides turned out to be a <u>cul de sac</u> in the search for a substitute natural rubber but he returned to the subject of vinyl and polyvinyl chloride some years later, not in Moscow but in the United States.

For rather different reasons Klatte's great body of work seemed, at that time, fruitless. Such was the lack of interest in and outlook for his materials that on the last day of 1926, "thirteen years after the granting of the first patents, they were allowed to lapse by Griesheim with Klatte's consent".[60] From the point of view of the world at large this renunciation of monopoly rights was a good thing; it opened up the paths of this rich field to all those who were interested in further prospecting. But why were the polyvinyl esters, upon which most of Klatte's attention was concentrated, and pvc so unattractive?

The answer is that Klatte's discovery came too early. At that time too many of the requirements for success were missing. There was as yet no really good process for the manufacture of the monomers. Nor was the large-scale polymerisation process satisfactory. This was hardly surprising since Staudinger's macromolecular theory was not yet available to illuminate the problem. More important however were first, the great desire of the Germans to have done with the <u>ersatz</u> materials identified with the privations of war and with inferior properties. The second reason militating against acceptance of these resins was their relative expense as compared with natural rpoducts. Even at the beginning of the 1930's they were about five times as expensive as linseed oil and natural resins. Thus the production of those plastics for which Klatte was responsible during the war did not survive the ending of it. PVC which never even graduated from the laboratory looked out onto a hostile world during all this time and had to wait for more than another decade before it tentatively ventured out.

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Chapter 3

The Preparation of the Monomer

In this chapter I shall trace the development of preparative and manufacturing methods used for vinyl chloride during the years between the end of the first world war and the beginning of the second.

At this time although the monomer seemed to be of little theoretical interest to the organic chemists, the foundation of its industrial exploration were being laid in the laboratories of the chemical companies. It is therefore not surprising that the relevant literature is to be found in the patent records since these, rather than the journals, contain chemical process development.

The first method for the preparation of vinyl chloride was devised by Liebig and Regnault in 1835. The second came some eighty years later from Klatte at Griesheim. Thus after 1912 vinyl chloride could be synthesised by one of two routes, the first based on ethylene and the other on acetylene. A great deal of work was done subseqently, as this section will show, to improve the processes and to contrive variations on these themes but ultimately the decisive factor was economic. Which route provided the cheapest monomer and thus the least expensive polymer?

Plötnikow appreciated the point early on in a somewhat different connection in a rather florid paper on the "Photopolymerisation of Vinyl Chloride and the Problem of Rubber". He observed that one could make the monomer from ethylene or acetylene and went on "Acoording to Ostromislenski one can convert vinyl chloride rubber into butadiene rubber [see Chapter 2] . If we can successfully make pure rubber ... the question then arises which is the best raw material, potatoes or coal". The chemurgical route to ethylene via alcohol that was universal then, made the dichloroethane synthesis the more expensive of the two processes and therefore although refinement and improvements recorded in contemporary patents indicated an industrial interest in the ethylene route, there was no question but that the acetylene hydrochloric acid reaction was the commercially viable one. It remained so until very recently when the operation of very large-scale petrochemistry, among other things, has revised the cost situation and dictated the use of ethylene.

Before considering the development of processes for making vinyl chloride it may be helpful to outline the basic reactions and their variants. They may be classified as follows:

<u>from ethylene</u>

$$CH_2 = CH_2 + Cl_2 \longrightarrow ClCH_2 - CH_2Cl$$

1,2 dichlorethane

a) treatment with caustic soda or potash

$$ClCH_2 - CH_2Cl + NaOH \longrightarrow CH_2{=}\ CHCl + NaCl + H_2O$$

vinyl chloride

b) thermal or catalytic elimination of HCl

$$ClCH_2 - CH_2Cl \longrightarrow CH_2 = CHCl + HCl$$

c) treatment of trichlorethane with a metal

$$Cl_2CH - CH_2Cl + Zn \longrightarrow CH_2 = CHCl + ZnCl_2$$

1,1, 2 trichlorethane

d) from sym. dichlorethylene

$$ClCH = CHCl + H_2 \longrightarrow CH_2 = CHCl + HCl$$

<u>from acetylene</u>

$$CH{\equiv}CH + HCl \longrightarrow CH_2{=}\ CHCl$$

I have already discussed the Liebig-Regnault reaction at some length and have also mentioned the Wurtz-Frapolli variation[2] in which they obtained vinyl chloride from 1,1 dichlorethane and sodium-ethylate. Ostromislenski used sodium hydroxide in place of Regnault's caustic potash and claimed a yield of 85%[3]. A group of Russians patented a more sophisticated continuous process based on this reaction[4], while a French company proposed the use of sodium or potassium hydroxide in the presence of glycols or some of their ethers[5].

All these reactions however remained of academic interest and the reason probably had something to do with costs. Inspection of the equation representing this conversion shows that half of the chlorine present in the dichlorethane is changed to the economically very low valued sodium chloride, so that however efficient the reaction the product is likely to be expensive. It is not surprising then to find only a few more references to it in a commercial context. One was a patent of I.G. Farbenindustrie, applied for in 1929[6] which claimed that the use of methanol rather than ethanol in the process "offers many technical advantages", another came from B.F. Goodrich in America[7] using aqueous solutions of caustic potash in the presence of ethanol or methanol while C.O. Young of the Carbide & Carbon Corp. proposed the use of heat and pressure in the reaction, with the temperature above the boiling point of the dihalide[8].

In 1929 I.G. disclosed that they obtained vinyl chloride of great purity using a process "in which 1,1,2 <u>tri</u>chlorethane is treated with zinc, iron or aluminium at 50°C or more, in the presence of water or steam"[9]. Shortly after, I.G.I. using dichlorethylene extended Biltz's work which demonstrated the production of vinyl chloride by the pyrolysis of this unsaturated chlorine derivative, in the presence of pumice.[10] A patent dated 1930[11] described how "acetylene and vinyl chloride are obtained by subjecting ethylene dichloride to a temperature of at least 800°C or to a substantially lower temperature in the presence of an inert diluent such as steam". Bearing in mind relative costs at that time, it is a little difficult to see how a process making the less expensive acetylene from the more costly ethylene could have reached large scale use.

In 1928 a Dow Corporation patent referred to the preparation of vinyl chloride by the pyrolysis of ethylene chloride[33]. This process represented a considerable advance on the reaction involving caustic alkali, since the chlorine abstracted from the dichloroethane appeared as hydrogen chloride rather than sodium or potassium chloride. It was to become the process which has replaced, at least in part, the acetylene route, in the last decade or so.

The Dow patent illustrated the technique as follows: "Ethylene chloride was pyrolysed at a temperature of between 600-680°C in an externally heated tube 30 feet long with an internal diameter of 1/8 inch, at a flow rate of 35 l. per hour in the presence of steam. Thereafter the product so obtained was subjected to fractional distillation to separate the vinyl chloride". It went on to claim a method of purifying the monomer by subjecting it to the action of concentrated sulphuric acid having a concentration of more than 88%.

Klatte in his pioneering patent of 1912[12] described a process "in which one leads a mixture of acetylene and hydrogen chloride over a [solid] catalyst at elevated temperature" and within a year he extended it to cover the situation in which the catalyst was dissolved or suspended[13].

He suggested that mercury compounds were outstanding in their catalytic effect but they were not unique since "metals, acids, basic oxides, salts and similar compounds have a greater or lesser catalytic effect".

At the same time H. Dreyfus, known particularly for his contributions to cellulose chemistry and technology, published a patent whose convention date was given as 1912[30]. It was concerned with "synthetic caoutchouc substances and intermediate products" and it listed a very large number of reactions and products. In a section describing the production of olefins, dienes and their derivatives he mentioned, in passing, a process by which "vinyl chloride may be prepared from acetylene and hydrochloric acid in the presence of a contact substance preferably using excess of acetylene...". Looking at the encyclopeadic nature of this patent one cannot help wondering whether the fertile Mr. Dreyfus was speculating about the reaction or whether this extract was based on experimental work. Be that as it may, it must be recorded that he proposed the synthesis of vinyl chloride from acetylene and hydrogen chloride at about the same time as did Klatte.

In 1918 H. Plauson let it be known[14] that "hydrogen chloride gas will react with acetylene without catalysts under an increased pressure of one to two atmospheres at 100-120°C". He went further and suggested that it was not necessary to isolate the monomer so produced. By increasing the temperature or time of the reactions "it is possible to obtain not only vinyl halides but also polymerisation products thereof". He made no comment on the nature or quality of these products.

Example 1 of the patent will illustrate the process.

> "26 parts by weight (pbw) of acetylene and 36.5 pbw of hydrogen chloride were mixed in an autoclave at 1-2ats at 100-120°C for 10 to 24 hours, then heated for a further 10 hours to 150-200°C. There was a yield of 36-37 pbw of pvc and 21 pbw of vinyl chloride. By further heating up to 90% of vinyl chloride can be polymerised. Polymerisation time can be reduced if the pressure is increased by the introduction of nitrogen".

Following up his idea of eliminating isolation and purification stages Plauson in a further patent suggested that one might go back in the process[15]. "The main feature of the present invention is the use of calcium carbide as the starting point. This eliminates the costly apparatus necessary for the manufacture of acetylene and its purification".

Ostromislenski, having moved from Russia to the United States after the war, recognised the possibilities of vinyl chloride polymers as interesting materials in their own right, rather than as intermediates for synthetic rubbers and published a number of patents to exploit his discoveries. He assigned one dealing with vinyl chloride manufacture to the Naugatuck Chemical Co. in 1925[16]. The details of this patent do not reveal any significant advance and the "invention" consists broadly in passing acetylene through a mixture of heated hydrochloric acid with a mercury compound dissolved in it. On the face of it the process did not vary very much from Klatte's, but Ostromislenski claimed that it lead to "a far Higher proportionate yield of substantially pure vinyl chloride while simplifying the means for bringing the reacting materials into contact without increasing the cost of the process".

Father Nieuwland using his catalyst mixture, well known in acetylene chemistry, found that when acetylene is led through the mixture containing cuprous and ammonium chlorides saturated with hydrogen chloride, then vinyl chloride is formed, among other things[17]. The Russians (or more probably Armenians) S. Arutyurian and S. Marutian tried to improve yields from the system by adjusting catalyst concentration, contact time and temperature[36]. They also investigated the mechanism of catalysis and decided that ammonium chloride played no part in the reaction. But this catalyst system obviously did not give such good yields as those already mentioned.

Indeed it seems that none of the procedures involving reaction in a liquid phase were as tidy and efficient as those in which the gaseous mixture passed over or through a solid catalyst. Hence the concentration in development and manufacture on this technique.

One problem that worried workers employing a solid catalyst was its relatively limited life. "The activity of a mercury catalyst diminishes after a short time because at the temperature of reaction the mercury compound is sublimed from the carrier". This was the view expressed by the Consortium für electrochemische Industrie in a patent of 1928[18]. The vapour pressure of mercuric chloride increases with increasing temperature according to the following table[32]

Temperature °C	Vapour Pressure mm Hg
200	25
225	75
250	150
301	760

To remedy the situation they proposed a catalyst based on active carbon or silica gel, in contrast to Klatte's coke or pumice, impregnated with a compound of the second or fifth groups of the periodic table. Its activity they claimed was unchanged after 100 hours [such a life span would be considered very short now or even during the war].

Along the same lines H. Berg and E. Kalb[19] disclosed a catalyst based on precipitated bismuth chloride on activated carbon or compounds of vanadium, antimony, aluminium etc. on highly active carbon-silica gel. This patent proposed further that one could improve the control of the process by using unpurified, technical, acetylene. Easily polymerisable vinyl chloride was promised this way but again there was no comments on the quality of the product.

Workers of I.G. Farben were so impressed with the volatilisation of the catalyst from the support in the course of time that they thought one might dispense with it altogether. The first claim of the relevant patent describes such a process as follows: " a process ... which comprises effecting the reaction at about 180° whilst employing a catalyst consisting solely of active carbon from which the activating agent has been removed or alternatively an active carbon prepared with the aid of phosphoric acid and still containing residual acid".[20]

J.P. Baxter of I.C.I. developed the idea by suggesting a preliminary activation of the carbon by subjecting it to the action of hydrogen chloride at a higher temperature than that used in the subsequent reaction[21]. Yet another variation on the catalyst theme was proposed in which the mixed gases "at elevated temperature were passed over active carbon while supplying mercury continuously or periodically".[22]

K. Jung of I.G. Farben went off on yet another tack by proposing that the addition of hydrogen chloride to acetylene with mercuric chloride as catalyst should take place in the presence of an anhydrous liquid carrier, such as a polyhydric alcohol, which acted as a solvent for the mercury halide[31]. In this way he hoped to overcome the loss of catalyst. A.B. Japs claimed that complex salts of mercuric chloride, such as $HgCl_2$ 2KCl and $HgCl_2BaCl_2$ deposited on bodies with a high surface action were not only less volatile but also gave increased conversion[32].

In fact while all these proposals may have produced a catalyst with a longer life none of them exhibited an efficiency comparable with that of mercuric chloride on carbon in terms of yield of product per unit time per unit volume of the reactor. As we shall see this catalyst became the preferred one in the very large scale production of subsequent years, when the range of operating temperature was reduced and no doubt the exothermic heat was subject to better control.

The exothermic heat of the acetylene-hydrogen chloride addition reaction was a worry to H.N. Stanley and T.B. Philips of Distillers, which was developing an interest in vinyl chloride at about the time of the outbreak of the second World War. They were concerned to minimise its effects and reported a method of doing this in 1940[34]. In essence it consisted of "causing the hydrocarbon to react with the hydrogen halides in several stages and this was done by reacting the acetylene with less than a stochiometric amount of chloride and then bringing the reaction product in contact with a further quantity of HCl. They claimed that this led to very high outputs per unit volume of catalyst while still maintaining adequate control of temperature.

Another sort of modification of the process was suggested by Ruhrchemie A.G., a company not very much interested in vinyl chloride to judge by the literature. It was concerned to improve the yield by the use of "an apparatus containing surfaces of higher temperature disposed opposite to surfaces of lower temperature"[23]. This process modification was further improved in that "bodies of good conductivity are inserted between the walls at different temperatures"[24].

As knowledge and experience of pvc grew, the overriding importance of monomer purity to both the polymerisation process and the quality of the polymers became obvious. The utter inadequacy of the Plauson process, whereby the product of the acetylene-HCl reaction could be polymerised _in situ_, without isolation[14], relegated it to historical studies such as this. The main burden of purification was carried out by fractional distillation but H. Berg and H. Mader of Wacker were so impressed by the effect of washing the monomer with a caustic solution that they patented this step[35]. They found it removed impurities which tended to promote the formation of low molecular weight polymers thus producing pvc whose properties are far superior to heretofore known products". The implication that high molecular weight products are necessarily superior to their lower counterparts may sound a little naive today, but the appreciation of monomer purity was certainly sound.

In the ordinary operations of "private enterprise" this examination of the patent literature would not necessarily lead to a knowledge of the details of processes used in the manufacture of vinyl chloride. Some cynics say that patents are manipulated to conceal more than they reveal. In fact we have an intimate knowledge of the plant and processes that were used by the Germans during the war, because following hard on the heels of the advancing Allied armies there were a multitude of civilian technicians and experts inspecting chemical, engineering and other technical establishments and interrogating their German opposite numbers on the operation of these plants.

The results of all this activity were duly recorded and published in the form of reports. British teams wrote British Intelligence Objectives Sub-Committee (B.I.O.S.) Reports; Americans, the Field Information Agency Technical (F.I.A.T.) Reports, and in addition there were Combined Intelligence Objectives Sub-Committee (C.I.O.S.) Reports.

Of course, not all German technicians and scientists collaborated enthusiastically in the exposure of German industrial secrets and to this extent the information revealed must at times be suspect. There is for example the classic case of Dr. J.W. Reppe, the man who led the I.G. Farben work on the chemistry of acetylene reactions under pressure. His attitude and lack of co-operation is described in the forward of the book by Copenhaver and Bigelow[25]. In a nutshell, he did not share the views of some of his compatriots, such as say Werner von Braun.

However there is an extensive and crosschecked documentation in the case of vinyl chloride production which has been summarised by DeBell and Goggins[26]. Monomer production was limited to Schkopau, Rheinfelden and Burghausen, the first two of which belonged to I.G. Farben and the third to Alexander Wacker. Schkopau produced the lion's share of the total output. All three were operating at the beginning of the war. The processes at Rheinfelden and Schkopau were very similar and the following extract from "German Plastics Practice" describing that of the latter will serve for both. Further details are available from other sources[37,38,39,40,41,42].

"Acetylene and hydrogen chloride were combined in the presence of a mercuric chloride catalyst. Reactants were carefully dried, the acetylene by potassium oxide and hydrogen chloride by concentrated sulphuric acid. For the catalyst, charcoal in approximately ¼" cubes were treated with mercuric chloride solution, then dried to give 10% by weight of mercuric chloride. This was packed in vertical reaction tubes of iron, 3m long and 50-80mm in diameter. These were assembled in furnaces about 3m high and 2 m in diameter, heated or cooled by water, although oil was previously used. Each furnace contained about 150 tubes.

"To start, the furnace was swept out with nitrogen and the mixed gases were passed through new catalyst at 120°C with 10% volume excess of hydrogen chloride. When catalyst is old temperature may be raised to 200°C [catalyst could be used for about 10 months before renewal].

"Pressure was atmospheric. Reaction was strongly exothermic so heat was removed by the water. Reaction product was condensed by running directly into a nearly saturated solution of 25% calcium chloride in water -40°C. By warming this solution the impure monomer was distilled off. It was purified in two twenty-foot 36" diameter columns, originally with plates, now packed. The first distillation delivered vinyl chloride plus 0.1% acetylene at the top and unsymmetrical dichlorethylene at the bottom. Yield was 96-98% on acetylene and 80-90% on hydrogen chloride.

Reaction was very complete and with fresh catalyst frequently no acetylene could be found. Detectable amounts of acetylene gravely affect polymerisation rates of vinyl chloride. The cooled vinyl chloride [about 99.9% pure] was stored in steel tanks or shipped in steel tank cars under 99.9% nitrogen and no polymerisation trouble was ever experienced".

Cost of monomer was about 40 pfennig per kilo[27].

The Wacker Burghausen process differed in a number of respects[28]. The catalyst consisted of active carbon containing barium chloride and a trace of mercuric chloride (30% $BaCl_2$ and 1% of $HgCl_2$).

The purification process involved extracting the vinyl chloride from the effluent gas with trichlorethylene. This no doubt stemmed from the fact that Wacker made and sold the solvent on a large scale. Incidentally, they made their hydrogen chloride for the reaction by cracking tetrachlorethane to trichlorethylene in the presence of a barium chloride catalyst.

$$\underset{\text{tetrachlorethane}}{Cl_2CH - CHCl_2} \xrightarrow[300^\circ]{BaCl_2} \underset{\text{trichlorethylene}}{Cl_2C\cancel{H}= CHCl} + HCl$$

(This interest in chlorinated hydrocarbons was reflected some years earlier in a synthesis for vinyl chloride in which "a gaseous mixture of acetylene and a chlorinated ethane having at least three chlorine atoms, is passed over a catalyst consisting of one or more porous contact substances, metal chlorides or porous substances in conjunction with metal chlorides, at a raised temperature"[29]. As their large scale process shows, Wacker did not develop this synthesis).

American large-scale processes for making vinyl chloride at this time were of course not subject to this sort of publication while England and the rest of the world had not moved beyond laboratory scale preparation at the outbreak of war.

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Chapter 4

Polymerisation

In attempting to delineate the progress that was made in the polymerisation of vinyl chloride one is faced with at least two difficulties. In the first place, with our present profound theoretical understanding of the nature of polymers and the polymerisation process it requires a great imaginative leap to appreciate the background of theoretical ignorance against which workers carried out their investigations a mere thirty to forty years ago.

The second problem stems from the fact that the pattern of progress was woven from a number of threads. For example various polymerisation techniques were established. Further, owing to the intractable nature and heat sensitivity of pvc a number of modifications of the product were introduced including a variety of copolymers and the post-chlorinated material. It is the purpose of this chapter to trace these developments in the period 1920 up to 1940.

1920 was a most important year in the history of polymerisation. That was the year in which Staudinger published the first paper[1] of a series which was destined to establish our present concepts. But it required more than a decade before his basic theory of the macromolecule was accepted and another ten years before the mechanism of addition polymerisation was worked out. The impact of these discoveries was not immediate nor did it permeate the thinking of all practicising chemists at the same rate. So much is obvious from the literature, in which the explanations of various experimental observations betray an ignorance of polymer theory that was being evolved.

This was especially true for research in pvc since it figured in so little theoretical work. Handling difficulties diverted workers who were elucidating problems of polymerisation to more tractable materials and it is interesting to observe for example that in a mass of correspondence between Staudinger and I.G. Farben polymer research laboratories he only once referred to vinyl chloride, by way of a request for a sample[2]. It is equally significant that pvc is mentioned just once in the index of Staudinger's classic work "Hochmolekularen Organischen Verbindungen"[3].

PVC therefore contributed little to the growth of the general body of polymer theory, but as might be expected the influence of the theoreticians permeated more and more into the laboratories working with vinyl chloride as the 1930s progressed. Academic work had a greater and more direct influence in the parallel development of the polymers of methyl methacrylate, vinyl acetate and styrene and as these were being studied in industrial laboratories which had close contacts with pvc workers there was a powerful indirect entry for theoretical ideas.

PHOTOPOLYMERISATION

Photopolymerisation, by which Baumann first made pvc in 1872, is now of no technical interest whatsoever in the manufacture of this polymer. However, it continued to dominate the approach of most workers for more than fifty years, in their efforts to work out practical methods for its manufacture.

Klatte proposed the use of heat or light in his original patent on the subject[4] but light seems to have been the preferred agent, judging from the patent which followed soon after in which he showed that useful products could be obtained from pvc[5]. Further, one must remember that Klatte and his colleagues were working on a number of vinyl polymers at this time and of these polyvinyl acetate claimed more of their attention as it showed rather more promise than pvc. Thus the latter tended to develop in the wake of the commercially more successful materials. During World War I Griesheim Elektron produced 40,000 kg of polyvinyl chloracetate by a two-stage process which Klatte described as follows[6]:

" 1) Prepolymerisation in enamelled equipment in charges of 50-100 kgms by heating with benzoyl peroxide to a thick syrup. This requires two hours.

2) Polymerisation in daylight in bottles of about five litre capacity. The conditions are most favourable when the bottles are exposed on south-facing platforms. The time varies between 8 days and 8 weeks depending on the weather and time of year.

"We still use this process [1929]. It has been confirmed again in recent years and our so-called 'glass-bottle method' is suitable for larger scale operation ... By this method we are dependent on daylight - direct sunlight is not necessary - and we cannot produce uniformly quickly during the twelve months of the year. Intensified production from March to October allows production to be maintained at a high level.

"Our process working with daylight has the particular advantage that a fully polymerised product is made and this obviates the need for the subsequent removal of residual monomeric ester. It has been repeatedly shown how important is the complete removal of monomer in the application of our vinyl resins and our peculiar glass-bottle method has an obvious advantage in that it achieves a completely polymerised product without further work or expenditure of energy whereas this cannot be done by heating alone.

"We should naturally like to become independent of the non-uniform light during the course of the year ... and interesting experiments are under way ... which may establish whether it is possible to achieve a technical polymerisation process based on artificial light sources".

Klatte's observations on photopolymerisation have been quoted fairly extensively here, not because his description is uniformly applicable to pvc but because it indicates the modus operandi in larger scale working with light as the source of energy and some of the problems that arose and finally condemned the process to extinction. It also shows that it was still being used on a significant scale as late as 1929, a fact which must have had some relevance to thoughts on ways of polymerising vinyl chloride up to that time.

Reverting a few years, back to the post-war period, a paper by J. Plotnikow added to the knowledge of and interest in the light polymerisation of vinyl chloride[7]. This worker came to the problem as a result of his studies in the then new photochemical research laboratory of Agfa in Berlin. He had been earlier stimulated by the work of Ostromislenski and since he found that simple ethylene polymerised slowly and does not give a uniform product on exposure to light, he turned to vinyl chloride which polymerises easily and uniformly in the extreme ultra-violet rays of a quartz lamp. His paper fell into two parts: the first discussed "Qualitative results of product investigation" and the second reported "photokinetic measurements of vinyl polymerisation". The intention of the measurement was to throw some light on the mechanism of the process but at the end of his exertions the author could understand it no better.

Plotnikow carried out his reaction in solution, in ethanol or methanol, and insoluble pvc precipitated after exposure to the rays of a quartz lamp. He found that, contrary to Baumann's report, only the quartz lamp would effect polymerisation in pure solvent. Neither sunlight nor ultra-violet influenced this reaction. "The photo-reaction only proceeds in the extreme U-V., i,e. only a limited range of the mercury spectrum is used. It would be desirable to accelerate the reaction and also to make the material sensitive to other wavelengths. It would be of considerable significance if sunlight were effective". His researches showed that the salts of a series of metals acted catalytically to a greater or lesser extent and his paper provided data on the effect of a variety of catalysts and solvents, but uranium salts were much more effective than any others. He therefore suggested that a process could now be worked out for the large scale preparation of pvc in sunlight. This is most interesting in the light of Klatte's subsequent efforts to get away from the limitations imposed by dependence on natural light.

Plotnikow was obviously interested in the nature of his photoproduct and when a few years later he became director of the Physical Chemistry Institute of the Technische Hochschule in Zagreb, he set one of his research students, G. Flumiani, to work on the elucidation of the problem. He published a part of his doctoral thesis in 1926 and showed thereby that the so-called colloidal behaviour of polymer solutions presented most intractable difficulties at that time[8].

Elementary analysis indicated the formula $(C_2H_3Cl)_n$ that is, "a simple polymerisation product". Flumiani fractionated it from various solvents and examined the resulting precipitates. Their chemical and even physical properties could be immediately recognised as pvc. Thus on the one hand "we are apparently dealing with a single chemical substance". On the other hand concentrated solutions of photopolymers in various solvents such as cedar wood oil, aniline, camphor etc. give waxy, Vaseline-like and solid substances in certain conditions. To throw some light on this matter Flumiani set out to determine the molecular weights of the particles dispersed in the solvent medium. He might thus obtain a measure of the degree of dispersion and at the same time establish some relationship between this and the optical properties of the colloidal solution.

The bulk of the paper consists of an account of the estimation of molecular weight in nitrobenzene, acetophenone, phenanthrene and naphthalene by depression of the freezing point, and also of the microscopic examination of these colloidal solutions. The results however did not disperse the confusion since there appeared to be no simple relationship between anything and anything else. The degree of dispersion varied with concentration, temperature and the time for which the solution had been standing. Further the way in which it was prepared was also relevant. Finally there was no direct proportionality between depression of the freezing point and the number of particles in the dispersed phase.

A second paper presented by Flumiani in Kolloid-Zeitschrift on colloidal solutions of photopolymerised vinyl chloride took matters no further[9]. This time he studied a series of solutions under the microscope, using different solvents from those mentioned previously, and tried to systematise the occurrence of various particle sizes and their behaviour in solution. This sort of investigation could not in the nature of things throw any light on the structure of pvc, photopolymerised or made in any other way, as macromolecular studies were even then showing.

In 1926 Ostromislenski, who had previously tended to concentrate his attention on polyvinyl bromide, published a patent on what he called "a polymerised vinyl chloride modification"[10]. In it he harked back to his earlier studies by naming his photoproduct "Kaupren chloride" and noting the α, β, γ and δ forms corresponding to those bromide polymers which he described in his paper of 1912[11]. His main claim in this patent was "that one of these modifications which I have produced and identified for the first time, can be made into films and other articles which avoid the disadvantages hitherto encountered, brittleness and discolouration".

This β kaupren chloride could, he said, be prepared in several ways, but all of them involved exposure to ultra-violet light. For example "vinyl chloride is placed in a hermetically sealed transparent container and is exposed to U-V rays as from a mercury lamp, until a good yield of the β form is obtained by partial polymerisation ... Any α polymer is removed by acetone and then the β form is dissolved in chlorbenzol to separate it from any γ and δ modification". If the monomer was so exposed for twelve hours at about 20°C, 90% was converted to solid polymer which contained all the forms. Of course the intensity of the light affected the rate of conversion.

Alternatively he used sunlight to effect the polymerisation with or without soluble lead salts as catalyst. The reaction could also proceed in the presence of such solvents as alcohol or monochlorbenzene to produce a good yield of β polymer. Finally he disclosed that it was possible to convert the insoluble γ and δ modifications into the desired β by heating them, for example, in aniline oil.

The idea of conversion of one form into another led quickly to a further patent, which was essentially an extension of the first[12]. "Broadly speaking", he said, "I first produce α kaupren chloride by the action of light, isolate it and then convert it to the β form. This conversion can be brought about either by prolonged exposure to U-V light only, prolonged heating, say between 50-135°C, or to both heat and light".

Du Pont in 1928 appears to have applied for the last patent involving photopolymerisation of vinyl chloride[13]. In it they announced that ozone is an excellent catalyst for the polymerisation of a wide range of vinyl derivatives and mentioned vinyl chloride in several examples of its actions. Thus with vinyl chloride in solution in methanol, which had previously been subjected to the passage of a stream of an ozone-air mixture, 77% of polymer was produced, of which about half consisted of the α and β forms.

This patent must have contained one of the last references to these Greek designated modifications of the polymers. It is true they continued to appear infrequently in the literature, but that only demonstrated the lack of the author's contact with polymer theory, because by about

1930 the concept of "mean molecular weight" of a polymer was denying any significance to the differentiation of polymers by solubility. Staudinger made this quite explicit in 1930 in one of the few theoretical studies on polyvinyl halides of that period[14].

"The polymerisation of vinyl bromide or vinyl chloride takes place in the same way [as formaldehyde and styrene]. A chain reaction leads to a high molecular weight product as soon as light activates the monomer ... when on polymerisation numerous molecules add together to form chains, one does not obtain a single body, as Flumiani assumed or even the three products of Ostromislenski but rather a mixture of high and low polymers comprising about 50 polymer homologues.

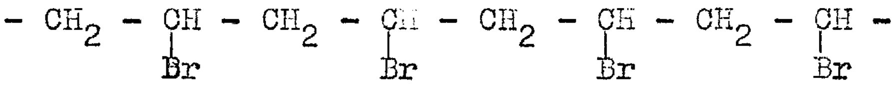
"The lower members of this mixture are more easily soluble than the higher ones ... [and] when Ostromislenski decided that his soluble (α) kaupren bromide had a degree of polymerisation of 16, he was not dealing with a single substance but a mixture with this average degree of polymerisation. There is no point in distinguishing between α, β and γ kaupren bromide, because as with polyindene, polystyrene and polyoxymethylene, such a mixture can only be characterised by an average molecular weight".

Staudinger made several other interesting observations in this paper. For example, he explained why the very different manifestation of polymerisation behaviour as between vinyl chloride and say styrene did not reflect any profound differences in polymerisation mechanisms, in spite of the fact that the styrene polymerised through a transparent and progressively increasing viscosity whereas vinyl chloride became cloudy and precipitated in a sludge.

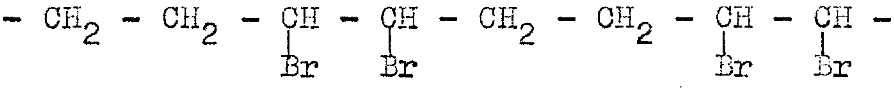
The difference arose simply from the fact that while polystyrene is soluble in its monomer and vice versa, pvc is insoluble in vinyl chloride[15].

He also referred to the difficulties inherent in the determination of the molecular weight of pvc, because while it was not readily soluble in the cold, heating led to decomposition of the heat (and also light) sensitive polymer. In fact he thought that some of Flumiani's observations on the fall in molecular weight on prolonged warming and the influence of the method of preparation of the solution on its molecular weight, might well be ascribed to changes consequent on dehydrochlorination[16]. He estimated that polyvinyl halides corresponding to Ostromislenski's kaupren bromide had an average degree of polymerisation of over 100. An estimate which later investigations showed was much too low.

Staudinger also addressed himself to the more detailed structure of polyvinyl halides in this paper. Was polyvinyl bromide based on a head to tail (I) or head to head linked chain (II)?

(I) 

$$-CH_2-\underset{\mathrm{Br}}{\underset{|}{CH}}-CH_2-\underset{\mathrm{Br}}{\underset{|}{CH}}-CH_2-\underset{\mathrm{Br}}{\underset{|}{CH}}-CH_2-\underset{\mathrm{Br}}{\underset{|}{CH}}-$$

(II) 

$$-CH_2-CH_2-\underset{\mathrm{Br}}{\underset{|}{CH}}-\underset{\mathrm{Br}}{\underset{|}{CH}}-CH_2-CH_2-\underset{\mathrm{Br}}{\underset{|}{CH}}-\underset{\mathrm{Br}}{\underset{|}{CH}}-$$

He tried to answer the question by chemical conversion of the polymer into hydrocarbons which he could recognise, but none of the reactions were clear and decisive enough for him to be able to draw unequivocal conclusions. For example he surmised that treatment with zinc alkyls might produce a hydro-methyl rubber whose characteristics could be identified and which would point to a head to head structure. Alternatively, the reaction would lead to an unsaturated isomeric hydrocarbon derived from formula I. Neither product was isolated. Reduction of polyvinyl bromide with metals or hydrogen iodide and attempted hydrolysis to polyvinyl alcohol, to compare it with material made by the conversion of polyvinyl acetate were similarly fruitless.

THERMAL POLYMERISATION

Polymerisation by simply heating the monomer rather than by exposing it to light was a suggestion made by Klatte in one of his pioneering patents in 1913[17]. In that case he was referring to vinyl acetate but it required no great stretch of the imagination to apply the process to vinyl chloride. Plauson did that in passing, when he made pvc from acetylene and hydrogen chloride without bothering to isolate and purify the monomer[18]. In Example 1 he proceeded as follows: "26 parts by weight (pbw) of acetylene and 36.5 pbw of hydrogen chloride were mixed in an autoclave at 1-2 atmospheres at 150-200°C. This yielded 36-37 pbw of pvc and 21 pbw of vinyl chloride. By further heating up to 90% of vinyl chloride can be polymerised. The time can be reduced if the pressure is increased by introduction of nitrogen".

Plauson patented his process but he was not concerned with the product. If he had been he would very soon have discovered that what is in principle a simple and straightforward matter is anything but that in practice. The difficulties, not yet understood at that time, stemmed from the large quantity of heat liberated on polymerisation associated with the very low thermal conductivity of the resulting polymer. Thus the heat could not be easily dissipated hence there was a rapid increase in the temperature of the polymerising mass, which was not uniformly distributed and this often resulted in thermal decomposition leading to darkening of the polymer and to irreproducible results. This irreproducibility was emphasised by varying amounts of impurities present in the monomer.

The situation was well described in a patent which aimed to improve the process[19]. "The preparation of synthetic resins particularly those of the type derived from vinyl compounds has been attended in the past by uncertainty. Those batches of polymer which showed excellent colour and good yield would often have a viscosity so high as to make their use as coating compositions difficult [This application requires a low molecular weight]. Other batches, made under identical conditions, would have good viscosity but would be very dark in colour and would be produced only in low yields. The polymerisation of these resins when carried out by heat at temperatures above 130° although accompanied by an advantageous lowering of viscosity was accompanied by a darkening of the product which made it substantially useless. The reasons for these variations has previously [sic] not been understood and has resulted in an inability to secure a uniform product".

Unfortunately the method proposed for eliminating the difficulty showed that the reasons for it were still not understood. The inventors suggested that the solution lay in regulating the amount of acid present in the reaction. To the extent that residual HCl was present in varying amounts in the monomer, this action doubtless helped to produce a more uniform situation. Berg and Mader subsequently dealt with this situation rather more effectively by washing the monomer with caustic alkali[20], but removal or control of acid content alone could never adequately deal with the problem.

A. Voss and E. Dickhäuser tried a more gentle approach and by slowly and progressively raising the temperature generated the polymerisation exotherm slowly, thus allowing it to be dissipated[21]. "100 parts of vinyl chloride are introduced, while applying pressure, into a bomb internally enamelled or lined with a noble metal. The bomb is then heated for several hours at 30°, then for some hours successively at 40, 50 and 60° during which operation the final temperature is maintained at 60° for 12 hours or even longer, the time being determined by the fact that completion of polymerisation will be indicated by decreasing pressure. The contents of the bomb consist of a white very solid mass, which is purified by dissolving it in chlorbenzene and re-precipitating it from benzene or alcohol. After drying, a white powder is obtained which shows neither a dark colouration nor any signs of splitting off HCl but is perfectly fast to light and air".

One would hope that after all that treatment the product would be good but that process would hardly be economic. The recrystallisation stage was perhaps gilding the lily.

Klatte, towards the end of his active life, returned to vinyl chloride and suggested that incomplete conversion of polymer gives "a polymer which is more uniform than the average product of complete polymerisation"[22]. Unlike the previous instances of thermal polymerisation Klatte used a catalyst. Thus "1000g of vinyl chloride is maintained at 34-45°C for 24-30 hours in a stirring autoclave in the presence of 6g of benzoyl peroxide and

6g of acetic anhydride. At the end of this period the unconverted vinyl chloride is distilled off and about 500g of white powdered pvc is recovered".

In speaking of the use of catalysts I have already noted that in 1913 Klatte had listed a number of compounds which could accelerate polymerisation. He mentioned among others, organic peroxides, organic acid anhydrides (both of which appeared in the last example), ozonides, perborates and percarbonates. The list was extended in a number of patents in the years up to 1939, but on the whole no really new types were revealed. Additions, were, for the most part, more highly oxygenated substances of the peroxide and peracid type. The important discovery of redox catalyst systems, associated more particularly with polymerisation in aqueous dispersion, had to wait another three years or so and was applied only after the end of the war.

As we have already seen Du Pont claimed the advantages of ozone as an accelerator[13]. They also suggested sodium bisulphite and barium peroxide[23]. Another patent proposed the product formed by the reaction between sodium perborate and acetic anhydride, in certain solvents, as a catalyst[24]. Carbide and Carbon Chemicals discovered (1932) "that acetyl benzoyl peroxide is an excellent polymerisation catalyst especially for the polymerisation of vinyl halides etc."[25]. At about the same time this company found that the effect of a normal polymerisation catalyst may be enhanced by the presence of metals "of the group lead, tin and aluminium"[26,36]. F. Douglas, the inventor, offered an explanation for the effectiveness of the acid which illustrates the thinking on mechanisms of initiation some two or three years before the elaboration of free radical theory of polymerisation, involving the three phases of initiation, propagation and termination. He had observed that "when a batch of vinyl compound to be polymerised is mixed with a catalyst and brought to polymerisation temperature, a period of inactivity generally precedes the initation of activity. This may be due to the fact that more or less time is required for the peroxide to begin to liberate the "nascent" oxygen, presumably required to promote polymerisation. The presence of the acid probably reduces this time".

We know that oxygen, "nascent" or otherwise, is not the direct initiator and that the decomposition of the peroxide in the conditions at issue occurs at the link between two atoms of oxygen and without its evolution. But molecular oxygen does have a very noticeable effect on the polymerisation of vinyl chloride in that combination with the free radicals generated by the added initiator prevents them from initiating polymerisation and so inhibits initiation until all the oxygen has been removed. This phenomenon is not restricted to but is particularly marked in the case of vinyl chloride.

F.K. Schoenfeld of Goodrich put this in a positive way in his patent by his statement that "I have discovered that the rate may be greatly increased if polymerisation is carried out substantially in the absence of oxygen"[28]. He therefore proposed that air be purged from the reaction by the use of nitrogen, carbon dioxide or an atmosphere of vinyl chloride itself. This purging of oxygen from the polymerising system has been used and is an important feature of the manufacture of pvc.

It is perhaps interesting to observe in passing that this patent, written in 1937, still referred to α, β and γ polymers. Indeed the object of the patent was to make γ polymers, that is polymers of high molecular weight, quickly at low temperatures. One would like to think that the diffusion of basic theoretical ideas among research and development workers has accelerated since then.

SOLUTION POLYMERISATION

In contemplating the development of pvc, we may regard photo- and thermal polymerisation as forming part of its infancy. It is true that thermal polymerisation is now reappearing (because of the purity of the product made in this way) but it has returned in a much more sophisticated form and is even so responsible for a very small and specialised part of the total output.

Solution polymerisation in retrospect, must also be set, in part at least, in this infant phase. Ostromislenski was the first to record the use of the method as early as 1912, when he revealed in his patent that polymerisation "can easily be effected in solution, for example in bromobenzene, benzene, toluene, xylene or carbon disulphide"[29]. He extended the list of solvents in his patent of 1926,[10] which described the four modifications of pvc, by quoting alcohol or monochlorbenzene as good solvents for the production of the β form.

Voss and Dickhäuser in their patent which suggested that slow thermal polymerisation resulted in good pvc[21] also referred to solution polymerisation and took matters a little further by noting that "the selection of different solvents has a certain effect upon the solubility and other physical properties (viscosity) of the final product. According to the working conditions adopted polymerised products of almost any desired degree of solubility are obtained. Such polymerised products can be obtained as are insoluble in nearly every solvent, as are easily soluble but only in a quite limited number of solvents and as are soluble in many solvents". In speaking of "working conditions" in almost the same breath as "the selection of different solvents" the authors tended to confuse the effects of temperature, catalyst, catalyst concentration etc. with the effect of varying the chain transfer coefficient associated with different solvents, in relation to the monomer. Each of these parameters can of course produce a range of molecular weights and hence changes in the solubility of the polymer. However they did observe that the choice of solvent influenced the product in respect of its solubility and viscosity.

Pavlovitch in Russia in 1937 extended these observations by noting that mechanical properties were also profoundly effected by the solvent used in polymerisation[30]. Of polymers made in acetone, isopropyl alcohol and benzene, the first had the highest tear strength. Rather more recently we have become aware of the relationship between the polymer structure, which is largely determined by the solvent, and its physical and mechanical properties.

In 1928 Du Pont tried to adapt solution polymerisation to a continuous process particularly suited to the production of "a toluene soluble polymer"[27]. According to this patent "the present invention of polymer of vinyl chloride comprises continuously forcing a solution of vinyl compound and a catalyst through a heated reaction tube... It will be apparent that the temperature, pressure and rate of flow through the tube may vary ... By keeping the compounds under continuous movement products are obtained which are free from objectionable discolouration and generally a higher yield of polymer is obtained".

One of the examples read as follows: "A 38 per cent solution of vinyl chloride in chlorbenzene, containing 3%

by weight of benzoyl peroxide, calculated on a vinyl chloride, was forced under 200 lbs pressure through a one inch diameter, tin-lined reaction tube of 800 ccs volume, at the rate of 800 ccs per hour. The temperature averaged 118°C. The product was a light yellow coloured solution of a new polymer of vinyl chloride. 28% was polymerised. This new polymer is distinguished by its solubility in toluene". Commenting today one would hardly be surprised that polymerisation at such high temperature and high catalyst concentration with chain transfer to the chlorbenzene solvent should produce such a low molecular weight polymer soluble in toluene. The product would probably be soluble if it were thermally polymerised.

A second patent was published at the same time in which Du Pont claimed an "improvement in the process for making polymer of vinyl chloride"[31]. This was essentially aiming at the same objective as the first; they were trying to get a low molecular weight, soluble polymer, and the process was not dissimilar. It was solution polymerisation at the relatively high temperature of 80°C or more, but it was carried out as a batch rather than a continuous process.

In a third application on the solution polymerisation of vinyl chloride Du Pont explained their interest in low molecular weight pvc[32]. "Various methods have hitherto been developed for the polymerisation of vinyl derivatives and these resulted in the production of four different polymers of vinyl chloride, α , β , γ and δ . These polymers are all insoluble in aromatic hydrocarbons, thus making it necessary to use expensive solvents when utilising these polymers in the preparation of coating composition.

They went on, once again "we have discovered a new polymer of vinyl chloride which is soluble in most aromatic hydrocarbons and in toluene in particular" and once again they achieved this by a variant of the earlier continuous solution polymerisation process in which high temperatures, about 120°C, and high catalyst concentrations, about 3% on monomer are employed.

In these patents we can see how much investigators at that time (1930) were hampered by a lack of a theoretical base, how empirically they had to proceed when they regarded a polymer with a difficult molecular weight as a "new polymer" and when they did not yet appreciate the relationship between the conditions of polymerisation and the polymeric product.

If Du Pont was concerned to produce toluene soluble pvc for surface coatings Carbide and Carbon Chemicals thinking about other applications of the polymer, patented a solution process to resins "of which a preponderating proportion is insoluble in toluene".[33] The invention required heating to a temperature not above 40°C in the presence of a known polymerisation catalyst and a liquid medium of a group consisting of aliphatic alcohols, hydrocarbons, ketones and aromatic hydrocarbons. The patent did not really break new ground. It used low temperature polymerisation in the presence of a solvent to obtain a higher range of molecular weights. But its real interest resides in its increasing awareness of the nature of polymers.

"... also it has been discovered that vinyl resins prepared by known methods can be fractionated by the action of suitable solvents into fractions possessing average molecular weight of the resin.

"It is probable that the original resin is composed of a series of polymers of varying degrees of molecular aggregation and diverse solubilities. The fractions of lower average molecular weight are relatively soft, fusible and soluble. The fractions having higher molecular weight are harder, less fusible, more resistant to heat and more insoluble".

In this last quotation we have a real echo of contemporary theoretical advances and discussions and in particular the suggestion that "the resin is composed of a series of polymers of varying degrees of molecular aggregation" recalls the very vigorous polemic that was then raging between Staudinger and Meyer and Mark on what Staudinger called the "new micelle teachings".

In 1929 it occurred to workers at I.C.I. that the fact that monomers and their polymers are not necessarily soluble in the same solvents might be put to some use[34]. They could thereby "eliminate the old inefficient methods of separating the polymer from its solvent". This could be accomplished by polymerising in a solvent in which the unpolymerised constituents are soluble and the polymerised product is insoluble. Vinyl chloride was not mentioned as such in this patent but it was clearly as applicable in this case as in any other. They pointed out that the technique could be used in a continuous as well as a batch process.

The different solubility of monomer and polymer was employed in a more complex process by Carbide & Carbon several years later when they were trying to produce "vinyl resins of high average molecular weight in which a comparatively narrow band of polymers of different molecular aggregation is represented"[35].

This result was achieved "by ensuring that the proportion of monomer in the total vinyl compounds present is maintained high and substantially constant. In doing this we take advantage of the fact that when polymerisation is conducted in the presence of a medium which is a solvent for the monomer but a non-solvent for the polymer produced, such polymers are precipitated. This precipitation is not of itself sufficient to obtain the above proportion constant; to do this the polymers must be separated as they are formed and removed with little or none of the momomeric vinyl compound from the reaction system".

However in spite of the not inconsiderable probing from 1912 onwards into the possibilities of solution polymerisation, the method had only limited application in the industrial manufacture of pvc. Its inherent disadvantages made this inevitable in all but some special applications. The use of solvents immediately introduced an extra element of cost. Their recovery required an additional stage in the process apart from any hazards that they might involve and they led, in otherwise similar conditions, to products of lower molecular weight.* With the inefficiency of photopolymerisation and the difficulties associated with thermal polymerisation there was every incentive to look for alternative methods for making pvc.

* In the manufacture of lacquers however, there is an obvious advantage in using this method since the polymerisation product i.e. pvc in solution, can be used as such. The polymer solution is applied more or less as it is obtained from the manufacturing process. Thus, I understand without being able to establish the point, Carbide & Carbon Chemicals in the U.S. used this technique in their operations. But this was a special case.

DISPERSION POLYMERISATION

They came in the two major processes extant today; emulsion and suspension, or granular polymerisation. Both are carried out in aqueous dispersion and although they appear to be, and indeed are, very similar in operation the resemblance may obscure profound differences in detail and product. The essential common feature is the polymerisation of liquid vinyl chloride dispersed as tiny droplets in water. PVC is thus formed as particles which remain suspended, at least until the end of the reaction. Since the polymerisation occurs in small particles, each surrounded by water, the problems of heat transfer associated with considerable exothermic heat of reaction are swept away by the heat sink of the water surrounding each droplet.

The main difference between the processes resides in the nature of the dispersion. In emulsion polymerisation, the older of the two techniques, immiscible monomer is held in a more or less stable dispersion by the presence of a surface active, soap or detergent-like substance, an emulsifying agent. Emulsification is a common enough phenomenon in various fields such as for example in the preparation of food creams, in milk, in washing-up water and oil-water combinations in a number of technologies. Its application in vinyl chloride polymerisation was no doubt suggested by the use of similar techniques in the synthesis of butadiene-styrene and other artificial rubbers. This in turn was probably inspired by the emulsified form in which natural rubber exudes from Hevea Brasiliensis.

In emulsion polymerisation the monomer and water are mixed together in the presence of the emulsifier and once adequate mixing has been effected the system should remain unbroken, that is the two immiscible phases will not separate out. This is not so in suspension, when no emulsifying agent is present and the monomer stays dispersed only as long as the mixture is stirred. A so-called suspension agent such as gelatin or carboxymethyl cellulose is used to augment the stirring in keeping the particles discrete but being much less surface-active than a soap it does not bring about any emulsification. Thus in contrast with the end-product of emulsion polymerisation, when agitation ceases the solid pvc particles settle out and can be filtered away from the water. In this respect the two processes differ. The shape, nature and size distribution and freedom from contamination of the polymer particles resulting also differ enormously and herein lies the raison d'etre for the two processes today but more of this will emerge as we trace the development of these dispersion techniques.

The literature reveals that both types of process were examined but for certain reasons the Germans remained wedded to emulsion polymerisation, while the Americans, and later the British[37] (not feeling exclusively attached to it) developed the suspension process equally vigorously. They were spurred on by the need for uncontaminated pvc to replace the rubber used in electrical applications, when the Japanese occupied the rubber producing areas of the Far East.

Dr. George Wick, who was in charge of the major I.G. Farben pvc plant at Bitterfeld before and during the war, has told me that the Germans were well aware of the suspension process, particularly since Wacker of Burghausen used it during the war. But they did not think that the advantages of the product justified the many headaches which would follow the large scale introduction of the process by I.G. Farben. It must be appreciated in this connection that I.G. Farben produced the lion's share of German pvc. In the light of the recent tendencies, on a world scale, to switch more and more to granular polymerisation and to regard emulsion polymer as a rather specialist product, that particular decision does not look right. But then we are not now subject to the pressures and tensions of that period.

a) Suspension Polymerisation

The first report of suspension polymerisation appears to have been contained in an I.C.I. patent of 1933[38]. It was not concerned with pvc and it noted that "it has already been proposed to conduct the polymerisation of derivatives of acrylic acid and their homologues or vinyl esters and their homologues by emulsifying such derivatives in liquids in which they are substantially insoluble ..."

"We have now discovered that unsaturated esters can be caused to yield products in globular form provided the polymerisation is effected while the monomeric ester is suspended in a suitable liquid medium and that the suspension is agitated throughout the whole period of polymerisation. For this purpose we have found it necessary to employ a suspension medium free from both emulsifying and wetting agents".

The first example quoted the polymerisation of methyl methacrylate in a 5 per cent aqueous solution of glycol cellulose. Others used gelatin, gum acacia and soluble starch as suspension agents.

I.C.I. published a development of this patent in the next year which described the polymethyl methacrylate product as smooth spherical or lentil shaped granules which vary in size from 0.001 inch to about 0.1 inch. These were polymerised in aqueous solutions of "polyvinyl alcohol, an amide of polyacrylic acid or its homologues or mixture of the same" in concentrations varying between 0.1 and 10 per cent.[39]

In 1935 H. Berg of Alex Wacker outlined "a process for the preparation of granular or powder emulsion polymers" of vinyl chloride which was the first application of the method to this monomer[40]. He used partially hydrolysed polyvinyl alcohol as the suspension agent, specifying a saponification number of 80-100. This was a qualification of some importance. Sommer and Zoebelein have explained why Berg surprisingly called his product an "emulsion" product. It appears to have arisen from his search for a water resistant pvc film[41]. The then current I.G. Farben emulsion polymer gave films which became cloudy in water and Berg tried to remedy the defect by the use of different emulsifiers. He eventually found that polyvinyl alcohol could in certain conditions give a product in the form of large particles and this pvc was less water sensitive than the others. In his single-minded search he did not really notice the significant change in the character of the process and continued to call it emulsion polymerisation.

This method led to the large-scale process that was employed by Wacker from the outbreak of the War and was still in use when the Allied investigating teams came on their voyages of discovery. It has been described in a number of documents[42,43,44] but the following description is an amalgam from three specific sources[45,46,47].

The reaction was carried out batchwise in 10m^3 stationary autoclaves which were fitted with paddle stirrers rotating at 40 rp.m. The charge consisted of

Monomer	3,000 Kg
Water	6,000 Kg
Benzoyl peroxide	4 Kg
Polyvinyl alcohol (Sap.No. 100-130)	1,000 Kg of 5% aqueous solution

Two comments on this charge might be made in passing. It will be noted that almost three quarters of the contents of the reactor consisted of water which in the course of the process was heated, cooled and then thrown away. This inefficient use of reactor space was, and still is, a serious weakness of the process. The second point concerns the initiator, benzoyl peroxide. Without digressing into kinetics of dispersion polymerisation it can be said that the use of a monomer soluble catalyst, such as benzoyl peroxide, rather than a water soluble one, such as hydrogen peroxide or potassium persulphate, definitely characterises this particular reaction as suspension and not emulsion polymerisation.

The charge was heated for about 50 hours at 40°C. The molecular weight of the product was adjusted by varying the temperature between 40 and 60°C. At the lower temperature relatively high molecular weights were obtained (molecular size varies inversely with the temperature of polymerisation) and the operating pressure was correspondingly low. There is some conflict in the records as to how far the reaction was allowed to proceed. One source[45] maintains that after 65% conversion the remaining monomer was distilled off. This avoided the formation of low molecular weight polymer. Another says that "reaction was continued until pressure had dropped to 1-2 ats ... corresponding to 90-95% completion. (Previously the reaction had been stripped at 65% conversion in an attempt to eliminate the formation of relatively short chains towards the end of the reaction, but this practice had been abandoned.)"[46] The account since given by workers at Wacker speaks of 65% conversion[47].

The polymer settled out and was filtered, slurried again with water in a washing procedure and then separated from the water by centrifuging, after which it contained about 30% of moisture. It was finally dried in a hot air drier at 80-100°C in the 1½-3 hours.

This process accounted for about 7% of German pvc during the war and the pvc made cost 1.55-2 RM per Kg.

In England in 1939 L.B. and W.H. Morgan of I.C.I. found a method of making pvc which they said made it more amenable "to working on rubber machinery at rubber working temperatures" than polymer made by other means. The point was important because plasticised pvc was being contemplated as an alternative to rubber in a number of applications, more particularly cable covering and electrical wire insulation.

They were impressed by the form in which the polymer emerged from this process and entitled their patent "Flucculose vinyl halide polymers"[48]. In it they described the suspension polymerisation of vinyl chloride, and they specified polymeric acrylic or methacrylic acid or ester as the dispersing agent. They also suggested incorporating a plasticiser in the polymerisation.

In an example they quoted the use of 7 parts of a sodium salt of a methacrylate copolymer dissolved in 1400 parts of water. To this was added 120 parts of di-n-butyl phthalate plasticiser, 480 parts of vinyl chloride and 2.4 parts of benzoyl peroxide. All this was charged into a rotating autoclave which was heated for three days at 55°C.

At the end of this time after washing and drying the polymer was received as a "pale coloured, low density, fluffy, matted and flock-like mass ... The flocculose nature as judged by feel and the naked eye is characteristic of the invention".

b) Emulsion Polymerisation

Progress in the preparation of pvc did not occur in a vacuum. The development took place against the background of work done and discoveries made in connection with other polymers. I have made this point particularly in relation to polyvinyl acetate and chloracetate in the very early work of Klatte. Later progress with other polymers, such as polystyrene and polymethyl methacrylate became increasingly relevant to pvc. Nor were these polymers restricted to plastics. Contemporary research in synthetic rubbers was also helpful particularly in its lessons regarding emulsion polymerisation.

The origin and early development of the emulsion process has been admirably presented by Hohenstein and Mark and I can do no better than quote from their paper in Volume 1 of the Journal of Polymer Science.

"The idea of using a finely divided monomer in aqueous suspension or emulsion seems to have been first conceived about 1910 by Hofman and Delbruck[49] and Gottleb[50]. There were two main reasons for the desire to carry out the polymerisation of various simple dienes in the presence of a diluent: one, the fact that the use of metallic sodium as a catalyst, which was common practice at that time [the German name Buna comes from butadiene and natrium] led to highly heterogeneous materials and posed a rather difficult problem regarding the complete removal of the alkali metal from the final polymer. The more important incentive for the use of an aqueous system, however, was the fact that all native rubbers occur in the form of latices and that obviously, polymerisation in the plant takes place under mild conditions in an aqueous phase without the use of such catalysts as metallic sodium and alkali alkyls.

"The aim of reproducing physiological conditions occurring in the plant is mentioned in some of the earlier disclosures[49,50]. (compare also references[51-53]) and led to the preparation and stabilisation of the emulsions as described in these patents not with the aid of soap or water surface active agents but by the application of hydrophilic protective colloids such as gelatin, egg albumin, starch milk and blood serum ... It seems therefore that the early practice, as disclosed in the above mentioned patents, was substantially different from what is known today as emulsion polymerisation and was essentially a suspension polymerisation in which the protective colloids acted as suspension stabilisers and which was catalysed by the presence of small amounts of oxygen.

"It was only in 1927 that the use of soap and similar substances (ammonium, sodium and potassium oleates, sodium butyl napthelene sulphonate) was disclosed in patents by Dinsmore[54] and Luther and Heuck[55]. The examples cited in these disclosures approach present practice to a considerable degree: they specify the simultaneous use of emulsifiers and catalysts (water or monomer soluble peroxides) and describe conversions and reaction times of the same order of magnitude as reported in more recent scientific articles".

The link between the work described and the application of emulsion polymerisation of vinyl chloride was Buna-S, the rubbery butadiene-styrene copolymer. A patent for this method was granted to W. Bock I.E. Tschunker in 1912[56] and by 1929 the process had been developed quite considerably. It is reasonable to assume that within I.G. Farben, which was interested in both Buna-S and pvc, there was a good enough exchange of information to ensure that people working in pvc knew of these developments. At any rate Drs. Wick and Iloff, who were working at Bitterfeld on pvc at about this time, have told me in separate conversations that the emulsion polymerisation of pvc was a development of Buna practice. In fact this early experience of the emulsion process gave the Germans a significant lead over their international competitors.

H. Fikentscher, working at the Ludwigshafen laboratories of I.G. Farben, was responsible for the elaboration of the emulsion polymerisation of vinyl chloride. With a number of colleagues he patented and described the process in 1931[57]. It is clear from the patent that by the time of its publication a great deal of research had already been done. Fikentscher has himself recently recorded that he began work in Easter of 1929 on the polymerisation of acrylic compounds and this led, among other things, to the preparation of copolymers of vinyl chloride and acrylates[58]. For this purpose he used the butadiene emulsion polymerisation process which had been developed by C. Heuck in the ammonia laboratory at Oppau[59]. From this he went on to the homopolymerisation of vinyl chloride.

The process was outlined as follows: "The aqueous emulsions of vinyl halides may be prepared in the manner usual for the production of emulsions, for example with the aid of turbo-mixers or homogenising machines; generally stirring the said halide into water to which any of the so-called and well known dispersing and/or emulsifying agents are preferably added is, however, quite sufficient.

Vinyl chloride is gaseous at room temperature ... therefore the emulsification is carried out by mechanical treatment such as stirring, shaking etc. in closed vessels, i.e. under increased pressure.

"The polymerisation of the resulting aqueous emulsions may be carried out by heating to temperatures of from about 35° to 80°C, or by irradiation with chemically active rays, such as sunlight or light from a mercury vapour lamp or a combinations of these means, polymerisation accelerators such as nascent oxygen in the form of inorganic peroxides, for example ozone, hydrogen peroxide, lithium, potassium or sodium perborates and persulphuric acid or organic peroxides such as acetyl or benzoyl peroxides or peracetic acid, perbenzoic acid or acetone peroxide being added if desired".

In considering this outline it is interesting to note that the catalysts listed included both water-soluble and insoluble substances but each of the five examples quoted used a water-soluble compound. Thus although the inventors were not then cognisant of this important point, they were in fact working a truly emulsion polymerisation. (cf the discussion of suspension polymerisation).

A large number of emulsifying agents were proposed and of these the sodium salts of N-oleic-N alkyl taurides, N-oleic tauride, of the fatty esters of hydroxyl alkyl sulphonic acids were cited as being "specifically suitable". Fikentscher in his recent account of that work[58] has said that in fact initially they used the sodium salt of diisobutyl naphthalene sulphonic acid (Neckal BX) or Turkey Red Oil and after 1931/2 they used the sodium salt of oxyoctadecasulphonic acid (Amphoseife 18) almost exclusively. Amphoseife 18 was based on sperm oil, the supply of which was cut off by the Allied blockade at the outbreak of war. This disruption in the provision of a unique emulsifier was a serious blow ~~at~~ to the production of pvc which was then regarded as a strategic war material. Dr. Wick has described the feverish search for a replacement by modification of the so-called 'Mersolat' emulsifiers produced by the neighbouring Leuna plant of I.G. Farben[60]. After several months of collaboration with Farbenfabrik Wolfen "Mersolat K" emerged and this not only proved suitable but gave Bitterfeld a quite unlooked-for bonus.

With Amphoseife the maximum concentration of vinyl chloride in emulsion was about 25-30%. Above this it was unstable. But with Mersolat K, monomer concentration could be raised to 50-60% without running into any trouble. Thus without any additional equipment or the use of any extra energy output could be increased from 600 to 1200 tons per month. It is an ill wind that blows nobody any good!

However, to return to Fikentscher's patent of 1930. It recognised the need to regulate the pH of the emulsion since the quality of the polymer and stability of the latex are to some extent dependent on it. The preferred pH was 2.5 to 3 and this could be achieved by the addition of acetic or boric acid with a suitable buffer. As the proposed catalysts included acids such as peracetic, this had to be taken into account in deciding on the necessary quantities. In operating the emulsion process on the large scale at Bitterfeld after 1934 they found that a slightly alkaline condition gave better results[61].

In 1930 they thought to avoid subsequent treatment that the incorporation of the plasticiser into pvc was best done by including it with the monomer in the emulsion before polymerisation, and so in Example 2 of the patent

10kgs of di-ethyl mono(ethylene glycol n-butyl ether) phosphate were mixed with 90kgs of monomer at the outset. This prepolymerisation plasticisation was not practised for long however and by 1932 the preferred process involved plasticiser addition to the polymer.

However, the patent showed an early and lively appreciation of the deleterious effect of iron on the polymer. Workers at that time of course, knew even less than we do now about the mechanisms of pvc degradation and the catalytic effects of iron in these processes but they laid it down that "in order to obtain products which are particularly fast to light, it is preferable to carry out the polymerisation in the absence of iron, for example in enamelled vessels and apparatus. The same result can be obtained by removing any iron from the polymerisation product, which may be effected by washing with aqueous oxalic acid". Claim 8, of which this point was the substance, underlined its importance.

Methods for breaking or coagulating the emulsion were also set out in some detail in the patent and the list shows that they were then aware of the techniques which are now employed. Addition of acids, salts and alcohols was suggested and of these a solution of aluminium sulphate was preferred. In addition "cooling the aqueous dispersions to -5° to -8°C and cataphoresis" were proposed.

One further noteworthy process detail was the alkali stabilisation of the product in order to make it "more resistant to decomposition and discolouration on heating..." This discovery was subsequently of the utmost importance because it made possible the high temperature (160°C) processing of pvc.

Altogether the process outlined marked a decisive advance on previous techniques for the polymerisation of pvc. The patent was not inhibited in pointing out its advantages. The form of the polymer was most convenient. Handling the fluid latex was easy, as compared with the solution or block polymer. The coagulated powdered polymer could be washed readily and furthermore the fine particles dissolved relatively quickly in a variety of organic solvents. From the point of view of the chemist polymerising, it afforded "the opportunity of very conveniently maintaining the desired temperature and completely preventing any local superheating". This lead to products of "paler colour with greater fastness to light and heat" and a greater uniformity of polymer. Finally the polymer was cheaper because organic solvents were avoided and "the yield of polymerisation products is about double of that of the ordinary polymerisation methods, i.e. from 80-90% against from 40-50%".

From this time and for many years thereafter emulsion polymerisation became the dominant method for the manufacture of pvc. In I.G. Farben it was the only one. All work on the polymerisation of vinyl chloride at Ludwigshafen, the research centre and at Bitterfeld the production unit, was subsequently aimed at developing and improving the process.

At Ludwigshafen Fikentscher and his colleagues were mainly concerned with copolymers of vinyl chloride, (which will be described in the following chapter) and most of the developments which he pioneered derived from investigations in this field. The basic formulation used Amphoseife 18, hydrogen peroxide as catalyst and a reaction temperature of 45°-50°C.[62] and polymerisations were carried out in enamelled rotating and oscillating autoclaves. These were used rather than reactors with stirrers because the lubricant from the stirrer gland contaminated the polymer. Agitation by vibration was limited to vessels up to 201 in capacity and bigger reactors, up to 1000 litres (the so-called "elephants") were of the rotating variety. In a further increase of scale to a capacity of $12m^3$ the form of the reactor changed once more to what was essentially the modern kettle with its stirrer. This occurred in 1934.

A formulation modification was instituted in 1932 whereby the hydrogen peroxide initiator was replaced by persulphate in the manufacture of vinyl chloride copolyers. Fikentscher explains that this was due to improved coagulation characteristics in the presence of the persulphate.

In the course of their investigations, the Ludwigshafen laboratories carried out intensive studies of the kinetics of the process and as a result in a paper published in 1938 Fikentscher gave it as their view "that in emulsion, polymerisation is not (as frequently assumed) undergone by the portion of the vinyl compound which is emulsified as drops but by the portion dissolved in the aqueous phase. The latter is continually renewed from the liquid emulsion drops and thus remains constant throughout the polymerisation, as long as these drops remain"[63]. This discovery as to the nature of emulsion polymerisation provided a key to the understanding of the process and consequently to subsequent improvements in it.

Meanwhile work was proceeding at Bitterfeld in parallel with Ludwigshafen. There, in a direct line of descent from Klatte, as it were, but now as part of the I.G. Farben empire, investigations were concentrated on pvc and post chlorinated pvc, as distinct from vinyl chloride and copolymers. This resulted in a somewhat different approach and slant to their work but there was a broad base of common interest with Ludwigshafen. They were, after all, both interested in the polymerisation of vinyl chloride and in the application of the products.

Dr. Wick has pointed out the great significance of the adoption of the so-called Ludwigshafen emulsion polymerisation process at Bitterfeld[61]. It did much to overcome some of the weaknesses of pvc made by the block and solution polymerisation. In particular, by reducing the considerable very low molecular weight fraction it improved its stability and mechanical properties.

From many experimental formulations the following emerged as optimal in 1932:

20 l of an aqueous solution of 0.5% sodium oxyoctadecansulphonate
0.5% disodium phosphate
1.0% hydrogen peroxide.

was emulsified with 5kg of vinyl chloride. Heating at 45-50° raised the pressure to 8-9 ats and heating was continued for 18-24 hrs. The polymer was eventually coagulated by addition of aluminium sulphate.

The equipment which was available in Bitterfeld at that time consisted of two 40 l. nickel-plated rotating autoclaves. Their design was based on the ideas developed by Fikentscher. After coagulation the polymer was sucked down onto a Nutsch filter and finally dried in an oven at 60-70°C.

Somehwat later polymerisation capacity was supplemented by a 100 l. rotating autoclave designed and built as were the smaller ones. But a centrifuge replaced the Nutsch filter and drying was carried out at reduced pressure. Product made thus was used for semi-technical scale post-chlorination investigations.

This brief description of the early Bitterfeld process underlines the obvious fact that manufacture of polymer involves rather more than polymerisation. Isolation and drying are important phases of the operation and required a good deal of attention. In 1933 they tried a plate-dryer [Teller-Trockner] which was designed to operate continuously, in which the polymer fell down a series of turning plates against counter-current of warm dry air. This particular arrangement was unsuccessful because some of the polymer adhered to the wall where it became hot, decomposed and contaminated the rest of the dried product.

The idea of continuous working had attractions that were obvious to workers at both Ludwigshafen and Bitterfeld. Both groups recognised that higher space-time yields and a greater product uniformity might reasonably be expected this way and both explored the possibility. The Ludwigshafen conclusions were published in a Fikentscher patent of 1937 and were subsequently translated to full-scale operation at Schkopau.[64] The Bitterfeld work was described in <u>Kunststoff Handbuch</u>[65]. "In principle", said Wick "the process was based on the simultaneous addition of vinyl chloride and water containing emulsifier and catalyst, to a tube fitted for heating and cooling, under pressure. The proportions of monomer, emulsifier and catalyst, the entry temperature of the emulsion, the polymerisation temperature and rate of flow were all so amenable to regulation that a uniform product of the desired molecular weight was made". Some formulation and processing details were given but perhaps one of the most interesting features was the mention of a spray-drying plant (Nubilosa) for the removal of moisture.

This technique has since become quite widespread in the manufacture of pvc, as of other materials, and as a process spray-drying has much to recommend it. The emulsion is "atomised" in a warm atmosphere and the water is "flashed off" the very large surface area so produced, leaving the powdered polymer to settle on the walls and floor of the chamber. The snag inherent in this method lies in the inevitable contamination of the product. When the water is removed all the non-volatile constituents, for example the emulsifiers and buffer, remain with the pvc. There is no filtration and washing to allow of their removal. This provided a strong incentive early on to devise formulations in which non-monomer ingredients were kept to a minimum, or alternatively to the choice of such ingredients as were least objectionable in the finished product.

Although both Ludwigshafen and Bitterfeld elaborated methods for continuous emulsion polymerisation it seems that the former were rather more successful and convinced of its advantages. The latter came to the opposite conclusions and adopted the batch process for the big expansion of capacity which was planned in 1938. I imagine that to a certain extent these views reflected the preoccupations of the two groups, the research orientated workers were impressed with the greater elegance of continuous operation while the production people were concerned to meet the demands of the market as it was then, by processes which they knew and of which they had built up a fund of experience. This much is conjecture on the subtler influences that may have been at work. What is quite certain however is the fact that the multiplicity of grades of product, which was even then becoming manifest, was a very powerful argument for the batch process. So convincing, that most plants today work on this basis.

By 1938 the interest and demand for pvc in Germany and abroad encouraged I.G. Farben to initiate capacity for about 7000 tons per year. PVC production was moving out of the exploratory stage to an output of a significant scale. The layout of this plant at Bitterfeld, the change of monomer supply from Rheinfelden to Schkopau, the use of pvc in the chemical engineering of the pvc plant itself, all these details have been described by Dr. Wick[66]. What might be specially mentioned here are several interesting features and developments of the earlier process. The vessels in which the aqueous phase was prepared were lined with pvc sheet. In the fabrication and installation of such corrosion resistant material the Germans, impelled by Governmental policy to create a self-sufficient economy for the impending war, had developed techniques which were well in advance of practice abroad. Containers storing the pvc emulsion were also lined with pvc sheet because it seemed to inhibit premature coagulation. The whole piping and valve system of the plant was made of pvc. I.G. Farben was demonstrating its confidence in this material and experience showed that it was not misplaced. In 1946 the piping and valves were still in good condition.

The process and equipment developed and erected at this time was more or less the same as that described by the Allied teams at the end of the war. The aqueous solution of the emulsifier in deionised water, with some sodium phosphate was first charged into the autoclave and the monomer and catalyst (hydrogen peroxide) came next. The nickel-lined autoclaves (of which there were 15) were no less than 12 m long and 1 m in diameter and they were rotated at 4 r.p.m. These vessels accommodated 3,500 lbs of vinyl chloride per batch.

Reaction started after an induction period of four hours when temperature was maintained at 40-50°. Cooling was necessary to control the exothermic burst when the reaction did eventually begin. The end of the reaction, recognisable by the pressure drop, generally occurred after about 24 hours.

The yield, it was claimed, was 95% (conversion was 90%) and drying was effected in a Nubilosa spray drying plant at 160°C and 90% of the polymer emerged as a fine powder with particles of 3-5μ.

This plant went on stream in the autumn of 1938. The next year the Ludwigshafen continuous process was set up on a large scale at Schkopau and it was subsequently described in German Plastics Practice[67] and in a B.I.O.S. Report[68].

The process details given there will not be repeated here but the main features included a vertical mounted autoclave seven metres high and 1.5 m in diameter. Materials were metered into the reactor in three streams, namely soap solution, monomer and initiator. The emulsion all but filled the reactor, but only the top layer, one metre deep, was agitated by a paddle stirrer. An outlet at the bottom of the reactor allowed efflux of the dispersion at a rate that balanced the inflow and polymerisation occurred as the monomer moved down the reactor. By the time it reached the bottom, some 3½ to 5 hours after entering (depending on whether sodium persulphate or hydrogen peroxide had been used as initiator) about 85% of the monomer was converted to polymer of K-value ranging from 68-78.

By the end of the war Schkopau had a plant capacity for about 7000 tons per annum.

This description of production in Germany has so far almost implied that pvc was one material. But this was not so. By the outbreak of war the industry was no longer rudimentary and immature. It was serving a variety of customers and turning out a corresponding number of grades of polymer. I.G. Farben designated them as shown in the following table[67,70]:

<u>Grades of PVC</u>

Grade	Application	K-value*	M-number+
Igelit PCU-K (Kabel)	Cable insulation	66 ± 5	-
" -G (Gummi)	Rubber substitute	65 - 75	28 - 36
" -GH	Where specially tough G was required	75 - 80	36 - 44
" -P (Paste)	Artifical leather	65 - 75	28 - 36
" -R (Rohre)	Extruded tubes	60 - 63	18 - 23
" -F (Folie)	Sheet or film	-	-
" -L (Luvitherm)	Sheet of high strength	78 - 80	-
Vinoflux PCU-3	Lacquers	30 - 33	-

* K-value is a function of the mean molecular weight of the polymer and is obtained from the following equation, derived by Fikentscher, by measuring the viscosity of a dilute solution

$$\frac{\log\left({}^{N}s/N_o\right)}{c} = \frac{75\ K^2}{1 + 1.5\ Kc} + K$$

where N_s = viscosity of solution (with concentration at about 2%)

N_o = viscosity of solvent in the same viscometer

c = concentration of polymers in g/cc of solution

K = a parameter characteristic of the molecular structure of the polymer

\+ M-number gave an indication of the low molecular weight content of the polymer, i.e. some idea of molecular weight distribution.
It was defined as the number of grams of solvent (a mixture of one part of monochlorbenzene and three parts of epichlorhydrin) that will dissolve 1 gram of Igelit PCU at 80°C and then gel within three minutes when cooled fro 20 minutes. It was a very arbitrary test which gave results varying from one operator to another and has long since been abandoned.

The main variable as between the grades was K-value and this was regulated by the temperature conditions during the polymerisation. Control of the reaction, it was said, was good enough to give reproducibility within ± 1 K value. Where toughness and strength generally was required polymer of high K value was indicated, while lower molecular weights were desirable where easier processing conditions were necessary. The very low K value of Vinoflex was dictated by the necessity for solubility of the polymer to make lacquers.

But molecular characteristics were not the only relevant considerations, as a comparison of grades P and G in the tables makes clear. The shape, size and particle size distribution of the polymer particles were of extreme importance, particularly for paste polymers, but here the chemists exercised little control and thus grades were not so much produced to order but rather each batch was classified and graded according to its behaviour.
These polymer types will be discussed further in connection with the applications of pvc.

Progress in Great Britain

So far this account of the development of pvc has been mainly a history of events in Germany. It could hardly be otherwise since that country was so clearly in the forefront at that time. But investigations were being conducted elsewhere, including the United Kingdom.

The written record is sparse however and the data selected in this account of work leading up to World War II in the U.K. is largely the result of a series of interviews that I have had with people who were active in this sphere from about 1936 onwards. The limitations of such oral evidence are obvious, but I have been able to confirm the facts given here by checking the accounts and answers of my interviewees against one another. I therefore feel fairly confident about the accuracy of this story. In any event, in the absence of written records, either because of their destruction or the non-availability, we have no choice but to do the best we can.

Probably the major difference between the situation here and in Germany in the field of pvc was the lack of that urgent political and technical pressure in the U.K. that motivated the search for substitute materials in Germany. There was no drive to replace natural rubber in the U.K. Quite the reverse in fact. There were powerful natural rubber interests which discouraged the search for synthetic materials. Thus for example, the cable-makers' specification requiring natural rubber as the insulant made it very difficult to persuade manufacturers to examine the merits of alternative materials. This circumstance together with the ready availability of natural rubber, albeit with violent price fluctuations, provided little incentive for the development of pvc.

However once German material began to be imported into the country its obvious possibilities attracted more serious attention. In speaking of British activities in pvc before 1940, one refers primarily to the work of I.C.I. since only in its laboratories were there any significant developments. The Distillers Co. has of course contributed much in this field, but it made its entry just after that date. The company known as F.A. Hughes Ltd was also interested in pvc before the war but only as selling agents for German material.

I.C.I. interest in plastics during the 1930's evolved from their original concern with methyl methacrylate and the thermosetting phenolic and urea formaldehyde polymers which they took over when they acquired the Mouldrite Company. They were of course also active in the development of polythene, but this work was going on away from the two major centres of polymer research at Billingham and Blackley. Other groups within I.C.I. also developed their own interest in pvc, for example, The General Chemical Division elaborated the monomer synthesis, I.C.I. (Rexine) did experimental work on pvc coated fabrics and the Explosives Group used pvc for insulating detonator leads, but polymerisation and the polymer were primarily the concern of these two groups[69].

At Billingham a "New Resin" section was established and this small group of chemists was charged with the investigation of about a dozen polymers nearly all of which were called "speculative polymers". PVC was added to the number in 1938 when on examination of the German polymer they decided it was an interesting material in spite of its poor stability, its relatively high water absorption and inadequate dielectric properties. The group including Dr. E. Brookman and Mr. A. Gibson worked under the direction of Mr. A. Renfrew who was also responsible for the development of polymethyl methacrylate. It is therefore not surprising that the chemists working on pvc tried early on to adapt the granular, or suspension, polymerisation process used in the preparation of "Diakon" (an I.C.I. trade name for polymethyl methacrylate). The basic patent for this process, in the name of Dr. J.W.C. Crawford has already been referred to[38] and initial efforts in pvc consisted of the elaboration of formulations and conditions suitable for this polymer. Work along these lines had the added advantage that it might have helped produce a polymerisation process free of patent restrictions. This would not have been possible using the emulsion technique, but as it happened the war made such considerations irrelevant.

At Dyestuffs Division at Blackley the other group of I.C.I. workers came upon pvc because they were concerned with rubbers and rubberlike materials. In 1936, in the light of the evident progress of the Germans with butadiene rubbers, a team directed by Dr. R. Hill and Dr. L.B. Morgan began investigations in this field. In 1938, becoming aware of "Mipolam" and "Igelit" (from Germany) and "Vinylite" and "Koroseal" (from the United States) they turned their attention to pvc.

The Blackley team was much bigger than their "Plastics" counterpart and one of the latter group expressed the difference in this way: "I was surprised to find the level of sophistication in the polymer laboratories at Blackley when I first visited it. The Plastics division had no stirred pressure vessels, only tubes growing bigger into rotating and tumbling autoclaves. Blackley had a selection of stainless steel and lead lined stirred autoclaves. They were ahead of us. We had nothing to teach them".

Under pressure of the patent situation the group also did some work on suspension polymerisation, as Dr. Morgan's patent on "Flocculose Vinyl halide polymers" shows[48], but their major interest was in the emulsion process. All their previous work was orientated in this direction following their researches on butadiene polymers.

At first, their work was imitative. They were trying to achieve the products that the Germans and Americans were already selling. They looked for formulations which gave them polymerisation times of 5-10 hours and controlled exotherms that did not require "all hands to the pumps to play cold water on the reactor". They were after dispersions which coagulated conveniently and left little adhering mess on the walls of the vessel to avoid the need for frequent cleaning. They investigated different methods of coagulating and methods for incorporating plasticiser and stabiliser.

In some respects they improved upon the competitive products even at this early stage. For example, the Blackley team chanced upon lead stabilisers before the war. It happened thus: when the emulsion was coagulated by the addition of brine they found that relatively large amounts of the proprietary surfactant, Lissapol C, remained to contaminate the polymer. This was unacceptable as the pvc was destined for use as cable insulant. They therefore sought to reduce contamination, and in this respect it is interesting to note that their knowledge of the dielectric properties of polythene (which the Germans did not have) set them more demanding criteria than those to which the Germans worked. They argued that lead acetate as a coagulant would also precipitate the Lissapol C as the insoluble lead salt and thus facilitate its removal. It did and at the same time exercised a stabilising action. They also found that the use of lead reduced water absorption of the polymer quite markedly. Thus while alkali treated polymer was not acceptable for electrical applications in the U.K. the lead treated compound was. A little later they changed from the acetate to 2,4 dihydroxyquinoline which could be used in rather lower concentrations. Lead was not used with polymers that were to be spread as coatings for leathercloth for obvious reasons.

At the end of 1939 with the war already in progress I.C.I. decided to take up the manufacture of pvc principally for use as a cable insulant. From that moment the people concerned with it were working under great pressure; a pressure moreover that was to increase when our source of natural rubber was overrun by the Japanese. The first decision that had to be made was as between the granular and emulsion processes; which was to be adopted? Both had been developed in the laboratory but the Blackley investigators had reached pilot-plant scale and it appeared that emulsion polymerisation gave better yields in a shorter time.

Thus the emulsion process won the day in 1939 but it left within I.C.I. two schools of thought regarding the relative merits of the methods. The protagonists continued the argument and within a few years the granular process was established alongside the other one. After the war suspension polymerisation became the dominant technique, not only in I.C.I. but among pvc producers generally.

In I.G. Farben there was no such competition. All its pvc was emulsion polymer and its chemists were wedded to the process. Their relatively late switch to suspension polymerisation is probably not unrelated to this circumstance.

General Chemicals Division of I.C.I. made the monomer. Their experience of chlorine chemistry and their manufacture of dichloroethane on a large scale predisposed them to this route to the monomer. In addition time was of the essence. They therefore put up a 50 ton a year plant for monomer made this way but they also investigated the acetylene-hydrogen chloride route, of which they had no previous background experience of their own, on another 50 ton a year plant.

With the decision to go ahead on the production of pvc there was some discussion within I.C.I. as to which part of that organisation was the rightful home for this new product. It was resolved by making the Plastics Division responsible for the new venture. As a result Dr. E. Brookman and Mr. A. Gibson went from Billingham to Blackley to acquire the necessary know-how and with a young assistant became the first production team for pvc in 1939.

The Runcorn pilot plant (100 tons/year) came on stream in December 1940 and by that time the designs for a 500 tons a year plant were under way. They were realised in April 1942. The original emulsion process used ammonium persulphate as initiator and Lissapol C was the emulsifying agent but this was subsequently changed to a more effective agent. The former had to be used at relatively high concentrations and produced a long induction period followed by temperature "peaking". The latter was better in this respect.

Another important change effected in the second Runcorn plant was the introduction of spray-drying in place of coagulation and filtration of the polymer. This was made possible by the development of a polymerisation formulation giving reduced contaminants in the final polymer.

In describing I.C.I.'s progress in manufacturing pvc at this time it is difficult to restrict myself to my self-appointed terminal date of 1940 because this was a germinal period and thus a stage of intense development. However some discipline is necessary. Even so it may be of interest to record the discovery, at Blackley, of reduction-activation, or redox polymerisation in the period 1942-3, and now so widely used in the production of synthetic rubber as well as pvc. Details of this work was subsequently described by Dr. R.G.R. Bacon[71].

One of the weaknesses of natural rubber is its inability to withstand oils. Bacon tried to improve its oil resistance by polymerising acrylonitrile in rubber latex and hoped thus to bestow some of the oil resistance of butadiene-acrylonitrile rubber onto the natural variety. He thought he might graft polyacrylonitrile onto natural rubber by the process of chain transfer. But he found that no polymerisation occurred; there appeared to be some inhibitor present.

He therefore decided to study the phenomenon of inhibition more deeply and, dispensing with the latex, set up a system of acrylonitrile in water with ammonium persulphate and an inhibitor. Hydroquinone was the first he tried but instead of observing inhibition he found that the induction period was reduced from several hours to a matter of seconds. The phenomenon was fairly soon generalised.

Dr. Morgan has since ruefully reflected that if I.C.I. in patenting this discovery had protected the process for polymersing at low temperature rather than the formulation that made it possible, they would have been in a very strong commercial position.

PVC in the United States

Developments in the United States in the interwar years were not as advanced as in Germany but quite a way ahead of those in Britain. There seemed to be two motives behind the interest displayed in pvc. The first was a long tradition of interest in artificial rubber in the U.S. Chemical industry, partly because there was no rubber producing areas either in the United States or under its control. Perhaps an equally important factor was the lack of opposition to synthetic rubbers generated by interests in natural rubber. There was no question of an immense urge to self-sufficiency such as stimulated the Germans. Plasticised pvc took its place alongside polychloroprene and other elastomers as a material with properties, superior in some respects to those of natural rubber and as such it was of interest. Secondly vinyl chloride-vinyl acetate copolymers were interesting, among other things, as lacquers; this development is discussed in greater detail in the next chapter.

Three companies were active in the field of pvc, Du Pont, B.F. Goodrich and Carbide & Chemicals Corporation. The patent literature bears testimony to this fact. But Du Pont, for some reason never went into large-scale production. Goodrich became well known for its plasticised pvc, sold under the trade-name of "Koroseal" and Carbide & Carbon marketed their copolymer products as the "Vinylite" series.

At a distance of 3000 miles and with a sparse relevant technical literature I have found it quite impossible to build up any sort of satisfactory picture of the emergence of polymerisation processes for pvc in the United States. It is said that Carbon & Carbide used the solution method and Goodrich emulsion polymerised but I have not been able to confirm this and without investigating the situation on the spot I see no prospect of collecting the necessary data. Since I have had no opportunity of doing so, this part of the history of pvc will have to await the arrival of a local historian.

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Chapter 5

Modification of Vinyl Chloride Polymers

Even the earliest superficial observations of polyvinyl chloride made it only too obvious that here was an intractable, insoluble and unstable material. On heating it was, and is, quite liable to liberate clouds of corrosive hydrochloric acid, leaving a discoloured or even black brittle mass and on exposure to light other undesirable changes occurred.

Small wonder then that pvc was not the subject of quick and enthusiastic development. Such behaviour obviously set up great obstacles to its acceptance by both processers who had to use heat to shape and fabricate the material and potential customers who would have to watch their purchases deteriorate under the influence of light. However the problem of polymer unstability was not altogether new. Cellulose nitrate, while not so unstable when freed from manufacturing contaminants, provided similar difficulties for the fabricators and users of celluloid. Indeed in some respects its flammability and explosive hazards were even more embarrassing.

In that instance the dilemma was to some extent resolved by the addition of stabilisers, that is substances which retarded decomposition. Learning from this experience workers in the field of pvc adopted a similar approach and it helped. But it by no means disposed of the problem. A parallel, but flanking attack on the tendency to degrade on heating came with the incorporation of plasticisers into the polymer. This too was a technique borrowed from celluloid. While primarily intended to modify the properties of the polymer it also had the effect of reducing the temperature needed for processing and thus protected it, to some extent, from the ravages of thermal breakdown.

However both these palliatives involve the use of additives, or compounding ingredients as they are called, which will be considered at some length in a subsequent chapter. What I should like to discuss here are the attempts that were made to deal with this problem by modification of the structure of the polymer itself. This was done in two ways. In the first method polyvinyl chloride was chlorinated so that the chlorine content of the molecule rose from about 56% to 62-65% with a consequent change in properties. The second method involved copolymerisation of vinyl chloride with a smaller proportion of another, and sometimes more than one, monomer.

Post-chlorination was a uniquely German technique in the years leading up to the War. It was developed by I.G. Farben and manufactured only in Germany and so it has not been difficult to gather the material for a review of its origin and early manufacture. A few patents, some post-war Allied reports, discussion with Dr. Wick and reference to the relevant section of <u>Kunststoff-Handbuch</u> provide sufficient information for the degree of detail required here.

Increasing the chlorine content of the polymers by subjecting pvc to treatment with chlorine commended itself because by so doing its properties became rather more attractive. With pvc one has to choose between reasonably high strength and ready solubility. To achieve the former high molecular weight polymer is necessary. But only low molecular weight material is soluble in cheap, easily available solvents. After-chlorination however gives polymers which are strong, soluble and form good films.

C. Schönberg discovered this at Bitterfeld in 1931 and described the chlorination process in a patent dated the following year[1]. He put the situation thus: "This invention relates to a process in which by chlorination of polymerised vinyl chloride, obtained in any manner, an artificial mass is obtainable having a strength higher than that of the product made from pure pvc which has not been chlorinated. Whereas before it has hitherto been necessary to produce a polymerisation as fundamental as possible (sic) in order to obtain a high degree of strength and thereby to sacrifice solubility, it is now possible to produce by after-chlorination of, for example, polymer of a low degree of polymerisation having a good solubility but exhibiting little or no tendency to form films in consequence of its insufficient tensile strength, a product which is suitable for making valuable films, lacquers, sheets or fibres.

"The enhanced mechanical strength of the product due to chlorination renders possible a depolymerisation leading to a further improved solubility and a lower flowing temperature of the product".

The basic simplicity of the process was illustrated in the first example of the patent in which low molecular weight pvc (soluble to the extent of about 10% in butyl acetate) was suspended in carbon tetrachloride and chlorine was introduced into the suspension at 60-70°C. The polymer went into solution as chlorination proceeded and when a test portion showed that the product had good film-forming properties the reaction was interrupted. After the solution had cooled, the chlorinated polymer was precipitated by addition of methanol and then filtered from the solvent.

I.G. Farben was sufficiently impressed with the results to erect in 1932 a small experimental plant with a capacity of one ton per month. Two years later they scaled this up by a factor of ten in a semi-technical plant at the Works at Rheinfelden to evaluate the process further. One modification which was to be tested in this way was the precipitation technique evolved by G. Wick. Its purpose was to produce the post-chlorination pvc in a "sandlike form" which unlike the product made heretofore could be easily cleaned and freed from solvent. The appropriate patent described the method in this way[2]: "The solution of after-chlorinated pvc, for example in tetrachlorethane, is concentrated to about 10% by evaporation of the solvent and is then cooled until it begins to gel. The temperature varies with degree of polymerisation from 0 to -20°C. ½ to ⅓rd of the volume of a non-solvent, e.g. methanol, is then added with stirring, after it too has been cooled, and the product comes out as a white eminently filterable powder ... This precipitation technique is surprising as one might imagine that the gelled solution would be less suitable for precipitation than a warm dilute solution".

This technique for the isolation of the polymer was proved as was indeed the rest of the process, with a number of minor modifications. Sanction was therefore given in 1938 for a production plant with a capacity of 120 tons per month which was in operation at Bitterfeld by the outbreak of war. The product was called "Igelit PC".

As chlorinated pvc is off the mainstream of pvc development and the chlorination process is a straightforward organic chemical reaction and thus not of particular interest in this story, I do not propose to discuss it in any detail. Chapter and verse can be found in a number of sources, the most illuminating of which are probably the post-war Allied Reports[3,4,5,6,7].

It is however interesting to note that two main grades were made, corresponding to the two major applications of the material as fibres and as lacquers, with the former consuming the bulk of production. The two types were obtained by manipulating the chlorine content of the polymer and by varying its molecular weight. For fibres a high softening point is desirable and hence the pvc raw material had a K value of about 60 and the final product contained 62-64% of chlorine. Lacquers, on the other hand were most useful when they were easily soluble and so the molecular weight of the original pvc was much lower. One source quotes a K value of about 30[3].

The development of the necessary fabrication processes, in particular those required for making fibres, proceeded simultaneously with the elaboration of the production technique. It took place under the direction of F. Gajewski, P. Esselmann and H. Rein. These were the people who began their efforts to make fibres from "PC" in the laboratories of I.G. Farben (Agfa) at Wolfen in 1932. Their success marks the moment of manufacture of the first fully synthetic fibre anywhere in the world. It is true that "Viscose" and "Rayon" among others predated this but they were not wholly man-made. The basic cellulose was of natural origin. Nylon on the other hand was first synthesised two or three years later and was spun sometime after that. It made its commercial debut in 1938 some five years after chlorinated pvc.

The Wolfen workers adapted the wet-spinning process used in the manufacture of cellulosic fibres and dissolved the chlorinated pvc, which had already been produced ~~established~~ at Bitterfeld with 0.5% dioxyethylsulphate, in very dry acetone. After being forced through a spinneret consisting of 120 holes each of diameter 0.08 mm the filaments were passed through flowing water which coagulated the PC filament and removed the acetone.

Even at that time there was a rich fibre and textile technology, but here too a discussion of the esoteric points of the process would be out of place (even if I were equal to it). Suffice it to say that both continuous and staple fibre was manufactured in the ratio of one of the former to ten of the latter. The continuous variety was used for ropes,cordage, marine applications and chemically resistant clothing while staple was woven into cloth and used in non-burning parachute cloth, fish nets and rot resistant army tent bottoms. From these applications it might be deduced that the great attraction of PC fibres lay in their great resistance to water, to various chemicals and to bacterial and fungal attack. This last property so impressed an American investigator following the Allied armies sweeping through Germany that he reported "The properties of PC fibre make it a suitable candidate for insect screening ... for the Pacific area. A sample of insect screening has been sent to Washington for examination ... it may be possible to secure the PC fibre for the Pacific War effort".

In spite of these attractions however, the work on chlorination of pvc appears to have been an interesting excursion arriving at no place of significance. The inherent weaknesses of post-chlorinated pvc have allowed it to be overtaken and completely overshadowed by other synthetic fibres and lacquers. In particular its low softening point at about 80°C (cf the melting points of nylon 66 and polyester fibres at about 250°C) and its instability at elevated temperature limit its interest.

In thus dismissing PC it should not be forgotten that before 1935, when the way for pvc was finally opened, it was PC that was regarded as the important product and pvc as an intermediate in its synthesis. So much is clear from the designations used at the time. "PC" was the chlorinated material and "PCU" (i.e. PC unchlorinated) referred to pvc.

Copolymerisation

In contrast with post-chlorination, copolymerisation was, and remains, a concept and practice of great significance, not only in the field of vinyl chloride but in the whole world of polymers.

The idea can be traced back to the early interest in the polymerisation of dienes to make synthetic rubbers. In 1912 I. Kondakov discussed the elastomeric copolymer of butadiene and dimethyl butadiene[8] and about the same time Bayer of Leverkusen patented the copolymerisation of isoprene and butadiene[9]. The extension of the technique to vinyl polymers came very shortly after in Klatte's patent dealing with "processes for the preparation of technically useful materials from organic vinyl esters"[10]. His primary concern was conversion of vinyl acetate and vinyl mochloracetate to their respective polymers but he also indicated, in passing, the feasibility of copolymerisation by mentioning that "it has been found that useful products can be made by polymerisation of organic vinyl esters on their own or <u>mixed with one another</u> ..."

However these researches, and others, led to no immediate industrial consequence in pvc. This development had to wait until the late 1920's. But by then a number of companies had become alive to the possibilities of vinyl chloride copolymers. In fact three of them applied for patents almost simultaneously in 1928. They were I.G. Farben in Germany in June of that year[11], Carbide & Carbon Chemicals[12] and Du Pont[13] in the U.S.A. in May and September.

They came upon this phenomenon from different directions, as it were, and with varying degrees of excitement. E.W. Reid, of Carbide & Carbon, was primarily concerned with his materials for use as lacquers and his patent dwelt at length upon the novelty and usefulness of the concept of copolymerisation. It "provides an entirely new class of resins and processes of making them" he said.

A. Voss and E. Dickhäuser of I.G. Farben and W.E. Lawson of Du Pont, on the other hand mention the matter almost incidentally. The main purpose of both these patents was to protect a method polymerisation. The Voss and Dickhäuser patent began thus: "A process of technical value for preparing polymerisation products from a vinyl halide has not yet been known ... We have now found that polymerisation of the vinyl halides is easily effected by starting from pure products and heating same at very slowly increasing temperature ..." Lawson started in much the same vein: "Various methods have hitherto been developed for the polymerisation of vinyl derivatives but, so far as I am aware, all such prior processes involving the use of heat have been difficult to control ... I have found that by the use of the continuous flow process ..."

Only in the body of the respective patents did it emerge that they were also concerned with copolymerisation. Thus Lawson in the third and last of the stated purposes of the patent said "It is also an object of this invention to provide a process of polymerising vinyl derivatives containing mixed esters". The I.G. Farben application first made the claim mentioned in the last paragraph, then stated that the polymerisation could be carried out in an inactive solvent and finally made the point that the polymerisation could be carried out in the presence of substances which could themselves polymerise.

They all made the point, Reid and Lawson with some surprise, that the products of copolymerisation were decidedly different from a mixture of the separate polymers and rather superior in their properties. Reid considered the case of lacquers from vinyl acetate polymer and vinyl chloride polymers in some detail, Coatings of polyvinyl acetate he said had never been used commercially because while they had good adhesive properties, "they are too soft, too low melting and too easily soluble in common solvents ..." Polymerisation products of vinyl chloride "had also failed to find any commercial use in liquid coating compositions or plastics. My experiments have shown that they are somewhat harder, higher melting and less soluble than those of the acetate but they are brittle and deficient in cohesive and adhesive properties. Moreover films prepared from them tend to darken rapidly and become opaque when exposed to sunlight ... I have attempted to overcome these objectives by mixing together vinyl polymers of the hard and high melting type without success. I have however discovered quite a new phenomenon, viz, that when vinyl compounds which form both these types are polymerised while in mutual contact, products are obtained which differ profoundly from those which can be made by polymerising the same compounds separately or by mixing the products obtained when these vinyl compounds are polymerised separately.

"The products of this conjoint polymerisation are tough and strong and are much better adapted to the purposes of the lacquer and plastics industries with respect to insolubility, adhesiveness or stability than are the polymerisation products prepared from the single vinyl compound".

Reid went on to speculate that such conjoint polymerisations "result in chemical compounds of a new type", but gave no hint of what he had in mind, since he said "the validity of his ~~his~~ hypothesis has not been proved experimentally because of the practical difficulties involved". One cannot deduce from the discussion in the text of the patent how familiar he was with Staudinger's new ideas on polymers, which in 1928 were by no means generally accepted. It is therefore impossible to speculate on the validity of Reid's theories but it is interesting to see that they pointed the contrast between plasticisation as "ordinarily accomplished by incorporating appropriate high boiling solvents with the resins" and "conjoint polymerisation" from which "an inherently and internally permanently plasticised resin is formed, presumably by a chemical interaction during the course of polymerisation". The concept of "internal plasticisation" has now become part of polymerisation lore.

One wonders why Reid found his discovery so much more significant than did the others. Perhaps he was unaware of the earlier work on copolymerisation while the others were not. Perhaps his company saw a more immediate use for the copolymers. Certainly Carbide & Carbon were early in the market with their Vinylite lacquers.

Reid's patent dealt almost exclusively with the copolymers of vinyl chloride and vinyl acetate. Lawson, in so far as he dealt with copolymerisation, also restricted his examples to this co-monomer pair but he was rather more quantitative. In example one his co-monomer mixture contained 75% of vinyl chloride and 25% of vinyl acetate and with a conversion of 56%, the copolymer contained 72% of the chloride. Likewise in Example Two the initial mixture consisted of 80% and 20% of chloride and acetate respectively and with a conversion similar to the first, the product contained 80% of the chloride. The correspondence between the compositions of the co-monomer and copolymers compositions could be accounted for by the constant composition of the initial monomer mixture which obscured the differing reactivity of the monomers.

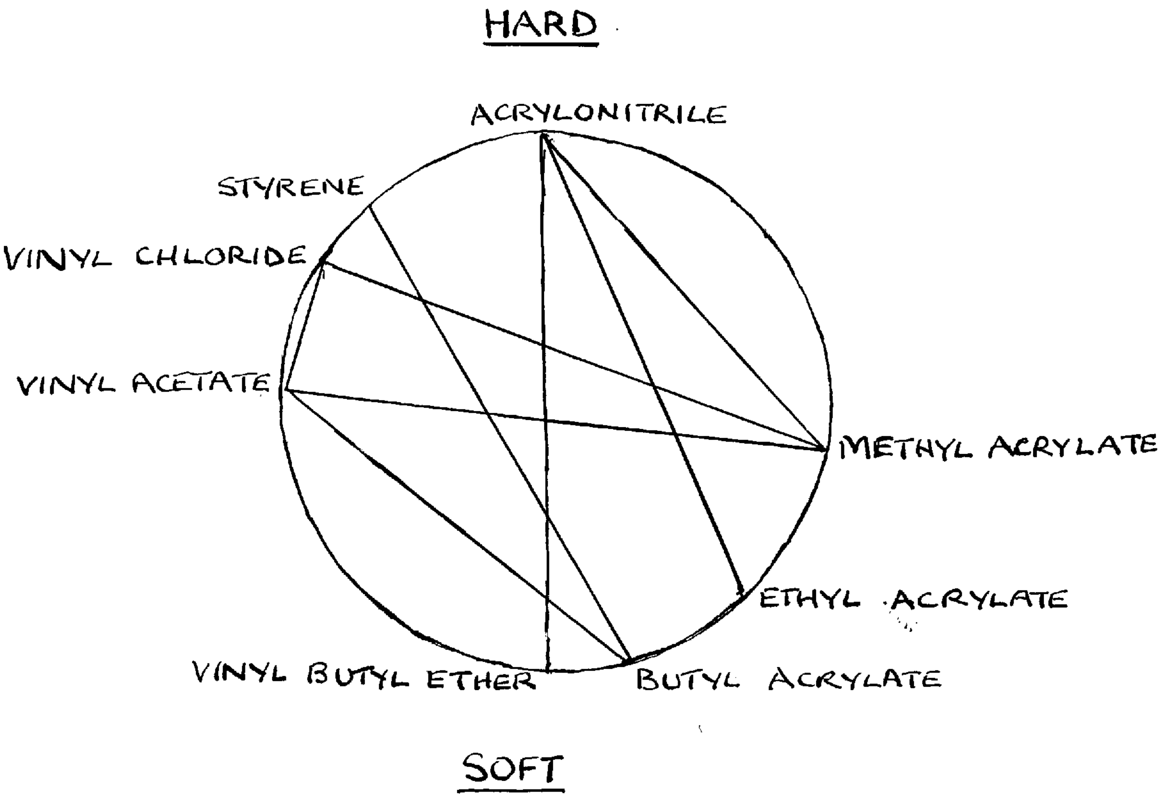
Lawson was aware of the difficulty of controlling composition, as he claimed that "the process set forth also permits a close control over the ratios of the two vinyl derivatives". But his explanation for such control shows that he had no conception of the origin of this problem. He thought it was possible "since there is no free space for the escape of one of the reactants". The true explanation, as we shall see, had to wait about eight years, until the work of Dostal.

Voss and Dickhäuser were more impressed with the copolymers of vinyl chloride and styrene than with the chloride-acetate and also quote in one example the copolymerisation of vinyl chloride and butadiene. They saw the future of their products "in electrotechnics, in the film industry" and, not to miss any possibilities, "in the manufacture of commodities of any kind".

In 1929 the work of Voss and Dickhäuser was followed up by Hans Fikentscher and his colleagues within I.G. Farben and through the copolymerisation of acrylic esters or vinyl ethers with acrylonitrile, styrene and vinyl chloride they too arrived at the principle of "internal plasticisation"[14]. This was a thought already expressed by Reid in his patent but there can be no doubt that the concept was much more meaningful to the Germans who were in close touch with the developing ideas of Staudinger.

From observations of the properties of their copolymers they generalised by placing the various monomers on the circumference of a circle. Those which produced rigid or hard polymers they graded on the upper half and the others they placed on the lower part, as in the figure below. When they drew straight lines between the monomers in the two halves they found that copolymers with about the same softening points fell at the same level.

MONOMER CIRCLE



Fikentscher and his colleagues found that while vinyl ethers would not polymerise with peroxide initiators, they readily copolymerised with vinyl chloride to produce useful products[15]. Copolymers of vinyl chloride and acrylic esters were investigated as non-flammable substitutes for celluloid. With a comonomer mixture of 80 parts of vinyl chloride and 20 parts of methyl acrylate the melt temperature was lowered sufficiently for the mass to be worked on celluloid equipment.

Thus the first commercial vinyl chloride polymers were copolymers based on this work in Germany and on Reid's work in the U.S. In America they came on the market as "Vinylite" in Germany they appeared as "Troluloid" (echoes of celluloid!) in 1931 and later as Igelit MP (misch polymerisate) "Astralon" and "Decalith" (in sheet form).

Apart from the comonomers already mentioned there were others recorded in the patent literature. Workers of the Phillips Petroleum Co. protected the white solid made from the sulphur dioxide and vinyl chloride, which could be moulded by heat and pressure[16], and I.G. Farben claimed the copolymerisation in emulsion of vinyl chloride and maleic acid esters[17] and vinyl chloride and esters of fumaric acid[18].

None of the patents discussed so far, with the exception of an oblique reference by Lawson, mentioned a problem which must have become apparent to workers in this field fairly early on in their investigations, namely the difficulty of controlling the composition of the copolymer. It was easy enough to decide on and fix the comonomer ratio but those people who examined their products carefully soon found that this ratio was not reflected therein. Fikentscher described their experience in this way[19]: "From the chlorine content of samples taken with increasing density, it became apparent that with the simultaneous addition of VC (vinyl chloride) and M (methyl methacrylate), M polymerised more quickly so that finally almost pure pvc was produced. The polymers were turbid". This was generally the situation with comonomer pairs. One was more reactive than the other so that the copolymer produced at the beginning was richer in the reactive component while that produced towards the end of the conversion contained virtually none of it.

While the reason for this behaviour could not be clarified in the light of current theory, Fikentscher and Joseph Hengstenberg devised a practical answer to the problem. In the relvant patent[20] they claimed that "unitary [meaning "uniform" presumably] mixed polymerisation products can be obtained by the polymerisation of at least two polymerisable unsaturated organic compounds of different speeds of polymerisation at about the rate at which it is used up to the compound having the lower speed of polymerisation".

They showed that the method worked by quoting a number of examples. With vinyl chloride and methyl acrylate samples taken during the course of the reaction had a chlorine content of 49.0, 49.0 49.6 and 49.2% as compared with the chlorine content of the final coagulated copolymer of 49.5%. The same uniformity of product was observed by noting the nitrogen content of acrylonitrile-styrene copolymer prepared in the same way.

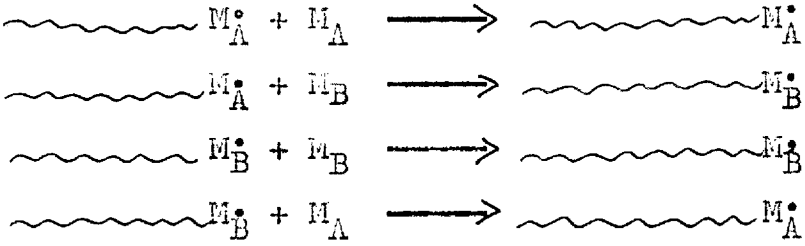
Thus in the absence of any theoretical guidance the industrial technologists were dealing with their problem in their usual *ad hoc* way. However the academic research workers were making some headway by the middle 1930's in the elucidation of nature and kinetics of polymerisation reactions, so much so that in 1936 H. Dostal of the University in Vienna was able to conduct the first probings into the unexplained phenomena of copolymerisation.

By then certain facts about addition polymerisation were more or less accepted. For example, Professor E.K. Rideal in his Introductory Address to the meeting of the Faraday Society on "The Phenomena of Polymerisation and Condensation" in September 1935 was able to say fairly confidently that "... the polymer grows by the addition of monomer to the ever growing chain of polymer. The mechanism presents several analogies with the chain reactions of classical kinetics and we may dissect the process of polymerisation in a manner similar to that adopted for chain reactions. The four factors as we know which have to be considered are the mechanism of chain initiation, chain prolongation, chain branching and chain termination"[21].

Many other contributions proceeded on this assumption. H. Staudinger made the same point thus: "The formation of real high polymers must be explained in another way; a molecule of the monomeric substance becomes activated by heat light or by a catalyst - and can therefore react with a second molecule. The newly formed molecule has an "active point" on each of its ends and the polymerisation can thus proceed further until an unknown side reaction makes the active centres disappear ... The reaction has thus the feature of a chain reaction"[22]. C.E.H. Bawn[23] and H.W. Melville[24] were among others who illustrated the general acceptance of a chain mechanism and of the three consecutive phases, initiation, propogation and termination.

Dostal himself in a paper with H. Mark on the "Mechanism of Polymerisation"[25] said much the same thing. One aspect of the subject however about which there was considerable uncertainty was the nature of the termination reaction and another was as to whether the length of the growing polymer chain had any effect on the speed with which monomer molecules added to the growing chain.

Against this background Dostal turned to problems of copolymerisation and with his short purely theoretical paper entitled "Bases of a Reaction Kinetic Scheme for Copolymerisation"[26] he laid the foundation stone for our understanding of this phenomenon. The essence of his approach was given in his sentence "It is clear that we must all the time pay attention to the terminal unit of the growing chain". With this in mind he set out the four competing reactions which can occur when polymer chains are growing in a mixture of two monomers, M_A and M_B. Two can occur with a chain ending with M_A and another two with the chain terminating at M_B.



He postulated that the rate constant for each of these reactions depended on terminal group and was independent of chain length or the composition of the chain behind the last monomer unit which joined the chain. The composition of the copolymer chains therefore was a function of the reactivities of the monomers towards the two growing radicals. Dostal worked out the equations governing the rate of polymerisation and the composition of the resulting copolymer but devised no experimental work to test his conclusions.

It followed incidentally from his assumption of uniform conditions during the reaction that the concentrations of the comonomers must remain substantially constant and this implied that when experimental determinations were carried out the results would only be valid over a small range of conversion.

In other words copolymer compositions had to be determined only within the first few per cent of polymerisation.

At about the same time as Dostal published his theoretical ideas on the kinetics of copolymerisation, S.D. Douglas and W.N. Stoops, of Carbide & Carbon, examined the molecular weight distribution in samples of vinyl chloride - vinyl acetate copolymers. They were concerned primarily to relate molecular weight and physical properties and so they separated the copolymer into a number of fractions of narrow molecular weight range by extraction or precipitation, that is taking advantage of the fact that polymer of higher molecular weight is less soluble than its lower molecular weight counterpart. Their paper[27] gave some detail of the techniques they used and it presented data on the dependence of some of the properties of the copolymer on molecular weight and the independence of others. These research workers however made no attempt to investigate the effect of copolymer composition on properties. In fact they regarded their vinyl chloride - vinyl acetate copolymers more or less as a homopolymer for the purposes of their work and so while the paper was of interest in other respects it took the understanding of copolymerisation no further.

Staudinger's and Schneider's paper published in 1939, the 231st in Staudinger's series on "Polymer Compounds", were given over to pvc[28]. It was one of the earliest systematic fundamental investigations of this polymer, which by this time was becoming recognised as a material of some significance. The opening paragraph stated that the physical properties of polymers depend on their structure size and form. "That is why it is important to examine pvc in relation to these considerations which are playing an ever more important role as plastics (such as Igelit) in the manufacture of tubes, leather, lacquers, fibres, and moulding ..."

Copolymers of vinyl chloride assumed a relatively small importance in this paper but the authors noted that "the properties of copolymers can be varied considerably according to whether one or other comonomers is present in greater proportion"[29]. They were therefore interested in copolymer composition and its relationship to the parent comonomer mixture. From a number of copolymers made from different comonomer proportions they selected one that was made from equimolar proportions of vinyl chloride and vinyl acetate for further examination by fractionation.

A solution of the copolymer in acetone was precipitated by the stepwise addition of the non-solvent methanol. "The less soluble high polymer product [which was precipitated first] had a higher chlorine content than the more soluble. In none of the fractions is the ratio of vinyl chloride and vinyl acetate 1:1 (as will be seen from the table)".

Analysis of the Copolymer

Fraction	C in %	H in %	Cl in %	Ratio of VCl to V.Ac.
I_1	43.26	5.88	39.85	9:3
I_2	44.49	5.60	38.20	7:3
I_3	46.48	5.58	31.35	5:3
II_2	52.86	6.81	19.58	5:7

Thus these workers confirmed by careful analysis of fractionated samples what Fikentscher and others had already observed more qualitatively some years earlier.

But for the explanation of this constitutional heterogeniety there was still no advance on Dostal's speculations of 1936. As a matter of fact Dostal and his colleagues in the laboratories of the University of Vienna had begun to verify his theoretical results experimentally but their team and work was broken up by the entry of the Germans into Austria in 1938, before they had reached any conclusions[30].

The next important step came with the work of F.T. Wall of the University of Illinois, U.S.A.[31] and it consisted of the recognition that copolymer composition did not depend simply on the rate constants of the four competing reactions of a comonomer pair but rather it depended on the <u>relative</u> reactivities of the monomers. He arrived at his general conclusion by the following steps:

"Let us consider first the formation of a copolymer from the reaction mixture. For convenience in future discussion let X represent one kind of molecule (e.g. vinyl chloride) and Y represent another kind of molecule (e.g. vinyl acetate). Suppose the original reaction mixture consists of n_{xo} molecules of X and n_{yo} molecules of Y. After polymerisation has proceeded to a certain extent let n_x and n_y equal the number of X and Y molecules respectively. Finally define N_x and N_y as the number of X and Y units which have been polymerised. Then evidently

$$N_x + n_x = n_{xo} \qquad (1)$$
$$\text{and} \quad N_y + n_y = n_{yo}$$

"Now there is no general reason to suppose that the X and Y molecules will polymerise at the same rate even though they copolymerise. There is however a basis for assuming that the polymerisation will be first order ... Assuming first order polymerisations we arrive at

$$\frac{dN_x}{dt} = - \frac{dkx}{dt} = k_1 n_x \qquad (2)$$
$$\text{and} \quad \frac{dN_y}{dt} = - \frac{dky}{dt} = k_2 n_y$$

eliminating t from equations (2) we see that

$$\frac{dnx}{dny} = \alpha \frac{nx}{ny} \qquad (3)$$

where $\alpha = \frac{k_1}{k_2}$ (4)

"It is obvious from equation 3 that unless $\alpha = 1$ the polymer found at any instant will not have the same composition as the reaction mixture. If we define x as the mole fraction of X units in the polymer forming at any instant then

$$x = \frac{dN_x}{dN_x + dN_y} = \frac{\alpha n_x}{\alpha nx + ny}$$

If α is more than 1, the first polymer that forms will be richer in X than the original reaction mixture. As the polymerisation proceeds the composition of the polymer forming will change continuously until the last polymer will consist of nearly pure Y. The average composition of the completely polymerised products must of course be the same as that of the original reaction mixture. In the case α is less than 1, the same arguments prevail except that the position of X and Y must be interchanged in the discussion".

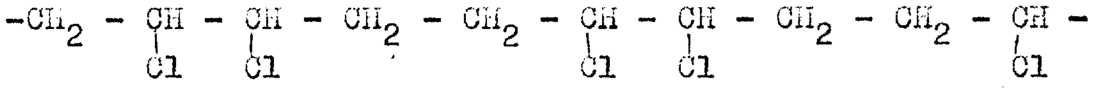
Wall's crucial concept was what he termed "α", the ratio of the rates of reaction of each monomer with the growing chain radical. In recognising this truth however, which as he pointed out, explained the Staudinger-Schneider observations[29] and also accounted for the efficacy of the Fikentscher-Hengstenberg[20] technique for obtaining more uniform copolymer composition, he lost sight of Dostal's suggestion that not only were there two different monomers adding to growing chains, these were also two types of growing chains to which the two monomers might add, There were in fact the four reactions noted earlier in this account with the corresponding rate constants k_{AA}, k_{AB}, k_{BB}, and k_{BA} (or in more modern terminology, k_{11}, k_{12}, k_{22} and k_{21}). These led to two ratios rather than Wall's one, namely $k_{11}/k_{12} = r_1$ and $k_{22}/k_{21} = r_2$ where r_1 and r_2 were the so-called "reactivity ratios".

This emerged subsequently in the simultaneous but independent researches of Mayo and Lewis[32] and Alfrey and Goldfinger[33] which resulted in the "Copolymerisation Equation". From it it has been possible to predict copolymer composition based on data on monomer concentration and reactivity ratios, at least in the initial phase of the polymerisation.

The development of copolymerisation theory was thus very much associated with the study of vinyl chloride copolymers. This contrasted with the elaboration of homopolymer theory. PVC was such a difficult material to deal with that academics preferred to avoid it in favour of more amenable polymers, such as polyvinyl acetate and polystyrene, for the elucidation of polymer generalisations.

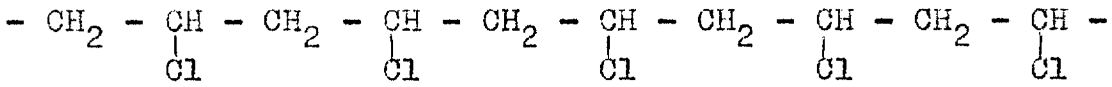
Although it may not be quite logical to include two further papers in this discussion of the progress of copolymerisation theory, it will nevertheless be convenient to comment on two theoretical researches, the results of which were presented before 1940.

One was on the structure of polyvinyl halides by C.S. Marvel and his colleagues[34]. Marvel made a great contribution to our knowledge of polymers in a large number of papers and this one established that of two possible polymer structures, namely head to head (I) or head to tail (II) pvc has its monomer units arranged in the latter fashion. In this he brought the unsuccessful efforts of Staudinger to resolve this matter some nine years earlier[35] (see Chapter 4) to a successful conclusion.



$$-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-$$

(I)

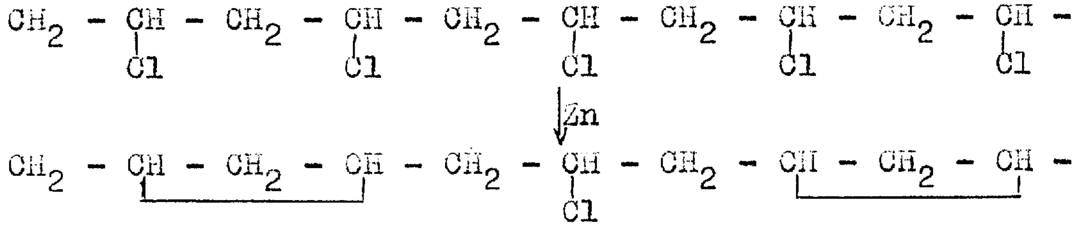


$$-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-$$

(II)

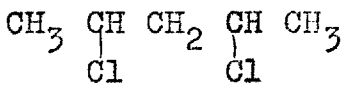
The evidence for this structure came from three types of experiment. First, dehalogenation of a dilute solution of pvc in dioxane by treatment with zinc led by a smooth reaction to a soluble product which always contained some residual chlorine. Under the most favourable conditions the amount removed varied between 84 & 87%. "The facts", the paper said "are particularly significant since Flory has shown that the random removal of pairs of halogens in a polymeric 1,3 dihalide should take out 86.47% of the halogen and leave 13.53% isolated from reactive neighbours and non removable, except by crosslinking of the carbon chains".

Secondly chemical examination of the dehalogenated polymer indicated that it "consists of cyclopropane units with isolated $-\mathrm{CH_2}$ CHCl - units". These would clearly have been obtained from pvc by the following reaction:



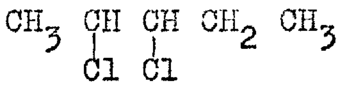
This supported the idea of the head to tail structure.

Finally comparison of the ultra-violet spectra of known compounds with pvc demonstrated its similarity with 2,4 dichloropentane (III) rather than 2,3 dichlorpentane (IV)



$\mathrm{CH_3\;\underset{Cl}{CH}\;CH_2\;\underset{Cl}{CH}\;CH_3}$

(III)



$\mathrm{CH_3\;\underset{Cl}{CH}\;\underset{Cl}{CH}\;CH_2\;CH_3}$

(IV)

This conclusion brought the structure of pvc into line with that of a number of other vinyl polymers whose molecular arrangement had already been ascertained.

The second of the two papers has already been referred to[28]. It reported on Staudinger's efforts to throw some light on the structure of pvc molecules by a study of their molecular weights as found by osmosis and viscometry. This investigation was stimulated in the first place by the anomolously low molecular weight of manufactured pvc as determined by viscosity measurements.

Using the Staudinger equation :

$$\frac{\eta_{sp}}{Cgm} = Km.\ M$$

where η_{sp} = specific viscosity
Cgm = concentration of the solution in bas mols. per litre
Km = a constant
M = molecular weight

The Km value used was that found for low molecular weight paraffins and paraffin derivatives in dioxane and tetrahydrofurane solutions. In these circumstances the pvc had molecular weights in the range 6,000 to 18,000. But polystyrene and cellulosic polymers, among others, of approximately equal chain length did not exhibit the strength or technically useful properties which were characteristic of pvc. Staudinger therefore regarded the pvc values as suspect.

He therefore determined the chain lengths by osmosis and found that in dioxane solution they emerged 5 to 8 times as big and in tetrahydrofurance they were bigger by a factor of 3 to 5. This brought the molecular weight range of pvc to 60,000 to 150,000, which adequately accounted for the physical properties of the polymers.

But why was there this difference between the values produced by the two methods? Perhaps it was due to the fact that industrially manufactured pvc was made from impure vinyl chloride which on polymerisation led to branched molecules for which the above equation was not valid. That relationship was developed from an Einstein equation for viscosity by assuming that the molecules in solution where in the form of straight chains rather than spheres. Examination of polymers made from specially purified monomer showed that the discrepancy between osmosis and viscosity was as great as ever.

It was not impossible however that branching might occur with pure vinyl chloride. Staudinger referred to the analogy of polystyrene in which it was known that branching was present, and when various polystyrenes prepared at different temperatures were examined they exhibited different Km values, "From these experiments" the paper went on, "we assume that unrecognised branching can occur during the chain reaction leading to pvc, which can result in deviations from the viscosity relationship presented in the equation". To support this contention Staudinger pointed out that for such side reactions the fact that almost all technical pvc contained a deficit of 0.5 to 1% of chlorine as compared with theory, was of significance.

Fractionation of both technical and laboratory prepared pvc and the subsequent determination of Km for different fractions showed a considerable variation between them.

In discussion of these results, and of similar phenomena noted in post-chlorinated pvc and vinyl chloride copolymers, the authors were principally concerned to explain the far greater molecular weight values obtained by osmosis as compared with viscosity. Incidentally this was equally true for polyvinyl acetate, polyvinyl alcohol and polyacrylic esters.

Staudinger had earlier suggested that by a consideration of osmotic and viscosimetric molecular weights jointly one could classify colloidal i.e. polymer molecules into three groups:

1) Colloids consisting of spherical molecules, as for example glycogen and some proteins.
2) Substances consisting of long chain molecules, such as cellulose and the polyesters.
3) Products with branched chain molecules.

PVC came in a fourth group of chain molecules whose precise structure was as yet unknown and whose behaviours in solution was therefore difficult to explain. He put forward two theories to account for the relationship between the osmotic and viscometric molecular weights found for pvc. He took it that the former value gave the true molecular weight and in the simpler proposal he assumed that the viscometric value represented the length of the chain. If the chain was extended the Staudinger equation would be valid and the value would coincide with osmotic measurements. Since it did not the chain was convoluted and the distance between the ends of the chain was not the same as the chain length. In these circumstances the Km constant of the equation varied with the degree of convolution. The order of the difference between osmotic and viscometric molecular weights was an indication of the degree of convolution.

"On this assumption two types of chain molecule can be distinguished:

a) extended chain molecules, e.g. cellulose, mannane and polyester; the viscosity equation is valid for these.

b) convoluted chain molecules, pvc and polyvinyl acetate are outstanding examples"[36].

The second explanation for the discrepancy between the two methods for estimating molecular weights has already been referred to, this was the suggestion that pvc polymers were not simple chains but more or less branched structures. To account for the changing Km values obtained for different fractions of the given sample of pvc he assumed that branching increased as did the chain length.

Why and where should branching occur? Staudinger thought it took place at imperfections along the length of the chain. For example if at some point head to head linking occurred instead of the normal head to tail then dehydrochlorination of the pvc was much more likely at that point with the appearance of a reactive position at which branching could grow.

Staudinger drew attention to some very significant differences between high and low molecular weight substances in this respect. Impurities in "ordinary" materials can be readily detected and removed by distillation or crystallisation. But matters are quite different with polymers. The products of variations from the main reaction are proportionately insignificant and therefore remain obscure in the polymer. Further these "by-products" are built into the polymer and cannot be removed.

Such polymer defects, small and difficult to detect as they are, are nevertheless of the utmost importance because they have a powerful influence on the physical behaviour of the polymer. Furthermore, upon such polymer defects the differences between osmotic and viscometric molecular weights can rest"[37].

But in 1939 Staudinger could not decide as between the two theories, convolutions or branching. He promised to resolve the problem by further study of other polymers, for this was of importance not only for pvc. "A valid determination of the structure of polymers is significant for an understanding of all plastics, because the physical properties of all these solid materials are most strongly affected by the form of their polymers".[37]

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Chapter 6

Plasticisation and Stabilisation

Early workers needed only a casual acquaintance of pvc for them to appreciate that on its own it was a useless material. Without additives to arrest~~s~~ its breakdown on heating, choking and corrosive clouds of hydrochloric acid were evolved in processing. Without substances added to increase the workability of pvc processing simply was not possible, because only in their presence was it feasible to operate at temperatures which would otherwise lead to chemical degradation. Thus early in the history of this polymer the art of compounding was acknowledged as a vital phase in the working of pvc.

One might generalise with the statement that plastics technology takes over from chemistry when the polymer, the end-product of the chemist, becomes the raw material of the compounder, were it not for the fact that the form of the polymer, for example its particle size and molecular weight, is very germane to subsequent stages of polymer processing. However there is some substance in the differentiation and in this chapter I propose to consider the development of pvc compounding and in particular to trace the origins of our current selection of compounding ingredients.

To begin, let us examine plasticisation. The International Union of Pure and Applied Chemistry (I.U.P.A.C.) defines a plasticiser as "a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability or distensibility"[1]. There are a number of interesting features about this definition but by confining ourselves for the moment to the parenthetic comment, it is clear that this phenomenon is by no means restricted to pvc. By the time Klatte, Ostromislenski and others had begun to grapple with this polymer a fund of experience had been amassed particularly in relation to celluloid and cellulose acetate and early pvc technology bears all the traces of the earlier work.

Plasticisers were first incorporated with a polymer by Alexander Parkes when he made "Parkesine", the forerunner of "Celluloid". When in 1865 he read a paper to the then Society of Arts on "The Properties of Parkesine and its Applications to the Arts and Manufactures", he disclosed that his material was "made from pyroxyline [cellulose nitrate] and oil, alone or in combination with other substances; the various degrees of hardness or flexibility are obtained in the easiest and most expeditious manner by varying the proportions of pyroxyline oil and other ingredients".

He went on to explain "... the oils employed are some of the vegetable and some of the animal kingdom [cotton seed, castor oil or other oils] ; they may be used alone or combined either in their normal condition or changed by a solidifying agent, chloride of sulphur being preferred, which has the remarkable property of solidifying the oils almost instantaneously... These solidified oils although unchanged by ordinary reagents are readily soluble in the author's solvents of pyroxyline, by which means the two ingredients are combined to form one of the descriptions of Parkesine".

Parkes used not only oils as plasticisers, "... so that the physical conditions of preparations of pyroxylene may be considerably modified to suit special applications [he used] gums, resins, paraffins, stearine, tar, glycerine and other substances combined therewith". In other words almost any substance with a relatively high boiling point which was compatible with cellulose nitrate was grist to his mill. He even used camphor in small proportions without appreciating its unique role as a plasticiser for celluloid. Of this range of substances however cotton seed or castor oil was the preferred plasticiser as his master patent of 1865 indicates[2].

Neither of these materials was really satisfactory either in processing or in the properties of the end-product. The ideal plasticiser emerged five years later with the work of John Wesley Hyatt in Albany, N.Y., U.S.A. This le~~a~~d to the successful launching of "Celluloid"[3,4]. Camphor and cellulose nitrate made such an outstandingly good plasticiser polymer combination, at least in the massive form, that it provided the criterion for future systems. It spurred technologists trying to evolve cellulose acetate as a non-flammable celluloid to examine hundreds of substances in the hope that they would find the camphor analogue for the acetate ester of cellulose[5].

One very early example, and probably the first reference to a phosphate plasticiser, was the use of triphenyl phosphate described by the Celluloid Company of New York in a patent dated 1910[6]. In it the Company claimed a process for the manufacture of "celluloid-like" material from cellulose acetate in which the polymer was mixed with triphenyl phosphate. Thus it hoped to overcome the dangers of flammability not merely by using "non-flam" cellulose acetate but to reinforce this by mixing it with a plasticiser which does not burn. The use of phosphate plasticisers to reduce the flammability of polymer compounds has since become widespread.

Shortly after that publication, Klatte in his pioneering pvc patent of 1913[7] (which I have already discussed at length in Chapter 2) demonstrated how various useful and processible forms of pvc could be obtained. Among other examples he described the preparation of non-flammable film by casting the polymer solution and "to increase the flexibility of the products, certain materials can be added to the solution [of polymer] in chlorbenzene. The same substances as have shown themselves particularly effective in the celluloid industry can be employed here, namely camphor, cresol, naphthol, phenol phosphate and carbonate, as well as many other compounds".

Klatte's comprehensive embrace of all the cellulose nitrate plasticisers for use with pvc turned out to be somewhat naive but this patent shows quite clearly the direct link that binds plasticiser technology in pvc and the cellulosics.

More than a decade later Ostromislenski was concerned with the same problem of making flexible films from pvc and his solution was substantially the same as Klatte's. In his patent of 1926[8] Ostromislenski claimed that his caoupren chloride (cf Chapter 4) was particularly suited to the preparation of films and that the polymer "is compatible with plasticisers of low volatility which impart useful properties to films". He went on to describe film manufacture from 15% monochlorbenzene solution by spreading the solution on to a suitable surface, such as glass or polished metal and drying it sufficiently to obtain flexible transparent sheets. Plasticisers such as ortho, meta or para dichlorbenzol, chlornaphthalene etc. might be added before the solution spreading operation. He went on, "these films being substantially non-inflammable are adapted for use in the motion picture industry for example. Their flexibility measured by the number of folds before cracking is far greater than that of ordinary nitrocellulose films even when kept under severe conditions such as in a warm dry atmosphere".

History suggests that the motion picture industry was not convinced of the advantages of pvc. Despite these blandishments it continued to use cellulosic films.

However, to return to our discussion, Ostromislenski in this patent further extended the range of possible plasticisers by listing "examples of plasticisers and solvents - naphthalene, or bromnaphthalene, tetramethyl chlorbenzol, diphenylmethane, acetophenone, orthochlorphenol, dichloracetone, benzyl chloride, ethyl methyl ketone, xylol, ethyl acetate, ethyl benzoate, chloral, benzyl aniline, trichlorethylene, glycol diacetate and anisole". By implication he classified those compounds boiling above 150°C as plasticisers when he said "Those which have a boiling point above 150°C are retained in the films very readily".

But it soon became evident that while an indiscriminate blanket acceptance of all high boiling point compounds as plasticisers for pvc was good enough for writing up patent specifications, it did not advance the technology of this polymer. Indeed many of the plasticisers developed for cellulosics proved quite unsuitable for pvc. This was because the attributes of an ideal plasticiser for pvc are different from those required for cellulosics and they are more demanding. They are sometimes mutually contradictory. In practice therefore pvc compound designers now make no effort to find an illusory "ideal" plasticiser, they settle for the one, or for the system, that best meets their needs.

Nevertheless there are minimum requirements. It must be able to withstand processing temperatures, which are considerably higher than those of cellulosics; that is it must not break down, nor must it volatilise away. It must not be lost in use by virtue of its high volatility or its solubility. It must be compatible with pvc so that when once mixed there is no tendency to separate out and appear as an oily layer on the surface.

These basic qualifications of any plasticiser for pvc soon eliminated most of the known candidates from serious consideration and left only dibutyl phthalate and tricresyl phosphate. The phthalates first appear to have been proposed as plasticisers for cellulosics by H.T. Clarke in 1920 with his claim for "phenolic esters of phthalic acid"[9], and this was soon followed by H.F. Wilkies' patent in 1922 describing diethyl phthalates as a high boiling solvent which could be used to produce clear coatings for films of cellulose nitrate or acetate under varying atmospheric and weather conditions[10].

With a boiling point as low as 290°C this ester was obviously too volatile for normal use and so attention shifted to the higher esters of phthalic acid. By 1930 and 1931 patent specifications were including dibutyl phthalate in their lists of proposed plasticisers without particular comment,[11,12,13] which suggests that it was an orthodox plasticiser at that time.

We have already referred to the early use of triphenyl phosphate in cellulosics for its non-flam characteristic[6] and to its inclusion in Klatte's list for pvc[7]. In 1929 the Celluloid Corporation of the U.S.A. patented a "composition of matter comprising vinyl compounds and aryl phosphates". The latter, proposed as an alternative to camphor which "leads to a serious reduction in the insulating properties", included tricresyl phosphate (TCP) but made no mention of vinyl chloride polymers among its vinyl compounds[14]. However in the following year a Du Pont patent protecting "a coating composition comprising ... a polymer of vinyl chloride and a softener", proposed tricresyl phosphate as a possible softener. Thus when plasticised pvc began to assume some importance, after about 1933 both dibutyl phthalate and tricresyl phosphate were the recognised plasticisers.

But both had their limitations, even the butyl ester was too readily volatile while TCP had disadvantages which became obvious as pvc compounds containing it were put to the tests of practical applications. One such was the poor performance at low temperature of phosphate plasticised pvc. The decade 1930-1940 therefore witnessed a growing interest and activity in the field of plasticisers and plasticised compounds. This, of course, in no way compared with the magnitude of research in subsequent years when thousands of compounds, also chosen quite empirically, were tested and evaluated for the many new applications that appeared after the war, but it nevertheless represented a considerable effort.

Some forty or so patents applied for during those ten years were concerned with aspects of pvc plasticisers or plasticised pvc. Detailed discussion of each of them seems hardly justified here but some relevant information is recorded in Table I.

But this discussion is leaping ahead of some developments that were vital for the emergence of plasticised pvc as a commercial material. It is one thing to be aware of a product, indeed to have made it on a laboratory scale; it is quite another to have the means to produce it at an industrial level. Klatte, Ostromislenski and others made their plasticised polymer by dissolving both components in a common solvent and then evaporating the latter. This is a very unsatisfactory process because in the first place these solutions contain only small concentrations of polymer. Above five per cent or so they become very viscous and this leads to the need to handle excessively large volumes of liquid. Secondly while it is relatively easy to remove the bulk of the solvent from the polymer, the last traces adhere tenaciously and disappear over a fairly lengthy period. Efforts to reduce this time generally lead to subsequent difficulties.

Alexander Parkes found this out to his cost some sixty years earlier when the Parkesine Company, set up to manufacture Parkesine, was forced into liquidation. He plasticised cellulose nitrate by bringing it into solution with castor oil in a common solvent. His ineffective steps to expedite solvent removal led to the production of combs and other articles still containing traces of solvent which volatilised subsequently leaving twisted and distorted purchases in the hands of customers. Their dissatisfaction led to the wind-up of the company.

The technical problem was solved by John Wesley Hyatt in the U.S.A. when by his discovery of camphor as a plasticiser he was able to dispense, more or less, with solvent. From that time Celluloid went from success to success.

So it was with pvc. When plasticisation could be carried out without a solvent the way to further progress was opened. The first step was taken in the laboratories of B.F. Goodrich in the United States and is recorded in a patent attributed to J.E. Wolfe at the beginning of 1932[15]. Viewed with historical hindsight the essential advance can be seen to be confused by other considerations but it was

Table I

Patents Dealing with Plasticisation of Plasticised PVC

Patent No.		Patent	Application Date	Plasticiser
B.P.	349,100	Du Pont	21.11.29	Diethyl phthalate
"	349,562	Du Pont	21.11.29	Aryl ester of a polyalcohol
"	366,461	Celluloid Corp.	29.7.29	TCP and TPP
"	379,292	Du Pont	3.6.30	TCP & DBP among others
"	389,914	F.H. Rerchal	15.12.30	DBP and other phthalates
"	398,091	Semon-Goodrich	17.9.32	Key patent on plasticisation of pvc
"	408,969	Hoffman - C & C	6.11.31	DBP, TCP, glycol or glycerol esters
"	412,442	F. Schmidt of Troisdorf	12.6.33	Phthalates esters, tributyl phosphate, etc.
"	419,586	Dynamit	27.6.33	Softeners
"	428,187	Dynamit	19.10.33	TCP, Tributyl phosphate, DBP
"	435,864	I.G.	26.3.34	Long chain esters of polyhydric alcohols
"	443,855	F. Schmidt of Troisdorf	20.11.33	TCP, DMP, Triacetin etc.
"	461,101	BTH	15.3.35	TCP
"	473,616	I.G.	25.5.35	Benzoic acid derivs. of long chain aliphatic alcohols
"	478,822	I.G.	10.8.36	Esters of monoaryl-ethers of polyhydric alchols
"	478,965	I.G.	27.6.35	Wick's discovery of pvc plasticisation

Table I (continued)

Patent No.	Patent	Application Date	Plasticiser
B.P. 480,592	I.G.	24.7.36	Subst. products of tetrahydronaphthalene
" 483,657	I.G.	26.10.35	Alkyl or aryl polynuclear aromatic derivatives
" 496,574	I.G.	16.6.36	Diethylene glycol benzoate etc.
" 497,001	Siemens	18.5.36	Benzyl stearate, palimitate oleates etc.
" 499,931	BTH	30.4.37	Ester of polymerised acid
" 500,298	I.G.	9.8.37	TCP - main example for paste polymers
" 503,787	I.G.	31.20.36	Araliphatic sulphides or polysulphides
" 527,407	BTH	12.4.38	Phenoxy propene oxide etc.
" 527,408	BTH	12.4.38	Dibenzyl sebacate etc.
U.S.P.1449156	H.F. Willbie- U.S. Industrial Alcohol	14.4.22	Diethyl phthalate
" 1972579	J.N. Wickert - Carbide & Carbon	12.5.33	Acetates, succinate phthalates, Di-2 ethyl butyl phthalate
" 2015677	W.E. Lawson - Du Pont	1.10.32	Phthalates
" 2050595	J.E. Wolfe - B.F. Goodrich	20.1.32	O-nitro diphenyl ether, DBP, TCP
" 211524	C.J. Rolle - Ault & Wiborg	30.7.36	Chlorinated diphenyl

Table I (continued)

Patent No.	Patent	Application Date	Plasticiser
USP 2115896	P.J. Wiezovich - Standard Oil	30.12.33	TCP, DBP, etc. etc.
" 2117283	S.L. Bass - Dow Co.	5.8.35	Triaryl phosphate
" 2118506	G.D. Graves - Du Pont	7.7.34	Long chain alkoxy-alkanol esters
" 2127400	C.F. Gibbs - B.F. Goodrich	25.6.37	Organic sulphones
" 2147242	C. Conover - Monsanto	27.4.35	Esters of benzophenone carboxylic acids
" 2151507	H. Fikentscher - I.G.	5.8.36	Aromatic carboxylic acid esters
" 2157697	M. Hagedan - I.G.	25.3.35	Benzoic acid esters
" 2193613	C.H. Alexander - B.F. Goodrich	18.3.37	Naphthalene or diphenyl derivatives
" 2191056	G. Wick - I.G.	26.7.35	TCP
" 2175048	C.H. Alexander - B.F. Goodrich	18.3.37	Complex aromatic alicyclic plast.
" 2193614	C.H. Alexander - B.F. Goodrich	1.9.37	Nitrated aromatic ethers
" 2193662	C.H. Alexander - B.F. Goodrich	2.8.38	Sebacates etc.
" 2227154	J.J. Russell - G.E.C.	12.4.38	Dibenzyl sebacate
DRP 674985	F.O. Merkle - I.G.	9.7.36	Naphthalene or aryl derivatives

there nevertheless in the sentence "The product, pvc, is then dissolved in a heated non-volatile solvent(plasticiser) with or without the aid of a more volatile solvent ..." In an example the inventor described how "10 parts by weight of powdered polymer is mixed with 75 parts of o-nitro diphenyl ether on a hot roll mill and is then moulded in a metallic mould to about 165°. At this temperature the solution is completed and the mass becomes thoroughly homogeneous in a short time".

It seems obvious that the hot milling must have taken place at a relatively low temperature, probably on a rubber mill at less than 100°C, since the author recognised that "about 165°" was necessary for gelation. The very high ratio of plasticiser to polymer is also noteworthy, as were the other plasticisers quoted, for example benzoyl benzoate, dibutyl phthalate and tricresyl phosphate.

Much of the patent was taken up with a process for shaping the plasticised pvc and exposing the moulded product to actinic radiation to increase its solvent resistance and tensile strength but this is hardly relevant to our present theme.

The next stage generally recognised as a great landmark in pvc technology, came with the work of Waldo Semon, also of B.F. Goodrich, and published in his patent entitled "Synthetic Rubber-like Composition and Method of Making Same"[16]. In it he claimed "the method of manufacturing a resilient rubber-like composition which comprises dissolving insoluble polymerised vinyl chloride at an elevated temperature considerably above room temperature in such proportions as to form a stiff resilient gel at ordinary temperatures and causing the composition to gel by cooling it". He explained that by the term "insoluble vinyl chloride" he meant pvc which is "insoluble in all ordinary solvents at room temperature though they may be soluble in many such solvents at elevated temperatures".

Semon was concerned to produce compositions duplicating the more important physical properties of natural rubber but without its chemical instability. He was also interested in finding a cheaper substitute for rubber and according to the patent he was convinced that "from the point of view of chemical inertness, cheapness and ease of manufacture, polymerised vinyl halides are almost ideal raw materials". In this patent, which was applied for some eight months after that of his colleague J.E. Wolfe, Semon set out clearly and simply the proposition that if pvc is dissolved in one of a large number of non-volatile solvents at high temperature, then on cooling one obtains a rubbery material. He suggested, as did Wolfe, that o-nitro diphenyl ether, dibutyl phthalate, tricresyl phosphate "are excellent solvents for the purpose" and he rejected a number of others for a variety of reasons. He noted that by variation of the proportions of polymer and solvent or by selecting a solvent or mixture of solvents a range of properties could be produced.

"An increased proportion of solvent in general gives a softer more resilient and more extensible product, whereas a decrease in the proportion of solvent gives a harder product of greater strength".

Having established that rubbery materials could be made this way Semon then went on to describe how they might be processed "The product may be readily moulded, extruded or otherwise formed to any desired shape by heating to a sufficiently high temperature. Two surfaces of the product may be caused to adhere to one another by heating the surfaces to a temperature approaching that to liquify the composition and then bringing them into contact. Fabrics may be impregnated or coated by spreading the composition over their surface while in a heated or liquid condition especially if the composition is softened by the addition of a volatile solvent such as xylene etc.".

In short Semon was suggesting that many of the processing techniques used for rubber were equally applicable to plasticised pvc. However, this did not as yet apply to the mixing of the pvc and plasticiser. The extension of the use of the mill to mix rubber and its various additives to pvc and its additives, instead of dissolving it at high temperatures, had to wait a while but it was this extension that made the plasticisation of pvc a viable industrial proposition.

This step was taken in the U.S.A. by Semon and his colleague S.L. Bro~~n~~us and in Germany by G. Wick in 1935. The former described their discovery in a paper in Industrial & Engineering Chemistry[17] and Wick made his disclosure in a patent[18].

The difference in approach between the two is interesting. Semon, as might perhaps be expected from his Akron domicile, looked at the situation from the point of view of a rubber technologist. His paper began "Rubber has found its widest use in industry because its properties can be altered and improved by compounding and cure ... but even better properties are needed to meet the demands of modern industry". Wick, on the other hand, seemed to proceed less explicitly from a rubber base and was obviously much more influenced by the cellulosics.

In spite of this difference the similarities between the documents on major items are even more interesting. Both made the point that the phenomenon of plasticisation occurs when the polymer and plasticiser are worked at elevated temperature. Semon put it this way: "Since Koroseal [the Goodrich trade name for pvc] is thermoplastic it can be worked under similar conditions and with the same equipment used for processing rubber. Koroseal in most of its forms may be plasticised on hot mill rolls. calendered to various gauges and extruded through dies". Wick said "The softening agent and the pvc may be mixed in a heated kneader, on rolls, under a press or any other suitable apparatus while heating to the temperature at which gelatinsation begins".

Wick however was impressed with the criticality of temperature. Mere kneading, as for cellulosics, was not enough to give the desired results with pvc. "The union of pvc and softening agent ... occurs at temperatures ... very nearly at that which pvc decomposes ..." This invention is based on the discovery that if certain softening agents are added to the pvc at certain well-defined high temperatures a transformation suddenly occurs, the mixture becoming homogeneous. While for example a mixture of 100 parts of pvc with 50 parts of tricresyl phosphate cannot be made homogeneous at 105° and 110°C even with prolonged kneading yet at 115° a sudden change in the behaviour of the mixture is observed which can be attributed to the setting in of homogeneity". Semon, for his part, merely noted that "mill roll temperatures approximate to 105°C".

The discrepancy between the milling temperature raises a question as to how it was that Wick found anything less than 115° inadequate while Semon had no difficulties at 105°. The answer might be that Semon was working with a significantly higher proportion of plasticiser, or that his polymer was of rather lower molecular weight or that his temperature readings were indeed approximate and were not accurate to within 10° or so.

It might be said in passing that 115° seems rather low for gelling and Semon seemed to imply as much in a subsequent remark that when the plasticised pvc was moulded into articles "the average moulding temperatures vary from 147° to 160°C depending on the stock and size of article to be moulded".

Wick and Semon both centred their discussion on the use of tricresyl phosphate as plasticiser while indicating that others could be employed. The former sweepingly claimed that "as softening agents all the known substances used for cellulose derivatives and other artificial materials may be used. The esters of phosphoric acid, phthalic, benzoic and adipic acids and the like are preferable". But this was largely "patent talk". The key plasticiser in his view, that is tricresyl phosphate, was the only one named in his "claims". Semon for his part also recognised the possible range but "to avoid confusion, all data given in the subsequent portion of this paper will be based on vinyl chloride compounds containing a single representative plasticiser - namely, tricresyl phosphate". There can thus be little doubt as to the preferred plasticiser around 1935.

Semon was evidently impressed with the advantages of plasticised pvc over rubber and among other things was convinced that "scrap Koroseal ... is easily reworked. Repeated milling and moulding does not present practical difficulties and apparently produces no deterioration in the material". General experience hardly bears this out but he produced experimental evidence to show that tensile strength was hardly affected by variation, within certain limits, of time and temperature of moulding. He did concede however that "Koroseal" in its uncompounded form is a translucent material whose natural colour varies ... with the extent of milling or moulding, from a very pale amber to a dark brown".

After discussing these processing matters both papers went on to describe the properties of plasticised pvc and its potential uses but we shall defer an examination of the early applications of pvc to a later chapter.

These two contributions made a powerful impact on pvc technology and established a firm foundation for subsequent work. They were put to immediate use in Germany and the U.S.A. and assumed a proportionately greater importance in the latter, since the Germans even at that time were developing the necessary techniques for the fabrication of rigid, unplasticised as well as plasticised pvc while the Americans were not. The Germans in their preparation for war were concerned to find domestic substitutes for imported metals, a factor which was of no interest to the Americans.

When once the basic conditions for plasticisation were known and the elementary criteria for suitable plasticisers had been met finer, though important points, could be considered. Other factors had then to be taken into account and these stimulated an active study of possible plasticisers. The availability of raw materials is one such consideration. This is of course related to another point of interest; price. Other things being equal, or nearly so, cost is a decisive item. But in the pre-war situation it was sometimes not so much a choice as between a cheaper or more expensive product. On occasions in Germany, certain raw materials were simply not available and hence given plasticisers were not possible even if they were technically and ecomomically desirable. This was a fact which resulted in divergencies in practice as between the Germans on the one hand and Americans and British on the other; one which was noted and commented on when Allied investigators reported on German industry towards the end of the war[19].

Another factor of importance in the choice of plasticiser is the nature of the properties demanded of the final product. Wick and Semon were well aware of this but clearly a certain degree of sophistication in the technology had to be reached before this became a matter of any real concern. The fact that tricresyl phosphate and dibutyl phthalate were so widely used in 1935, and several years later, suggests that that level had not yet been achieved. It was only after the war that the range of plasticisers in use was greatly extended.

Nevertheless it would be incorrect to leave the impression that there was no concern to find improved materials even before the war. The patent literature for that period provides clear evidence and even more direct proof comes from the archives of the erstwhile I.G. Farbenindustrie.

Until 1935 individual sections of this vast chemical combine were working independently on matters relating to plastics applications. In that year the Kunststofftechischen Kommission ("Kuteko") was set up in Ludwigshafen to co-ordinate their efforts. The minutes of its meetings were discovered in the post-war search through German documents and they provide a good deal of interesting information on the problems that occupied the attention of the people and organisations developing the use of plastics. Among other things, of course, they deal with the then newly emerging pvc. Dr. Kling has extracted these particular minutes in Kunststoff Handbuch Vol. 2, Part I[20].

At its first meeting on September 28th 1935 the pvc situation was reviewed and it was decided that there should be an extensive exchange of information on chemical and physical constants as well as on the properties that bore on the applications of chlorinated pvc (pc), pvc and vinyl chloride copolymers. The next meeting, a month later, summarised the results of this exchange and received a detailed study from Dr. H. Fikentscher on the processing and applications of vinyl chloride copolymers. One section dealt with plasticised polymer and noted under this heading that artificial leather was still at the investigational stage. "Rubber" tubes and various rubbery articles had been made but it seemed vinyl chloride copolymers were too expensive as a rubber as well as a leather substitute.

The cable situation was rather less tentative. For detonator fuse[21] and low-current cable tricresyl phosphate or one of the phthalates were used but for cables carrying stronger current special "electrical" plasticisers were required. These were Vulkanol B (benzyl naphthalene) and Clophen A60 (chlordiphenyl with about 60% of chlorine). One might note in passing that I.G. Farben patented the former group[22] and that chlorinated diphenyls were also described as plasticisers for pvc in 1936 by Ault & Wiborg in the U.S.[23] (They were concerned with coating compositions and claimed that "chlorinated derivatives of diphenyl possess a unique capacity as plasticisers to impart to coating compositions in which the resins are present, the unusual quality of adhesion, miscibility with conventional solvents and tendency to flow spread and dry to a smooth film under the influence of heat"). Cable sheathing, which had hitherto been made from lead, was produced in pvc plasticised with tricresyl phosphate or dibutyl phthalate and a heavy loading of filler[24].

At a further meeting in January 1936 the Deutsche Celluloid Fabrik branch of I.G. Farben reported that they were investigating the use of alkylated naphthalene added prior to polymerisation but they did not comment on the products.

A few months later it was reported at Kuteko that there was a very active interest in pvc and its copolymers in the cable industry. Their application in place of lead was now possible with the discovery of a good cold-resisting and less volatile plasticiser. Unfortunately the record does not indicate what it was, It went on to say however that a plasticiser with acceptable properties and adequate heat stability for use as an insulator was still not available.

In March 1937 pvc homopolymer and copolymer were said to be generating an ever growing response in the cable industry but still the search for suitable plasticisers had to continue. As substitute for leather however pvc copolymer together with plasticiser and filler gave shoe-soles which were to all events and purposes as good as rubber soles. Floor covering in pvc was equally satisfactory with a formulation such as 15 parts of copolymer, 15 parts of tricresyl phosphate and 70 parts of filler.

The record of these Kuteko meetings attest to the lively German interest in plasticisers at this time and particularly for the electrically demanding cable requirements. The parallel patent applications underline the contemporary concern. I.G. Farben proposed a wide variety of substances, for example esters based on long chain aliphatic alcohols and aromatic carboxylic acids[25], esters of monoaryl ethers of polyhydric aliphatic alcohols[26], derivatives of tetrahydronaphthalene said to be eminently suitable for safety glass, cable-sheathing, oil cloth, linoleum amongst other things[27], derivatives of polynuclear aromatic hydrocarbons[28] and a number of others.(See Table I).

Siemens in a patent of 1936[29] reviewed the plasticiser situation as they saw it. "To provide products from pvc chlorinated pvc or vinyl chloride copolymers softening agents are added. However these give either products of good mechanical properties effective within a wide range of temperatures but which detrimentally influence electrical properties or they impart good electrical properties, in which case the good mechanical properties are effective within a small range of temperatures. Tricresyl and triphenyl phosphates, diethyl and dibutyl phthalate and polyglycerine acetate belong to the first group and fluid mixtures of aromatic hydrocarbons and chlorinated aromatics belong to the second".

Siemens therefore proposed a group of compounds to "avoid the disadvantages of the known plasticisers", examples of which included benzyl stearate and dibenzyl-amide of oleic acid, none of which are of any significance today.

In the United States a very similar search for suitable pvc plasticisers was going on in the middle thirties, conducted by the five or six companies interested either in the manufacture of pvc or the selling of chemicals. But this can be traced only through the patent literature. Thus W.E. Lawson of Du Pont patented an extended range of phthalates[30] and L.P. Kyrides described the virtues of succinate plasticisers[31] while S.L. Bass of Dow went beyond tricresyl phosphate to analogous chlorophenyl phosphates[32].

In a 1937 patent C.F. Gibbs, a colleague of Waldo Semon, set out "a new class of plasticisers particularly useful in polyvinyl halide compositions described in USP 1,929,453 to W.L. Semon"[33]. These were organic sulphones which were said to be immune from leaching by petroleum solvents. C.H. Alexander of the same company was very active in this field at that time and claimed that complex disulphides, for example bis ethyl-o-phenylene disulphide conferred improved acid resistance and dielectric properties,[34] that various naphthalene derivatives were useful for electrical applications[35] and that aromatic ethers were useful for solvent resistance as well as their dielectric properties[36].

In 1938 Alexander patented "a composition of matter comprising gamma pvc, a plasticiser and an alkyoxyalkyl ester of a higher aliphatic carboxylic acid, said acid containing at least ten carbon atoms"[37]. This last constituent, for example di(ethoxyethyl) sebacate, he considered was a stabiliser. If present in proportions of 0.1 to 5.0% it lead to mouldings that were lighter in colour [i.e. less degraded] than a similar composition containing no stabiliser. But this observation turned out to be less significant than another in which he said: "Compositions plasticised with tricresyl phosphate alone rapidly lose their flexibility at temperatures below freezing and when low enough temperatures are reached they become so hard and brittle that they are easily cracked. A composition containing gamma pvc 57 parts, tricresyl phosphate 28 parts and 2-methoxy ethyl oleate 15 parts on the other hand remains flexible around -30°C and even lower. Another composition having good low temperature flexibility contains gamma pvc 57 parts, tricresyl phosphate 33 parts and di(2 ethoxy ethyl) sebacate 10 parts. The stabilisers may be included in the compositions in amounts up to about equal the weight of plasticiser ..."

In these proportions the sebacate and oleate were obviously not functioning merely as stabilisers. They were what we should nowadays call <u>secondary plasticisers</u> and in this patent Alexander was drawing attention to a group which are specially effective in producing pvc compositions with good cold flex properties. Sebacates are widely used today in such compounds. In "claiming" an ester of sebacic acid in 1938 Alexander was among the first to recognise the virtues of this type of plasticiser.

But he was not alone. The General Electric Company seems to have been interested in plasticised pvc at this time and J.J. Russell patented for them yet another "plasticised polyvinyl halide composition"[38]. This one incorporated a class of plasticisers of which dibenzyl sebacate was cited as an example. The application is interesting not only for its early suggestion of the use of sebacates, it also pointedly described the contemporary dilemma. For Russell the ideal plasticiser was one which "will withstand mechanical abuse as low as -10°F, not give more than a minimum loss from compositions at 125°C for 100 hours and will extrude onto wire". To achieve this order of cold temperature flexibility he decided the plasticiser must be of low molecular weight, must consist of a long aliphatic chain, have as few aromatic substituents as possible and must have relatively little branching of the side chain in the aliphatic substituents. On the other hand volatility is reduced when the compound has a high molecular weight, contains many aromatic groups, is highly branched and is compact in structure.

The reconciliation of Russell's conflicting requirements would seem to have been impossible but fortunately he announced that "I have discovered that esters formed by the esterificatio of relatively long chain saturated aliphatic dibasic acids ... and alcohols of the class $C_6H_5(CH_2)$ ... closely approach the total of the combination of properties desired in a plasticiser and impart low temperature flex, high tensile strength and low loss of plasticiser".

In 1937 a process worked out and patented by the Kötitzer Ledertuch und Wachstuch-Werke [Leathercloth & Waxcloth Co.] of

Dresden in Germany ushered in a new branch of the pvc industry based on pvc-plasticiser dispersions. These were very quickly dubbed "pvc-pastes". Kötitzer, among other manufacturers of leathercloth, had been using a process which involved the application of a solution of a polymer, generally cellulose nitrate, to a base, often textile, and then removing the solvent. Other processes were also in use but they all had one or other unattractive features. One of these techniques required the application of a solution of an aqueous paste of pvc onto the base, with or without plasticiser, and producing an adhering coherent layer by evaporating the water at high pressure and a temperature above the softening point of the polymer. The process had a number of disadvantages but it lead the Kötitzer workers to a much simpler and more elegant technique.

It was described in their patent[39], and its nub was to be found in the sentence: "It has now been shown that film formation from powdered polymer on a textile base without pressure, i.e. just by heating, can be achieved when the polymer is not pasted with water but is intimately mixed with plasticiser to form a paste". It continued "thus the polymer swells and pvc and its derivatives in particular are gelled to a greater or lesser extent by the plasticiser. As a result of this gelatinisation the polymer particles, enveloped by plasticiser, combine on heating, without pressure, to a coherent layer, which cannot be distinguished in its chemical or physical properties from polymer films prepared by the now normal processes".

The bulk of this patent was concerned with the details of the application of pvc pastes to leathercloth manufacture and as might be expected the final "claim" was for "a process for the preparation of materials such as artificial leathers".

I.G. Farben however, which was keeping a close watch on outlets for its pvc quickly appreciated the wider potential of pvc pastes and acquired the patent rights from Kötitzer. Professor Kurt Thinius, now Director of the Plastics Research Institute of the German Democratic Republic, and then working in the patent department of I.G. Farben, recalls that this acquisition proved quite costly.

The first work of I.G. Farben in this field was patented in the same year and was carried out by E. Escales[40], who tried to establish the conditions for the preparation and application of pastes. He quoted one example in which "50 parts of fine pvc powder are intimately mixed with 50 parts of tricresyl phosphate to a paste. This is then passed through a mill or attrition rolls which are cooled to below 20°C. In this way one obtains a thin lacquer-like paste which can be applied with a paint spray-gun or doctor-knife to all sorts of bases. Gelatinisation can be achieved by heating to at least 150°C. Thus one obtains a smooth and perfect coating". Escales continued "These dispersions of pvc or vinyl chloride copolymers with vinyl or acrylic esters can be applied to bases and surfaces to be lacquered or coated may be dipped in the paste with subsequent gelling at 150-160°C". This last sentence represented a significant extension of the application of pvc pastes.

Progress in the first year can be measured by examination of an I.G. Farben patent completed in the middle of 1938[41]. From the discussion and the thirteen examples given it is clear that a good deal of effort had been directed towards the elaboration of paste processing. A number of different types of mixers had been investigated including turbo-mixers, dough kneaders as used in bakeries, and an Eirich mixer. A variety of plasticisers had been incorporated in addition to dibutyl phthalate and tricresyl phosphate, such as diethylene glycol dibenzoate, triphenyl phosphate, dodecyl phthalate, the benzoate of the coconut oil fatty acid alcohols, diethylene glycol monomethyl ether phthalates and various combinations of these. Fillers such as talc, chalk and titanium dioxide as well as colourants had been incorporated.

The problem of paste viscosity had received attention, since the application of pastes in different processes demanded sometimes a thin paste and at others a more viscous flow. To meet specific needs the polymer-plasticiser ratio could, within limits, be varied. The paste could be subjected to mechanical shear or "by adding readily volatile diluents which are not capable of dissolving the thermoplastic substance the viscosity of the dispersions may be further adjusted as desired".

Processes were elaborated for making shaped articles in open moulds, for coating metal surfaces, for coating and impregnating absorbent substances such as paper and textiles, for making hollow articles and for insulating wires and cables. The patent described how to free the paste from air bubbles when these were unwelcome, by exposing it to vacuum and it also suggested how air bubbles might be included when porous articles were required. In fact it proposed the use of chemical "blowing agents" for this purpose. Thus "the paste may also have added thereto an agent developing gas under the gelatinising conditions, as for example ammonium carbonates". This compound would of course liberate carbon dioxide on heating.

In brief this patent demonstrates quite conclusively that the foundations of pvc paste technology were soundly established within the first two years of its discovery.

The development of these pastes quickly revealed that not all forms of pvc polymers were suitable for their preparation. Some, when mixed with plasticiser, gave anything but a flowing, homogeneous paste. Often an agglomerated doughy mass was formed. G. Wick and his colleague J. Grassl therefore tried to discover what were the characteristics that made the polymer suitable for paste-making and how they were produced. The investigators were only partially successful. In a 1939 patent application[42] they addressed themselves to the question of the manufacture of paste polymer and said "To convert the emulsified pvc particles into a finely powdered form, one uses the Nubilosa process [i.e spray-drying]. With this method of drying the pvc particles appear as spheres of less than 50μ [$\mu = 10^{-3}$ cm]. They thus have the smallest possible ratio of surface area to volume. The individual particles are enveloped in a thin skin of sintered pvc which holds them in suspension and retards their solution in the plasticiser below gel temperature". They had previously found that processing the emulsion in other ways produced unsatisfactory results. Drying in a so-called "Imperial" drier gave particles so soft that they absorbed plasticiser too readily and so resulted in a gel rather than a paste, while centrifuging conversely produced such hard particles of pvc that they did not easily gel with plasticiser at elevated temperature.

But even if this were a complete and adequate specification for paste polymer, the aim of the chemists was not always on target. Although I.G. Farben marketed a grade PCU-P (Paste) it transpired later that it was not polymerised especially for this application. Clayton F. Ruebensaal disclosed in a Field Information Agency Report at the end of the war[43] "that contrary to popular belief the pvc resin type

PCU-P used for pastes is not a polymer specially prepared for this one application". The reason was the inability at that time of polymer chemists to fix conditions that would invariably give a product which interacted with plasticisers to give pastes. Ruebensaal explained "despite ideal control conditions the polymerisation of any monomeric substance yields products of varying density, average molecular weight, molecular weight distribution and particle size. This variance occurs not only in batch reactions, but also, although to a lesser extent, if the process is continuous. Subsequent precipitation and/or drying and grinding operations tend to vary the nature of the product even more".

While these observations were undoubtedly true, subsequent research and development made it possible to "tailor-make" paste polymer and most effectively with the production by Distillers of Geon 121 in 1943. However both before and throughout the war I.G. Farben manufactured an emulsion polymer of K value between 70 and 75 with potassium persulphate as catalyst. They designated the product PCU-G (Gummi) as it was mainly used for its elastomeric properties. Each batch was tested for its paste making properties by mixing 50 parts of a polymer with an equal weight of tricresyl phosphate. If the mixture gave a paste of the required flow properties, the polymer was renamed PCU-P and sold for pastes.

This simple procedure provided an adequate means for selecting a suitable polymer from those available at the time but any ideal paste has to satisfy a number of criteria. It must be stable over a period, i.e. its viscosity should not have increased so much between manufacture and application that processing becomes difficult. Its flow should be such as to meet the needs of the leathercloth manufacturer, the moulder, the dipper or whoever else proposed to use it. Further the properties of the end-product, as well as the processing characteristics, must be adequate. These are the requirements of an ideal paste. They are rarely all satisfied today in a single formulation even with our present resources and were much less likely to be fulfilled at that time.

However by selection of the second component of the paste, the plasticiser, it was possible to make a series of pastes, each of which was suitable for particular applications. Thus the I.G. Farben plant at Bitterfeld, which made almost all the paste in Germany before and during the war, marketed the four main types described in Table 2.

Table 2

I.G. Farben Paste Formulations[43]

Paste Designation	PCU	Plasticiser				
		Mesamoll	TCP	Palatinol F	Plastomoll KF	Silica Powder
Paste F (for cheap General Purpose Use)	50	50 or	(50)	-	-	10
Paste M (for General Purpose Use)	50	50 or	(50)	-	-	-
Paste K (for resistance to cold)	50	20	-	30 or	(30)	-
Paste C (for harder products)	60	40 or	(40)	-	-	-

(Compositions are given in parts by weight)

Some comments on the plasticisers in the Table may be appropriate and perhaps the first one ought to be on the absence of dibutyl phthalate rather the presence of the rest. DBP, though widely used then in other formulations, proved unsuitable for pastes largely because of its viscosity. Compared with TCP and the others mentioned, dibutyl phthalate has a relatively low viscosity (20 centistokes as against more than 70 for the rest at 20°C) and since this characteristic of the plasticiser is reflected in the behaviour of the paste is meant that the high plasticiser content of the paste inevitably led to a paste of low viscosity and a gelled compound of low hardness when dibutyl phthalate was used.

Mesamoll however was well suited for the formulation of pvc pastes. It resembled tricresyl phosphate in its general behaviour and although it was rather more volatile and water sensitive the resistance of Mesamoll compositions to cold was superior. In fact this plasticiser assumed considerable importance in Germany before, during and even after the war because it was good. Further it was in reasonable supply, based as it was on the Fischer-Tropsch process which kept Germany provided with petrol in the absence of imported natural variety and because it was cheap. It was the only plasticiser in Germany whose price was less than that of the polymer.

The development of Mesamoll has been very adequately described by Dr. Von der Horst of the I.G. Farben Merseburg Ammonia Plant, where it was made, in two reports dated 1941 and 1943. These were translated and made available after the war in a B.I.O.S. Report[44]. The Mesamolls were in fact aryl sulphonic esters made from aliphatic hydrocarbons with a boiling range between 230 and 320°C, (mainly straight chain with an average chain length C_{15}) produced by the catalytic hydrogenation of carbon monoxide (i.e. the Fischer-Tropsch process). These hydrocarbons were chlorosulphonated and then treated with phenols, according to the following equation

$$\text{Alkyl } SO_2Cl + HO \text{ aryl} \longrightarrow HCl + \text{Alkyl } SO_2O \text{ aryl.}$$

The first products were rather dark in colour, had a marked smell of phenol, were acid in reaction, had a low resistance to water and gave a plasticised pvc which could not be used below -5°C. Dr. Von der Horst described how the product was improved in all these respects and played a big part in meeting the German requirements for plasticised pvc.

Returning to the plasticisers used in the paste formulations given in Table 2, Palatinol F was one of a series of phthalate esters, ranging from the methyl ester to esters of higher alcohols, containing up to ten carbon atoms, which were also made from Fischer-Tropsch hydrocarbons. Palatinol F was the diester of the C_7-C_9 alcohols and its good electrical properties, indifference to temperature variation, especially the cold and the good mechanical strength of compounds made from it, marked it out as a very good plasticiser for pvc pastes.

Plastomoll KF was the ester of triethylene glycol and Fischer-Tropsch fatty acids (C_6-C_{10}). It too conferred satisfactory resistance to low temperatures but could not be used as the sole plasticiser in any paste as the compounded tended to become sticky with the necessary proportion. It was therefore mixed with others as the table indicates.

These plasticisers did not, of course, exhaust the variety that was made and used in Germany before and especially during the war. New compounds were tried and brought into service not only to meet the requirements of different applications. They were also the response to shortages first in this direction and then in that. The indispensible role of Fischer-Tropsch based acids and alcohols in the German pvc industry will be obvious from this brief description. These compounds were not available to Britain and the USA and although the English were not quite so limited as were the Germans, Britain also suffered severe shortages, and in particular did not have the higher alcohols which come from the Fischer-Tropsch synthesis or petroleum processing. These were especially useful for plasticisers of low volatility.

A list of plasticisers that were in use in Germany during the war is given in Table 3. It is a summary of an appreciation of the plasticiser situation by Dr. Schulz of I.G. Farben at Hoechst which was included as an appendix in F.I.A.T. 464[45].

There has been little mention of the British contribution so far in this account of pvc plasticiser development. The explanation is simple. There was no interest in the subject until about 1937 when imported Mipolam, the I.G. Farben plasticised pvc, began to make some slight impact in the U.K.

As I have already had occasion to point out when discussing British research in pvc manufacture, the ready and relatively cheap availability of natural rubber made rubber users contemptuous of possible synthetic alternatives. This attitude was only too clear to F.A. Hughes Ltd who acting as agents for I.G. Farben in Britain introduced Mipolam (the plasticised polymer) in 1937 to an uninterested and unimpressed public.

Mr. Peter Delafield, who was then trying to sell the

Table 3

Range of German Plasticisers for PVC as Reported in a Survey of German Coated Fabrics Industry[45]

Plasticiser Designation	Composition	Characteristics
Elaol K	Ester of C_5-C_8 fatty acids with hexane triol	Good all-round plasticiser
Elaol 3	Ester of C_4-C_6 fatty acids with pentaerythritol	Impart good heat resistance but cold flexing properties decline markedly as proportion of plasticiser falls
Elaol 4	Ester of C_6-C_9 fatty acids with pentaerythritol	
Palatinol AH	Ester of phthalic acid and ethyl hexane	Good plasticiser conferring good properties at low temperatures even with relatively small proportion of plasticiser
Palatinol C	Ester of phthalic acid and butyl alcohol	Good plasticiser but too volatile - recommended only for applications where volatilisation is low, e.g. thick walled objects
Palatinol DP	Ester of phthalic acid with C_8-C_{12} alcohols from coconut oil	Does not process easily but confers good resistance to heat and cold
Palatinol HS	Ester of phthalic acid with Intrasolvan HS	Rather more volatile than Palatinol F or AH and not so resistant to heat
Palatinol K	Ester of phthalic acid with butyl glycol	Good processing properties not good in cold
Palatinol O	Ester of phthalic acid with methyl glycol	Like Palatinol K but more volatile

Table 3 (continued)

Plasticiser Designation	Composition	Characteristics
Plastol DG	Dixylenldiglycol ether	Resistant to alkali since it is not an ester - good plasticiser but not completely compatible
Plastomoll XF	Ester of C_6-C_{10} fatty acid with triethylene glycol	—
Plastomoll TB	Ester of thiodi-butyric acid with 1.3 butanediol	Used when resistance to benzene was required but mechanical properties of compound were not very good
Plastomoll TV	Ester of thiodi-butyric acid with C_1-C_9 alcohol	Recommended as a very good plasticiser
Tricresyl phosphate G	Tricresyl phosphate	Good plasticiser for all compounds except those exposed to low temperatures and films exposed to light - they discoloured
Mesamoll I	Discussed in text	Discussed in text
Softener 1980 Special	Ester of F.T. fatty acid with thiodiglycol	Particularly suitable for cable work
Clophen A.40	Chlorddiphenyl with 40-42% Cl_2	Do not have a high plasticising efficiency but they confer good electrical properties. Can be used with other plasticisers
Clophen A.60	Chlorodiphenyl with 58-59% Cl_2	
Teolan	Beta phenoxy methyl tetralin	
Vulkanol B	Benzylnaphthalene	
Plastomoll TAH	Ester of thiodi-butyric acid and ethyl hexane	The best plasticiser especially for electrical applications
Mollit BG	Ester of butyl hydroxy-acetic acid and a triglycol	An average product

material for F.A. Hughes, has told me in conversation that "in the U.K. before the war pvc hardly got off the ground". He recalled that consumption in the year or two before the outbreak of the war was no more than 200-300 tons and explained that the Cable Makers Association, by far the largest potential users at that time, felt that even if the price of pvc came down to that of rubber, from about 2/6d to 1/6d per lb. they would still not be interested in using pvc since they saw not the slightest reason to disturb the even flow of their work.

But hostility to pvc was not universal and F.A. Hughes managed to turn an honest penny in Britain by importing the I.G. Farben polymer Igelit and compounding it with plasticiser according to formulations and processes supplied by the Germans and then selling the product as "Chlorovene". This was probably the first time pvc was compounded in the U.K. A little later, at the beginning of 1939, Dr. Harry Barron, working for the Pirelli Company began his investigations in this field along what he has called "the generally accepted lines, that is the lines laid down in W.L. Semon's work on Koroseal. The plasticiser most widely used was tricresyl phosphate".

"Koroseal",a second source of plasticised pvc in the U.K. and Vinylite QYNA a vinyl chloride copolymer product of Carbide & Carbon Corporation represented the United States effort to develop the local market. But both these compounds were small as compared with German quantities and they all amounted to very little in total. Of course, to these manifestations of pvc developments abroad one must, to obtain a complete picture, add the activities of I.C.I., but since these were confined to the laboratory they had at that time not made any impact on the market.

Such then was the plasticised pvc situation in Britain in 1939. With the outbreak of World War II the indifferent attitude to this material changed. The need to reduce imports engendered a more receptive frame of mind and Pearl Harbour made pvc production a matter of greatest urgency. One consequence was the early establishment of the Plastics Committee (Committee No. 3) of the Cable Makers' Association, which came to spend much of its time in facilitating the maximum output of the most suitable compounds for various wartime cable applications.

Many people who were then active in this sphere recall this committee as an important focus of developments. Sir John Dean, who was its chairman, told me in an interview that it included representatives of the major cablemakers, I.C.I. and plasticiser producers Boake Roberts. It met once a month and to begin with it was asked to elaborate the necessary specifications for pvc but as the war progressed it became a forum for the exchange of information on compounding. Dr. Barron, a member of the committee, recalled that though the palette of polymers and plasticisers was very limited much work was done in varying the proportions of ingredients to produce the required properties. A number of oils and hydrocarbon distillates were considered as plasticisers, to relieve the acute shortage and to find alternatives for tricresyl phosphate and dibutyl phthalate but not much of lasting interest emerged.

The predicament was expressed in a paper on "Thermoplastic Cables" which was read in 1944 on behalf of the committee to a meeting of the Institution of Electrical Engineers. "The choice of plasticiser is of the greatest importance and profoundly influences the behaviour of the materials. Many hundreds of plasticisers have been examined in pvc compositions. The number which have been found suitable for large scale applications is however very small. The most important are tricresyl phosphate, dibutyl phthalate and certain other phthalates. A few special plasticisers have latterly come into use in order to give improved properties at low temperatures".

The "special plasticisers" referred to sebacates which had been developed in the United States and were at that time becoming available in the U.K.

The paper drew attention to another procedure for meeting the shortage of materials used in the conventional plasticisers. "In this country a technique has grown up in the use of certain materials such as Cerochlors [chlorinated waxes, as the name suggests] and aromatic extracts (from petroleum) as extenders". These materials were not sufficiently compatible with pvc to be used as plasticisers on theirown but they could be used in smaller quantities to replace part of the latter and so lead to some economy. Though Cerochlors and the like are still used to effect cost economies, they did not represent any major advance in the range of plasticisers. Indeed these quotations from the paper read in 1944 show quite clearly that up to that point the U.K. contribution to plasticiser technology was limited. The paper also indicates however that the country had joined the mainstream of pvc development.

<u>Stabilisation</u>

I have already commented on the instability of pvc. It is affected by exposure to heat and light with consequent embrittlement, discolouration and other manifestations of mechanical, optical and electrical deterioration. This weakness seriously inhibited the development and application of pvc in the interwar era, particularly outside Germany where there was no urgent need to exploit its properties.

The more exacting criteria for acceptance of the new material in the U.S. probably explains why stabilisation was an area of pvc technology in which the Americans made an outstanding contribution. A cursory glance at Table 4 shows quite clearly that they initiated most of the stabilising systems that are now in use and this is confirmed, in Britain at any rate, by the fact that even today nearly all the companies specialising in the supply of pvc stabilisers have a link with U.S. companies, which gives them access to American know-how.

The pressing need to find means to cope with the ready degradation of the polymer became evident as soon as workers began to try to evolve processing techniques. Professor Kurt Thinius has told me that in the early 1930's when experimenting at the Deutsche Celluloid Fabrik at Eilenburg, he and his colleagues tried to adapt the old celluloid equipment to pvc. This involved mills and calenders operating between 75 and 100°C and at these temperatures the then pvc decomposed so vigorously that they had to work in gas masks to cope with the hydrochloric acid. Their respiratory equipment was protected but the effect of the corrosive acid on the processing equipment can be easily visualised.

Dr. Harry Barron, speaking of early work in England, about 1939, illustrated the same point by recounting an incident in which he was extruding some pvc compound. For some reason it was inadequately stabilised and this led to decomposition within the barrel which produced an explosion violent enough to crack the heavy metal extruder.

Such were the consequences of heating unstabilised or insufficiently stabilised pvc. Equally unwelcome, if less dramatic, were the results of exposure of the polymer to

Table 4

PVC Stabiliser Patents Applied for Between the Wars

Patent No.	Patentee	Application Date	Type of Stabiliser
British Patents			
336,237	I.G. Farben	16. 11. 28	Amines
384,639	Du Pont	1. 3. 30	Ethylene oxide
418,230 (DRP656,133)	I.G. Farben - G. Meyer	22. 4. 32	Ethylene oxide
450,856 (USP2,141,126)	Carbide & Carbon - A.K. Doolittle	15. 3. 34	Lead salts
451,675 (DRP679,896)	Deutsche Celluloid	11. 2. 35	Removal of low molecular weight polymers
451,723 (USP2,075,543)	Carbide & Carbon - F. Groff & M.C. Reed	10. 7. 34	Cadmium laurate and other soaps
451,725 (USP2,126,179)	Carbide & Carbon - F.W. Duggan	31. 7. 34	Phenol derivatives
454,232	Deutsche Celluloid	25. 3. 35	Amino acids
464,302	Deutsche Celluloid	15. 12. 34	Methyl and ethyl acrylate
467,167 (DRP633,220)	I.G. Farben - H. Fikentscher & W. Franke	8. 11. 35	Sodium salts of acrylic acids
470,380	BTH	7. 3. 36	Lead oxide
492,558 (USP2,157,068)	Carbide & Carbon - T.E. Carruthers & C.N. Blair	16. 10. 36	Aryl esters of benzoic acid
497,879 (USP2,219,463)	Carbide & Carbon - V. Yngve	31. 12. 36	Alkyl or aryl tin or lead
532,425	BTH	31. 8. 38	Lead salts of phenol
536,297 (USP2,256,625)	Carbide & Carbon - W.M. Quattlebaum	13. 2. 38	Alkaline earth alcoholates
540,127	Stoner - Mudge		Alpha pyroazyl ethylenes
542,141	I.C.I. - J.R. Lewis, L.B. Morgan, & W.M. Morgan	24. 6. 40	Various mercaptides
542,505	I.C.I. - J.R. Lewis, L.B. Morgan, & W.M. Morgan	11. 7. 40	Lead salts of 2,4 dihydroxyquinoline
German Patents			
633,220 (BP467,167)	I.G. Farben - H. Fikentscher & W. Franke	8. 11. 35	Sodium salts of acrylic acids
656,133 (BP418,230)	I.G. Farben - G. Meyer	22. 4. 32	Ethylene oxide
659,042	I.G. Farben - G.V. Susich & H. Fikentscher	28. 8. 32	Alkali treatment of polymer
679,896 (BP451,675)	Deutsche Celluloid	11. 2. 35	Removal of low molecular weight polymer
729,419	Siemens - Schuckertwerke	11. 2. 35	Lead or silver oxides or hydroxides
U.S. Patents			
2,011,132	Carbide & Carbon - C.O. Young & S.D. Douglas	11. 4. 31	Metallic lead, tin and aluminium present during polymerisation
2,013,941	Carbide & Carbon - C.O. Young & S.D. Douglas	28. 3. 31	Amines
2,050,843	Coe Laboratories - I.M. Jacobson	6. 4. 33	Morpholine, sulphydryl, xanthate
2,075,543 (BP451,723)	Carbon & Carbide - F. Groff & M.C. Read	10. 7. 34	Cadmium laurate and ether salts
2,103,581	Hazel-Atlas Glass - D.M. Grey	25. 4. 34	Organic bases
2,111,395	Pittsburgh P. Glass-O.J. Hartwick	28. 8. 34	Inert metallic oxides
2,126,179 (BP451,725)	Carbide & Carbon - F.W. Duggan	31. 7. 34	Phenol derivatives
2,130,924	Stoner - Mudge - A.W. Johnson & G.H. Young	5. 2. 37	Tar base
2,140,518	Carbide & Carbon - A.K. Doolittle	24. 3. 34	Aluminium, cadmium, magnesium and various sulphites
2,141,126 (BP450,856)	Carbide & Carbon - A.K. Doolittle	15. 3. 34	Lead salts

Table 4 (continued)

Patent No.	Patentee	Application Date	Type of Stabiliser
2,157,068 (BP492,558)	Carbide & Carbon - T. Carruthers & C.M. Blair	16. 10. 36	Aryl esters of benzoic acid
2,157,997	B.F. Goodrich - S.L. Brous	16. 6. 38	Oxides and salts of iron, zinc, aluminium, etc.
2,160,060	Carbide & Carbon - A.K. Doolittle	12. 12. 36	Acid phosphates and sulphides
2,160,061	Carbide & Carbon - A.K. Doolittle	12. 12. 36	Acid phosphite or sulphide
2,160,948	Dow Chemicals - R.H. Wiley and H.R. Slagh	23. 10. 37	Sodium phosphates
2,161,024	Carbide & Carbon - A.K. Doolittle		Compounds of lead and antimony
2,161,026	Carbide & Carbon - A.K. Doolittle	23. 7. 37	Antimony oxide
2,169,717	Stoner - Mudge - G.H. Young	7. 3. 38	Quinoline
2,171,334	G. E. C. - R.M. Fuoss	10. 3. 37	Lead oxide, resinate, Fuller's earth and carbon
2,179,973	Carbide & Carbon - C.H. Alexander	16. 7. 38	Metal silicates
2,181,478	Carbide & Carbon - K.K. Fligor	22. 12. 36	Sodium or potassium acetate with stearates
2,190,776	Du Pont - E.K. Ellingboe & P.L. Salzberg	21. 7. 37	Polymeric amines
2,193,662	Carbide & Carbon - C.H. Alexander	2. 8. 38	Esters of higher aliphatic carboxylic acid
2,208,216	Stoner - Mudge - A.W. Johnson & G.M. Young	28. 7. 38	Hetero cyclic nitrogen bases
2,217,170	- - J.M. Hunter	-	Metal titanates
2,219,463 (BP497,879)	Carbide & Carbon - V. Yngve	31. 12. 36	Organo lead and tin compounds
2,224,944	Stoner - Mudge - G.H. Young	19. 1. 39	Tar base, e.g. quinolidine
2,232,933	Dow Chemicals - R.M. Wiley & J.E. Livak	10. 4. 39	Dialkyl and aralkyl ethers
2,256,625	Carbide & Carbon - W.M. Quattlebaum	13. 12. 38	Alkaline earth alcohols
2,258,243	Carbide & Carbon - A.K. Doolittle	24. 3. 38	Sodium and calcium
2,261,611	Carbide & Carbon - D.M. Young & W.M. Quattlebaum	23. 2. 39	Product of lead salt with alkali metal salt
2,267,777	Carbide & Carbon - V. Yngve	23. 6. 38	Organo-tin and lead oxides and hydroxides
2,267,778	Carbide & Carbon - V. Yngve	23. 6. 38	
2,267,779	Carbide & Carbon - V. Yngve	23. 6. 38	alkyl tins
2,274,555	B.F. Goodrich - A.B. Japs	4. 12. 37	Ester of drying oil acid and alcohol
2,307,075	Carbide & Carbon - W.M. Quattlebaum & D.M. Young	2. 8. 40	Metal diketones
2,307,090	Carbide & Carbon - V. Yngve	16. 12. 39	Organo lead compounds
2,307,092	Carbide & Carbon - V. Yngve	9. 11. 40	Alkyl tin esters

daylight or, even more, to sunlight. These agencies produce a discolouration; at first only slight, but becoming progresively more intense. While discolouration is also a feature of heat degradation, a distinction was drawn between the effects of heat and light. In a patent applied for in 1934[47] the inventor described the situation simply. "Some of these compounds [proposed stabilisers] are slightly superior to others in their ability to impart to resins resistance to discolouration by sunlight. This ability bears no relation to the properties of these compounds as heat stabilisers".

The difference between the effects of heat and light arises from the varied chemical decomposition mechanisms involved. These are of more than academic interest since they determine what type of compound will effectively inhibit or retard degradation. However, it is one thing to appreciate the significance of pvc degradation mechanisms amd quite another to know what these are. We know little about them today. They knew even less at that time. The search for stabilisers was therefore a quite empirical investigation with little theory to guide it.

But the relevance of acid to the instability of the polymer was at first intuitively felt and later accepted almost as an article of faith. Thus the first patent that I have found dealing with the problem, applied for in 1928 by I.G. Farben[48], said "Known polymerisation products from vinyl esters have the disadvantage that they contain a certain amount of free acid. This quantity is generally very small, however even this small proportion suffices to cause injurious effects when the product is used for certain technical purposes, such as polyvinyl acetate in lacquers. This liberation of acid also acts detrimentally in another respect. Thus a lacquer coating prepared from pvc when exposed for a long time to a temperature between 80 and 100°C assumes a more or less dark colour".

The simple solution to this difficulty was obvious: add a suitable dose of basic substance to react with the acidity. This patent proposed just such a solution. "According to this invention the said disadvantages are obviated by incorporating in the polymerised product a small proportion of a basic substance ... These basic substances not only render innocuous the free acid already present but also act as a stabilising agent in preventing a new formation of acid in the polyvinyl compound". The stabilisers claimed were organic bases said to be applicable to vinyl polymers generally, and they were exemplified by such compounds as diphenyl guanidine hexamethylene tetramine and cyclohexylamine.

A similar solution to the problem of the instability of pvc emerged in the patent applied for by C.O. Young and S.D. Douglas, of Carbide & Carbon Chemicals, in March 1931[49]. These too incorporated small amounts of substances having basic properties, which they confidently felt "render them [the vinyl resins] entirely stable". In retrospect Messrs. Young and Douglas seem to have been somewhat optimistic, but then they were at the beginning of a long and tortuous road.

Their "basic substances" included not only the amines which formed the core of the I.G. Farben patent, they also encompassed inorganic basic compounds, for example, alkaline earth metal and heavy metal oxides and carbonates and ammonia.

These "inventions" were, however, destined to become just additions to the patent record. Of far greater importance was the idea developed by Drs. Fikentscher and Susich, of the alkali treatment of emulsion copolymer and subsequently homopolymer. This method became part of the manufacturing process in 1932 and persisted through the war and beyond as a characteristic of the I.G. Farben technique for the production of pvc. It made processing possible at temperatures up to 150°C and gave the Germans a pvc which was adequate for most of their needs.

As first described[50] the method involved the coagulation of the latex and then the filtration of the coagulum followed by washing to neutrality. At this stage the polymer was treated with a dilute alkali solution (about one to two per cent) at about 60°C for one or more hours and then it was washed free of all water-soluble components: later with the elaboration of the spray-drying technique the alkali solution was mixed with the emulsion just before it was charged into the dryer. The process as observed at the end of the war was described in a number of B.I.O.S. and F.I.A.T. Reports and this account given in one[51] is typical. "The emulsion is dried in a Nubilosa ... At the same time as the emulsion is sprayed into the drier, sodium carbonate is injected through separate nozzles so that the finished product contains 0.4-0.5% of alkali. This procedure results in an adequately stable finished product".

But although "prestabilised" polymer was generally satisfactory, "the stabilisation of vinyl chloride polymers with alkali alone was not sufficient in all cases. This was particularly true when they were processed in the absence of solvents and plasticisers". So said Dr. Fikentscher in 1963 when he enumerated various additives which were employed to improve the situation[52]. For example he and his colleagues found that copolymerisation with a few percent of unsaturated carboxylic acids or acid amines was helpful and two patents, one attributed to Fikentscher and Franks[53] and another to the Deutsche Celluloid Fabrik[54] deal with acrylic acid esters and amides.

In this connection it is interesting to note that when I.C.I. workers combed through the patent literature at the outset of their own pvc research programme some four or five years later, they noted the claim for improved heat stability through copolymerisation. They tested the claim but could not substantiate it by their own investigations and therefore rejected it[55]. What they did not appreciate at the time was the German practice of alkali treatment. In these circumstances the presence of a few percent of acrylic acid or ester comonomer helped to retain the sodium carbonate which the Germans used but which the I.C.I. workers did not.

I.G. Farben patented another type of hydrochloric acid "absorber" in 1932, namely ethylene oxide derivatives[56]. This followed an earlier application by Du Pont[57] which tried to meet a number of requirements "... Another object of this invention is the development of a process by which vinyl resins of consistently uniform quality may be obtained. Another object of the invention is to control the colour and viscosity of the vinyl resin". "These objects are accomplished by the careful regulation of the amount of acid present or generated during polymerisation ... According to our invention we regulate the amount of acid so that it is greater than 0% but does not exceed 1% ... This may be achieved in several ways e.g. by the addition of the requisite quantities of mild inorganic bases (such as sodium carbonate, amines, butyl alcohol, lead tetraalkyls, lead trialkyl chloride, dioxan and especially ethylene oxide and substances of the ethylene oxide type". Here then was the origin of the epoxide stabilisers.

I.G. Farben was more single minded in its 1932 patent. It was solely concerned to improve stability. It drew attention to the Du Pont specification and said "the products resulting from this Du Pont process will thus always contain a small quantity of free acid. In contradistinction thereto the present process is employed in order to avoid the presence of free acid in the resulting products even after prolonged storage and exposure to light or heating".

In its patent of February 1935 Deutsche Celluloid Fabrik published a rather different and more fundamental approach to the stabilisation of pvc[58]. Instead of adding, it removed something. It recognised that the nature of the polymer itself was relevant to its stability and observed that "a material freed from low molecular weight substances exhibits a glass clear appearance, complete absence of colour, essentially enhanced stability to light, a considerably higher softening point and an essentially increased stability of the colour towards heat". Claim 1 of the patent therefore proposed "a process for improving the stability to light and heat of simple or mixed highly polymeric bodies containing chlorine, which consists in subjecting it ... to a substantially complete extraction with the aid of an organic liquid which has no, or only a slight, swelling action on the highly polymeric body".

Such a process was not commercially feasible and was in any event made unnecessary by the achievement of a greater control of the polymerisation process and hence to an elimination of the very low molecular weight component. But the general idea is interesting and may well have relevance to future efforts to improve the stability of pvc. If pvc can be manufactured in such a way that the polymer chains contain few points at which degradation can be easily initiated then there will be less need to stabilise it.

Today the bulk of pvc is stabilised by lead salts of one sort or another and the first published suggestion for this type of stabiliser seems to have been contained in A.K. Doolittle's patent of March 1934[59]. There he developed his theme in a nice logical way. "Heat stabilisers for vinyl chloride copolymers are of two general groups. First metal (powder) which forms insoluble chlorine derivatives and then oxides, hydroxides and salts and second, substances which have a mild reducing action. Heat stabilisers of either of the above groups are improved if they are additionally slightly basic. Also, stabilisers may be selected which are members of both classes and their action is for that reason improved. If in addition the stabiliser is also slightly basic it will be still more efficacious. Thus lead sulphate is somehwat less desirable than basic lead sulphate and lead sulphite, a member of both groups, is better than other lead salts or other sulphites. Mixtures of basic lead sulphate and lead sulphite are particularly effective".

This rationale did not preclude the use of salts or metals other than lead and the patent did in fact claim antimony oxide, mercurous oxide, silver sulphite etc. etc. Nevertheless lead compounds were the centre of interest of this patent (and another published at about the same time[60]) which provided the foundation for lead stabilisation of pvc.

In the preamble of the patent, Doolittle explained that the reason for his interest in the subject sprang from the use of vinyl chloride copolymers as lacquers and the need, on occasions, to bake them. This inevitably lead to the decomposition of the polymer and consequent discolouration. The behaviour of these lacquers was of considerable concern to his company, The Carbide and Chemicals Corporation, because at that time it saw surface-coatings as the major outlet for this product. Stoved lacquers were exposed to the full rigours of degrading agencies. They were heated to well above 100°C and then in the nature of things left exposed to the attack of light and hostile atmospheric agencies. Little wonder then that the company devoted a lot of effort to the stabilisation of pvc (as illustrated by their many patents on the subject).

Another stabiliser type coming from Carbide and Carbon laboratories was the metal soap, also inspired by its acid absorbing capacity. In July 1934 F. Groff and M.C. Reed claimed a process in which vinyl chloride polymers or copolymers contained "a small amount of one or more alkali metal, cadmium, lead or manganese salts of a weak carboxylic acid"[61]. Lead and cadmium soaps were the real concern of the inventors who chose lead oleate and cadmium laurate as specific examples. The patent also suggested the use of a mixed soap "such as mixed cadmium-lead stearates", which might be regarded as a forerunner of what are now called "synergistic mixtures" of stabilisers. But this might be claiming too much for these workers, since there was no suggestion in the text that the efficiency of the mixed soap was greater than the sum of the efficiencies of each constituent soap.

The development of pvc as a lacquer soon revealed the need for protection of the polymer against the degrading effects, in some circumstances, of the substrate to which the lacquer was applied. It transpired that some metals act as catalysts for the decomposition reaction and that stoving pvc lacquers on iron, zinc and copper surfaces quickly led to the appearance of colour. G.H. Young in his patent listed the temperature at which copolymer decomposes in the presence of various metals[62]. For tin it was 300°F and for iron, zinc and copper it was 290°, 280° and 330° respectively. All of these temperatures are within the range normally used for baking the surface coatings. His solution was to incorporate quinoline and isoquinoline as stabilisers. A.K. Doolittle in dealing with the same problem proposed the use of acid phosphates and sulphides since "they react with the metal surface which is thus non-reactive with any acid decomposition products of the vinyl resin"[63], while D.M. Grey had recourse to a series of amines, including urea and its derivatives[64].

Still in 1934, F.W. Duggan, on behalf of Carbide & Carbon applied for a patent specifically concerned with the light stabilisation of vinyl resins[65]. His invention was based "upon the discovery that it is possible to treat an unstabilised vinyl resin, or one that has been stabilised against heat, so as to further stabilise the resin against deterioration and discolouration upon recourse to light, whether from a natural or artificial source, while preventing or substantially retarding the formation in the resin of objectionable fog or colour". The compounds which proved effective for this purpose were mononuclear aromatic substances having a single hydroxyl or amino group attached to the nucleus in the ortho position to a nitro, alkoxy or esterified carboxyl group. "Suitable compounds for use in the present invention are eugenol, methyl salicylate and guaiacol... Phenol derivatives containing one or more carboxylic ester groups attached to the benzene ring in many instances possess outstanding merit as light stabilising agents for vinyl polymerisation products".

In the event these substances have not achieved any importance as stabilisers for pvc but it is not difficult to recognise the influence of contemporary rubber technology in this particular investigation.

People concerned with elastomers were (and still are) very interested in their ageing characteristics and with means to prevent or delay perishing. Since oxidation was the most potent form of attack, stabilisation of rubber required the presence of an antioxidant and phenols were of use in this role. In a contribution to a monograph on the Chemistry and Technology of Rubber published in 1937[66], Waldo L. Semon (of pvc plasticiser fame) asserted that "phenols have definite protective action" and went on to cite a number of examples of their use in rubbers, including one patent dated 1870[67]. Phenols are widely used with rubbers today.

The influence of rubber practice may also account for the early selection of amines as pvc stabilisers. The reader will recall that amongst the earliest patents for pvc stabilisers were two which selected amines for these acid absorbing properties[48,49]. Since amines were amongst the most effective rubber anti-oxidants, workers knowledgeable in rubber practice might well look to see if they were equally useful for pvc. Indeed it may have been no coincidence that nearly all the amines quoted as stabilisers in the early I.G. Farben patents were aromatic, the type which is of greatest interest in rubber compounding.

Another line of enquiry, described in a Du Pont patent of 1937[68] which, like the phenols, has since proved of no practical advantage in the stabilisation of pvc, is nevertheless of interest. The authors, E.K. Ellingboe and P.L. Salzberg were concerned about the loss of stabilisers through volatility, particularly when the polymer was applied as a thin surface coating. In that situation the ratio of surface area to volume is at its highest and so conditions are most favourable for evaporation. They therefore proposed the use of "non-volatile, film-forming polymeric basic amino compounds" and as examples they quoted "a reaction product of phenolformaldehyde resin and a non-aromatic primary amine" and an amino alcohol ester of an alpha substituted acrylic ester.

About ten years before this patent, the first I.G. Farben stabilisation patent concerned with pvc, which we have already discussed[48], quoted in Example 4 the use of a product of two parts of a urea-formaldehyde resin and 0.4 parts of dimethyl aniline. In that case however the author did not specifically comment on the non-volatile nature of the stabiliser,

A more fruitful field of research was inaugurated with the work of Victor Yngves of Carbide and Carbon when he examined the stabilising effect of organo-metallic compounds based on tin and lead. His pioneering patent covered the use of an organo metallic aryl and/or alkyl compound of tin and/or lead and of these compounds those containing three or more carbon atoms were said to be particularly effective[69]. Tetrapropyl, propyl triphenyl lead, dipropyl diphenyl tin, tetra phenyl tin and other such substances were typical examples of the class which Yngves had in mind and what especially impressed him about them apart from their actual stabilsing capabilities, was the fact that unlike pvc compounds containing the popular lead stabilisers, "resins incorporating these metal alkyls show practically no tendency towards discolouration in the presence of hydrogen sulphide".

The initial tin alkyls were followed by other organo-tin compounds in particular by more complex structures such as dibutyl tin laurate[70] and later dialkyl tin maleate[71] and the organo-tin mecaptides, all of which represented improvements on the original and so eventually completely replaced it.

It will be quite evident from this discussion of progress in the stabilisation of pvc that the major contribution emanated from the U.S.A. That this progress was reflected in the quality of pvc on the market was evident from an incidental comment in a paper published in 1940 on the "Accelerated weathering of transparent plastics"[72]. Said the authors "specimens 81 and 95 present an amazing contrast in the behaviour of two copolymer vinyl chloride-acetate plastics. Specimen 81 is the old type of sheet material, originally received by us in 1935, whereas specimen 95 is a modified composition of this same type of plastic received in 1939. The latter material is practically unaffected after the 500 hour test in the accelerated ageing apparatus whereas the former product is nearly opaque from discolouration. This difference in behaviour of these two samples has been duplicated in roof exposure tests".

The Germans for their part were reasonably happy with the stability of the alkali treated polymer. A study of the available minutes of "Kuteko" (Kunststofftechnischen Kommission) during the period 1935-40 shows no concern with the problems of inadequate stability. However there were certain applications where sodium carbonate was unsatisfactory. One relatively major reason was the "blowing" of the carbonate, that is its tendency to evolve carbon dioxide. This resulted in porosity when processing by extrusion and compression moulding, both of which required high temperatures. Sometimes, urea was used instead of sodium carbonates[73].

As can be imagined the need for additional heat stabilisation became more apparent when dealing with unplasticised compounds rather than plasticised compositions because of the higher operating temperatures used for the

the former. In fact one of the Allied investigating team following in the wake of the advancing armies reported the situation thus: "With unplasticised pvc it may be necessary to incorporate lubricant and stabiliser although polymer was bought with these i.e. sodium carbonate already incorporated"[74], the implication here being that it was not necessary in the plasticised form. This was confirmed by Dr. Fikentscher on interrogation, when he said that at Gendorf they never added stabiliser to the pre-stabilised pvc which they calendered into film[75].

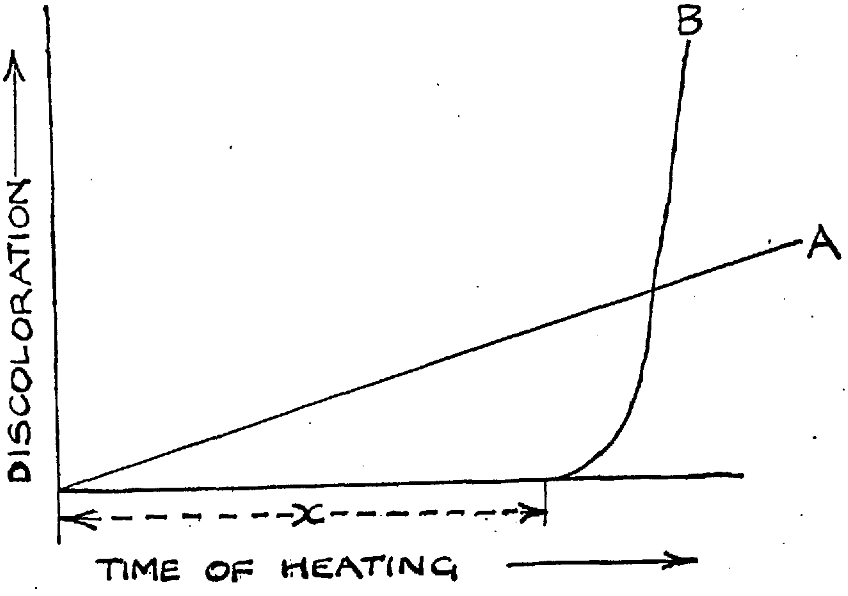
But as pvc became more widely used and standards of adequacy rose, there developed a growing need for material which could better withstand the attack of heat and light. The Germans therefore developed a series of stabilisers which differed from those used in the U.S.A. and Britain because their effectiveness was related to the presence of the sodium carbonated in the prestabilised polymer.

About a dozen compounds were reported as German pvc stabilisers by the Allied investigating teams (cf. Table 5) but of these only two seem to have been of any consequence. They were α (or 2) phenyl indole and diphenyl urea[74].

Table 5
German Stabilisers for PVC[76]

Stabiliser Designation	Composition
P	Phenoxy propylene oxide
DBG	Diisobutyl phenyl glycidyl ether
HRA (AH)	Adipic acid hydrazide
BS	Butadiene sulphone
-	Thiodipropionic acid hydrazide
I (J)	α phenyl indole
C	Diphenyl thiourea
MPTH	Monophenyl thiourea
A	Methyl (3 amino/phenyl) sulphone
D	4,4 diamino diphenyl sulphone
-	Methanol

The German, or more accurately the I.G. Farben experience and attitude to these two was discussed most comprehensibly in a post-war Dutch Report on the German Plastics Industry[77,78]. From it, it appears that the protection offered by alkali (sodium carbonate) was rather different from that afforded by stabilisers I and C. The difference is explained by the curves A and B in the following graph



Whereas the alkali stabilised polymer begins to discolour very soon after heating begins (Curve A) the indole and urea derivatives protect the polymer from discolouration for the period x but once this has elapsed the rate of degradation is very fast (Curve B) as compared with Curve A. In fact beyond a certain time the decomposition represented by Curve B is much more serious than that of A. It will be understood that the behaviours of α phenol indole and diphenyl thiourea are not identical. Curve B is merely intended to illustrate the pattern of breakdown.

Stabiliser I was said to be better than C in some applications while the reverse was true in others. α phenyl indole however was itself more light sensitive and therefore tended to colour the product on exposure. Professor Thinius illustrated this unfortunate fact with an experience in Leipzig, in East Germany. In 1945 in the destruction and shambles at the end of the war there were, of course, many broken windows. Though there was no replacement glass available there was some pvc. It was therefore decided to use phenyl indole stabilised pvc film in place of glass. This was highly satisfactory until the sun shone and then the windows went first yellow and then blue. Yet another unfortunate experience of "ersatz".

A question that intrigued many investigators of the German pvc scene was why did the Germans not use lead stabilisers. Various answers were given, some more convincing than others. In any event it was not quite accurate to say that lead was not used in Germany. It was not used or recommended by I.G. Farben but Alexander Wacker preferred lead stearate as stabiliser. However this use represented only a very small proportion of the total volume of stabiliser.

One reason given was that the basic patents for lead stabilisers were held by British and American companies and the Germans did not wish to infringe these patents[77]. Here is a delicacy which many will not recognise as characteristic of Nazi Germany. More credible explanations involved the shortage of lead salts, the more stringent factory legislation controlling the use of lead compounds, their discolouration under the influence of hydrogen sulphide in the atmosphere and a conviction that their own stabilisation systems were comparable with lead compounds.

In assessing the progress achieved in the field of pvc stabilisation by the outbreak of war, or very soon after, one must be impressed with the fact that all the basic systems used today had already been recognised. In an authoritative monograph on "The Stabilisation of PVC" published in 1963, the authors classified stabilisers in the following groups: 1) salts of mineral acids, 2) salts of carboxylic acids, 3) organometallic compounds (largely tin), 4) other organic compounds of metals and metalloids, 5) epoxides, 6) amines of all types, 7) esters (mainly organic phosphites, 8) organic acids, alcohols and phenols[79]. Using this classification as a yardstick a study of the foregoing chapter will show that the pioneers did their work well.

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Chapter 7

Processing

In the preceding chapter we have considered, at some length, the evolution and maturation of methods for the preparation of pvc as raw polymer and in compounded form. In brief, we have looked at emergence of pvc as a material. Clearly production of the raw material is the essential first step but even so without further processing, white powdered pvc is of little interest. Only when it has been shaped, that is converted into a useful article is the manufacturing process completed.

This chapter is therefore concerned to trace the development of the machines and techniques necessary for the latter phase. It aims to deal with the stuff of plastics technology rather than chemistry, which has been our main preoccupation so far.

The first point that stands out in any study of the machines is that they did not have to be invented for the processing of pvc and other plastics. The prototypes existed already. The advent of the materials that today we call plastics seems to have occurred in three phases. PVC formed part of the second wave, the surge of which so significantly extended the range of substances available to craftsmen and technologists. The first one arrived in a rather leisurely fashion over a period which reached from the time before the beginning of Queen Victoria's reign up to the first decade of the present century. It included rubber, gutta percha, celluloid, casein, cellulose acetate and phenolic plastics. These formed the group of materials upon which the pioneer rubber and plastics engineers "served their time" and received their first lessons in the manipulation and processing of polymers. These experiences laid the foundation of today's plastics techniques and of pvc in particular.

The youthful rubber industry conceived most of the important processes, certainly as applied to pvc. For example mixing, the vital operation which makes a homogeneous material from polymer, stabiliser, plasticiser and so on, which is then shaped, has long been carried out on a so-called "open roll" or "two roll" mill. This machine was invented in the very early days of rubber technology and was adapted with minor modifications to accommodate the higher working temperatures required for pvc. There is therefore no need to dwell on this item here, since pvc stimulated no important innovation.

Again the first calender to rubberise fabric without the use of solvent was patented by E.M. Chaffee in 1836[2]. He called his invention the "Mammoth" because he thought it was so big. He would hardly use that name alongside today's monstrous calenders, but size notwithstanding the modern version shares the basic principles of the original.

The hydraulic press with its steam-heated platens devised to vulcanise rubber mouldings was taken over to exploit the possibilities of thermosetting resins and now, in modern form it produces thousands of tons of phenolic urea and melamine mouldings. Extruders have been traced back to 1797 when Joseph Bramah was said to have made lead piping with a hand operated plunger and die. Later this type of machine was used to extrude soap and macaroni among other things and then gutta percha and rubber.

Injection moulding was a technique that did not derive from the rubber industry. It was first applied to celluloid by the brothers J.W. and I.S. Hyatt who designed a machine in 1872[3] for moulding rod which was then developed six years later to cover metal buckles with a coating of celluloid[4].

Thus by the time pvc came on the scene as an industrial product the machines and processes that were to be used in its fabrication were already extant. All the techniques that have been enumerated here have been used at one time or another in connection with pvc but they have not been and are not of equal importance in the economy of pvc. Compression moulding is basically not a method which lends itself to the economical exploitations of thermoplastic materials and so apart from some unimportant and a typical situation is has not been used for pvc.

Injection moulding on the other hand is widely used for thermoplastics but even so has not figured prominently in the development of pvc. Until the fairly recent advent of screw preplasticising machines, unplasticised pvc defeated the best efforts of technologists to mould it by injection without an unacceptable degree of decomposition. However, though the plasticised variety was formed quite satisfactorily in this way injection moulded pvc never assumed great significance because the pattern of applications dictated the use of other techniques.

This is far from being the case with extrusion and calendering, processes which between them accounted for the bulk of pvc output. Experiemce soon demonstrated that the striaght application of machines as used for rubber was most unsatisfactory; that considerable modifications were necessary to ensure products of good quality and outputs at speeds which made operations economic. These requirements, set by developing pvc technology, imposed greater demands on extruders and calenders and this spur provided the major impulse for their progressive improvement and sophistication.

I will therefore devote this chapter to a consideration of the influence of pvc processing on the development of these two machines,

Extrusion

Extrusion is a process which in principle is as simple as squeezing toothpaste from a tube. The Shorter Oxford English Dictionary says that "to extrude is to thrust forth, to urge out, to expel". The history of the extruder is an account of the refinement of the methods used to "urge out" various materials in shapes confirming as closely as possible to those required.

In some cases the operation poses no great problems. The dimensions of the strip of toothpaste, for example, are not critical. In the extrusion of metal tubes, the flow characteristics of the molten metal allow of the fairly striaghtforward technique that was first elaborated in which preheated lead was forced through a suitable die by means of a hand operated ram.

The extrusion of plastics however has turned out to be a much more complicated and subtle exercise and the equipment is correspondingly complex.

Extrusion, as the elementary process defined in the dictionary, has doubtless been practised for centuries but the recognisable antecedent of the sort of process that we are considering here is said to be a machine invented and patented by Joseph Bramah in 1797[5,6,7,8]. In spite of wide currency of this belief however, there is no definite reference to the patent. My own searches through the Patent Office records give no indications of such a patent. Bramah was indeed a fertile inventor. Between 1778 and 1814 he claimed no less than 18 inventions. The first dealt with water closets, the last with "applications of species of earth to destroy dry rot" and in between he contributed to paper making, printing machines, locks for doors and the "clarification, preserving and drawing off of malt and other liquors" among other things. But the patent records show no trace of an extruder. It might be that Bramah published the details of his machine for the extrusion of lead piping elsewhere, but if so, I have not been able to track it down.

Whether or not a Bramah extruder existed there is no doubt that it was the advent of telegraphy and the need for electrically insulated wiring and cables that provided the powerful stimulus for the early development of extruders. The possibilities of electrical telegraphy had been convincingly demonstrated in the early years of the nineteenth century and by the 1830's the growing railway network in Britain was demanding some such form of communication. William Cooke and Professor Wheatstone had set up in partnership to meet this need and in 1842 they connected Paddington and Slough along the route followed by the Great Western Railway. The potentialities of electric telegraphy were dramatically demonstrated when "a suspected murderer was seen to board a London bound train at Slough. The news was telegraphed to Paddington and he was arrested on arrival and subsequently hanged"[9].

One result of this episode was the founding of the Electric Telegraph Co. in 1846 by Cooke and Wheatstone, which in the following six years installed no less than 4,000 miles of telegraph in Britain. Initially the conductors were carried on poles uncovered except at the points of support, where they were insulated. But inevitably the wires had to come down to ground level and below, at some points and then some electrical water proof insulation was essential. "At first the insulated wires were of copper, wound round, or lapped, with fibrous material afterwards saturated in such substances as tar, wax or pitch. As may be imagined such insulation was unsatisfactory even when, as in some cases, the covered wire was drawn inside a lead tube. It remained one of the technical problems of the day to find an insulating cover which would continue stable in the presence of moisture"[10].

The challenge was met quite quickly with the application of gutta percha, a new material which Dr. William Montgomerie had found in his travels in Malaya. In 1843 he wrote a detailed account of its occurence, how the natives extracted the gum from a tree and of the properties of gutta percha. The account and samples of the material were transmitted to the Society of Arts and this led to a fairly wide dissemination of the information. "On one occasion Michael Faraday remarked to his friend William Siemens, that such a substance being impervious to damp might prove useful as an insulator of electric current, whereupon Siemens obtained a piece from the Secretary and sent it to his brother in the Prussian Army with the suggestion that it might be tried on the German underground telegraph cables"[11]. The suggestion was taken up and some lengths of gutta percha insulated copper wire laid as submarine cable.

In Britain the Gutta Percha Company was set up by Charles Hancock (brother of Thomas, the "Father of the Rubber Industry") and Henry Bewley to exploit its special properties. The company produced a range of moulded articles from Gutta Percha (some of which were on display at the Great Exhibition of 1851), such as "Small and cheap Railway Conversation Tubes" which enabled parties "to converse with ease and pleasure" and the "Hearing Apparatus" fitted up in Lismore Cathedral for the use of His Grace the Duke of Devonshire which ran, out of sight, from the pulpit to His Grace's pew. These and other such possibly even more important applications are listed and illustrated in catalogues of the company but its major activities very quickly focussed on telegraphy.

This was made possible by the extruders developed by Bewley and Brooman in 1845.

Richard Brooman's specification concerned an invention "communicated to him by a foreigner residing abroad", and dealt with the "Manufacture and Application of Gutta Percha Thread"[12]. Such threads, according to the patent, could be used for all sorts of useful purposes, but our interest lies in the manner of their production. The patent described the operation of the machine with reference to the diagrams reproduced here. (Figs. 1 and 2).

With the piston D withdrawn, a roll of gutta percha was introduced into the cylinder B. The replaced piston was then "forced steadily downward by hand or other suitable power upon the gutta percha, which becoming softened at the lower end by the die box, C (heated by steam passing through hollow chambers F), escapes from the pressure through the orifices E, E in a series of threads, which as they drop into and are cooled by water in the tank, A, are carried round a roller W".

This appears to be the first recorded description of the extrusion of a thermoplastic.

The process was developed somewhat further in Henry Bewley's patent of the same year in which the extruder was modified for the manufacture of "flexible syringes, tubes, hose, and other like vehicles and vessels wholly of gutta percha"[13]. The modus operandi can be seen from the diagram which was appended to the patent (Fig.3). Here A is the cylinder and B the piston, C is the die box, also kept hot by steam. C^1 represents a disc with a number of holes through which the gutta percha is forced into a cup C^2, whence it passes round the core D and descends as a tube into the receiver E, containing cold water.

[redacted]

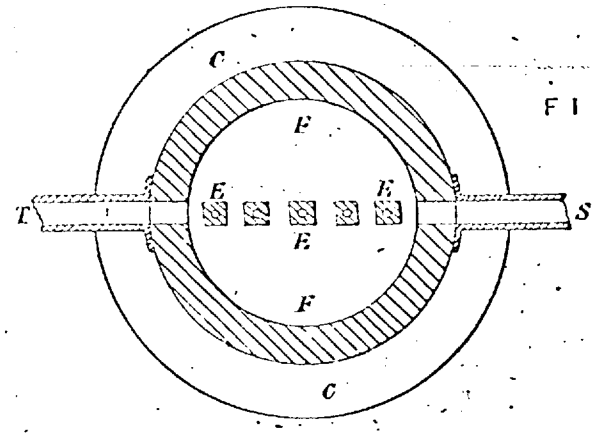

FIG. 2.

A PLAN OF THE DIE BOX

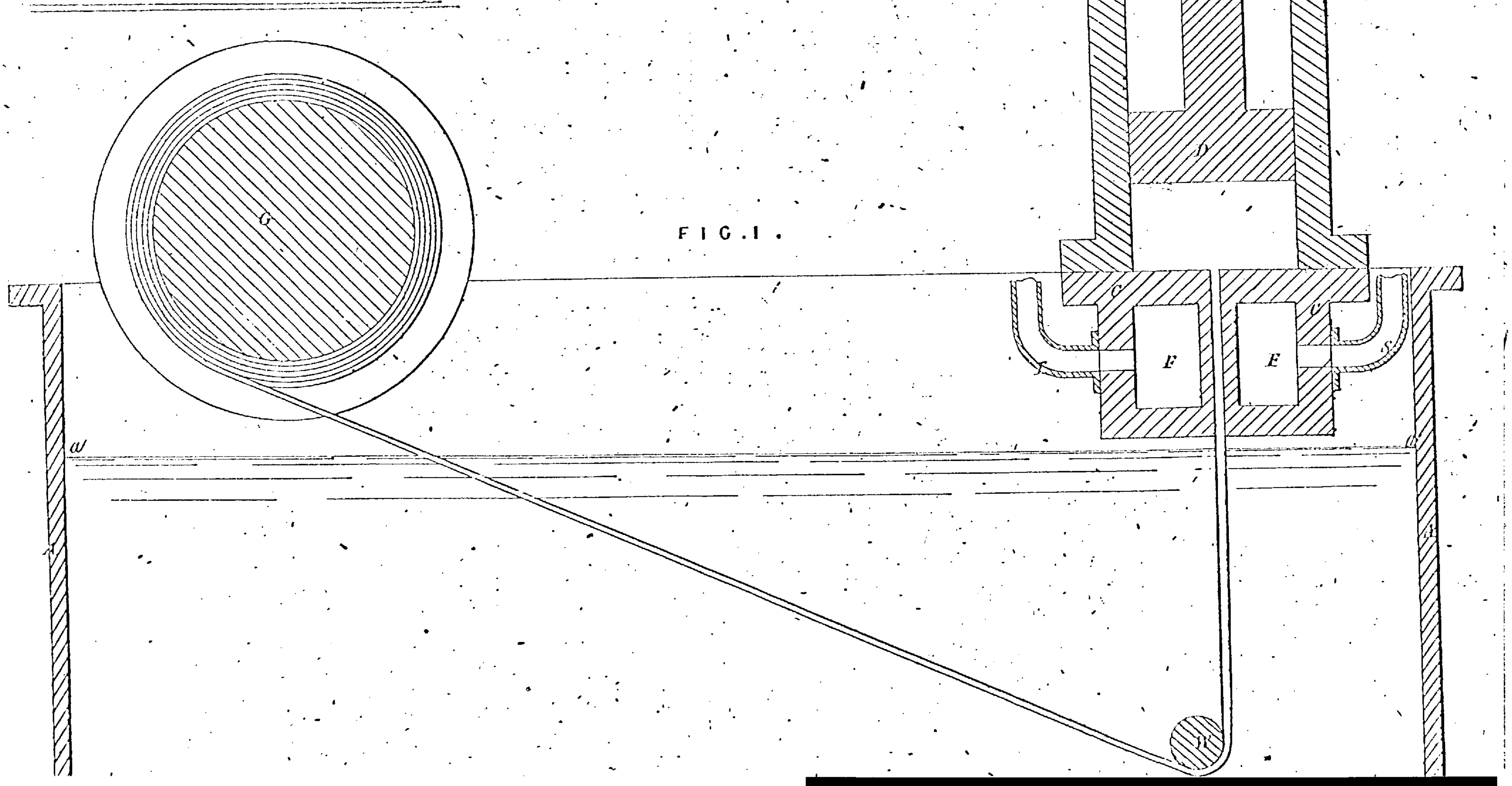

FIG. 1.

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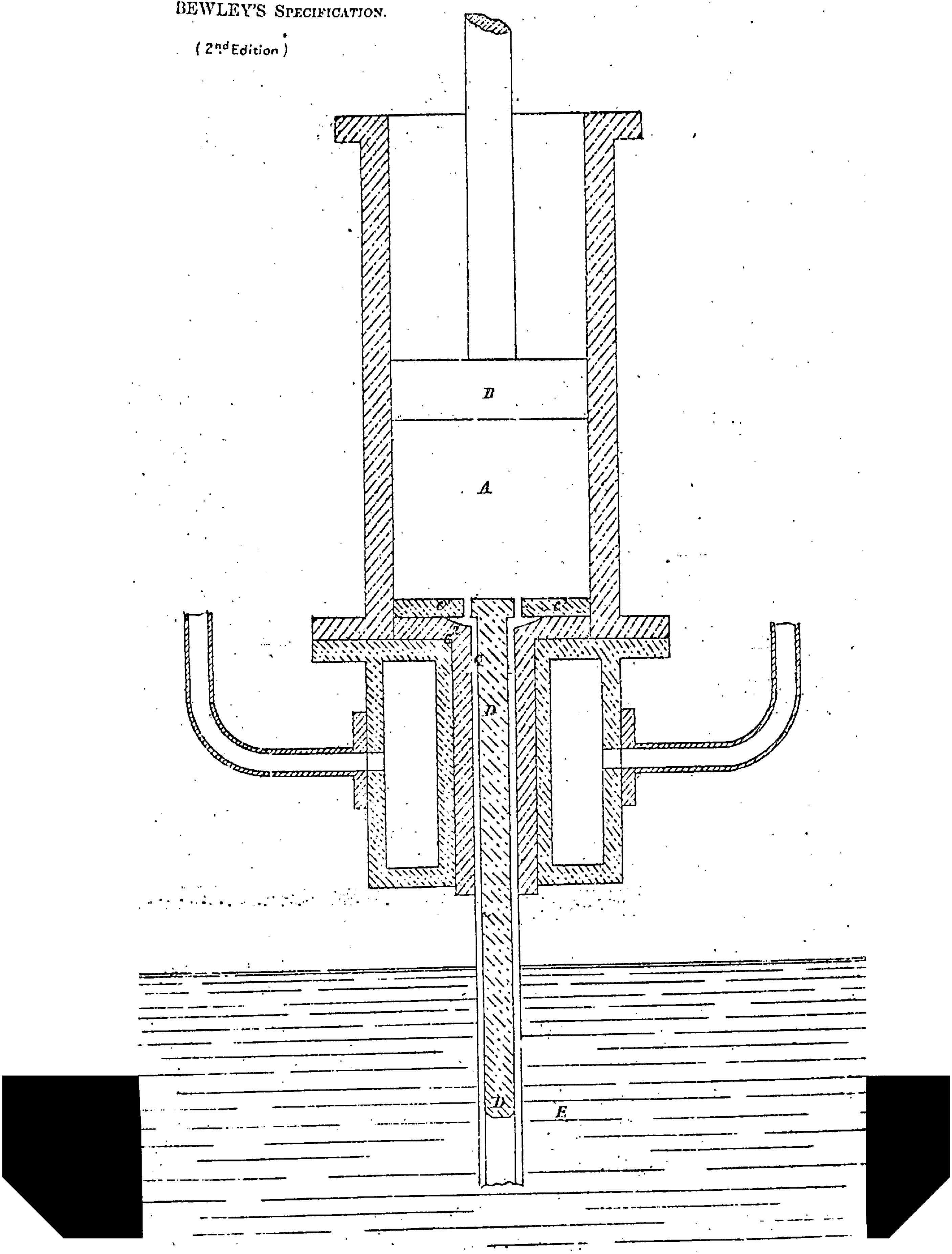
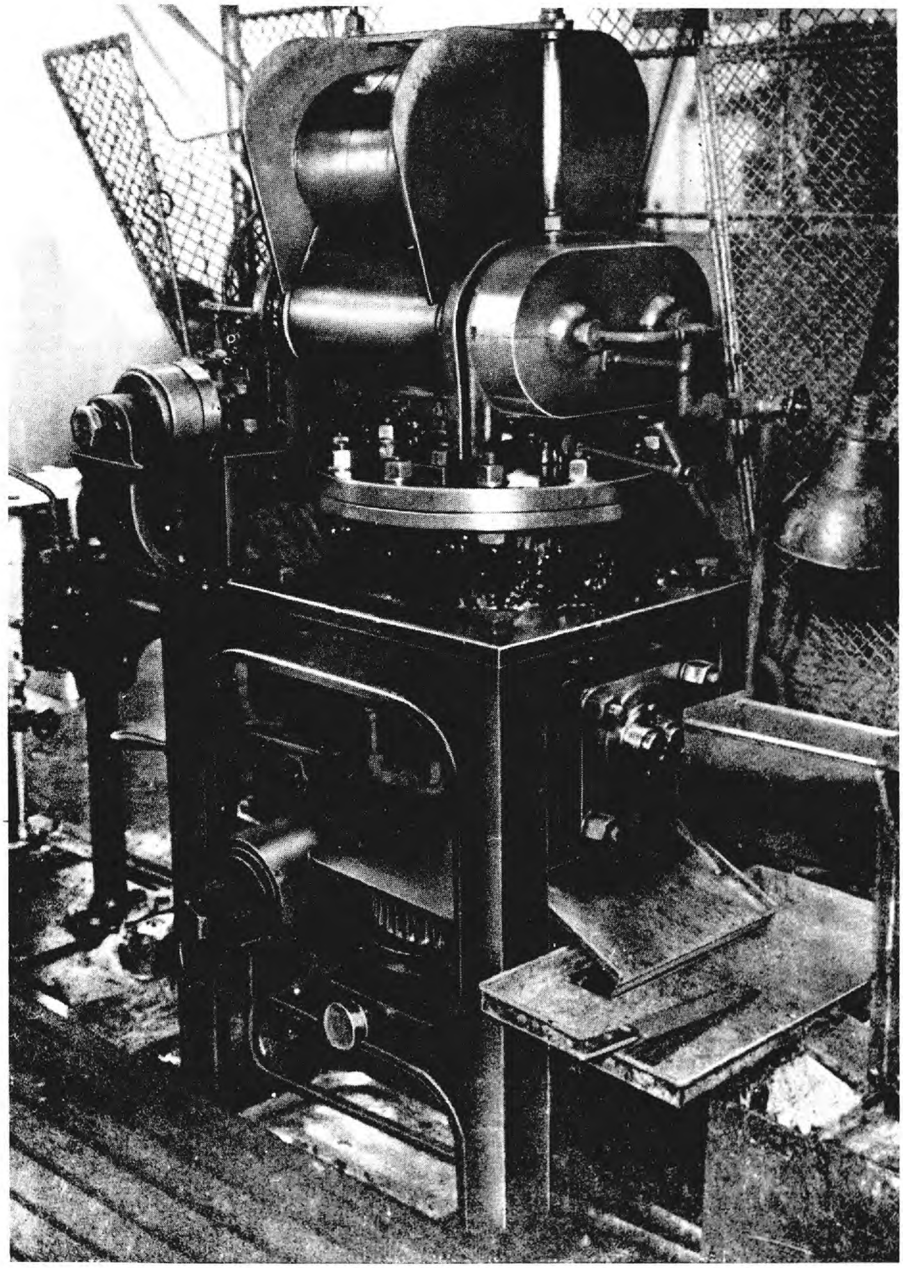
Fig. 3.

A.D. 1845. Sep. 4. No 10,825.
BEWLEY'S SPECIFICATION.

(2nd Edition)





PHOTOGRAPH a

This machine was in turn adapted by Bewley's partner in the Gutta Percha Co., Charles Hancock, to serve as a wire covering machine[14]. He did this by passing the copper conductor through the die box as the gutta percha was forced out, thus covering the conductor with a layer of insulant. The first submarine cable, laid between Dover and Calais in 1851, was covered in this way.

Such extrusion technique however was hardly consonant with the production of mile upon mile of cable. The need for a continuous process rather than this intermittent means of insulation would have seemed clear. But it was not until 1887 that Willoughby Smith, an employee of the Gutta Percha Co. patented improvements in "Apparatus for Covering or Insulating Wire"[15].

The invention was concerned with the processing of gutta percha and it provided for a continuous feed from a hopper through hot feed rolls into a chamber which was fitted with a gear pump. The material was thus fed under pressure into a box which was traversed horizontally by the wire which was to be covered, the wire when covered, leaving the box through a die. (Photograph (a)).

The Smith machine persisted in use for gutta percha cabling until the naturally produced insulant was completely replaced by the more efficient, modern and synthetic, polyethylene. With the demise of gutta percha the ram and gear type extruders have become almost extinct, though the former type continued in use for the processing of celluloid and indeed is still used to extrude phenolic tubes, amongst other things.

Since the extrusion of celluloid had a direct bearing on some of the techniques initially employed in the extrusion of pvc it might not be inappropriate to describe briefly the method used for the production of celluloid tubes. It was characterised as the "wet process" and was so called because the polymer was softened by the addition of some solvent. This was necessary because celluloid is a highly flammable material which might be ignited if it was processed in the dry state.

Typically the extruder consists of a cylinder about "30 inches long and 7 inches in diameter heated by an external jacket. The roll of (softened) celluloid is placed in the cylinder and one end is closed by a firmly secured head which carries the die assembly. A closely fitting hydraulic ram, lightly compressing the material against the head of the machine closes the other end of the cylinder. The die and the cylinder are then heated to about 185°F and after allowing two hours for the roll of material to warm up, the hydraulic pressure on the ram is increased to 2000 p.s.i. causing the celluloid to extrude from the die. When empty the cylinder is recharged by cooling the die, withdrawing the ram and putting in a fresh roll of material"[16]. (Photograph (b)).

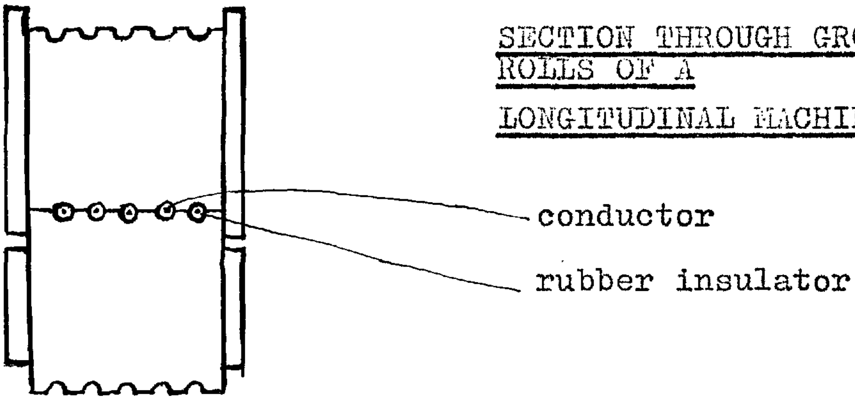
Another type of continuous extruder was produced and brought onto the market by Iddon of Lancashire. In this machine rubber was fed between rolls and as it emerged it was forced from the rolls into the throat of a tube whose far end was closed by a die. Iddon continued to make these extruders for a number of years for the production of solid tyres for cabs.

A machine which provided a method for insulating wires with rubber although it was not an extruder, was the so called "longitudinal covering machine"[17]. It is mentioned here because for a brief period towards the end of the 1930's and in World War II intensive efforts were made to use it

PHOTOGRAPH b

for pvc insulation. The earliest form of the process consisted of passing the conductor between two sheets of rubber into two single grooved rolls, which moulded the insulation in tubular form around the wire. In later versions the single grooved rolls were modified so that many grooves, eventually 36, could produce many coated wires simultaneously (Fig. 4).

Fig. 4.



SECTION THROUGH GROOVE ROLLS OF A LONGITUDINAL MACHINE

Mr. Harold Wilson of Telcon, a firm which is a direct descendent of the Gutta Percha Co., has told me that this process was very widely used by cable companies between the wars. When pvc came onto the scene, his company tried very hard to substitute it for rubber in the longitudinal machine but all to no avail. While the natural tack, or stickiness, of the rubber ensured a good bond between the two calendered sheets when they were brought together in the groove, pvc, without this tack, never welded adequately and generally broke down electrically along the weld line. This experience was confirmed. in a paper by H.J. Tew[18].

The most fruitful development in this field of processing, however, has been that of the screw extruder, the birth of which is generally linked with the patent of

Matthew Gray in 1879[19]. There is evidence, however, suggesting that this invention was anticipated both in Germany and the U.S.A. The Pheonix Gummiwerke has published a drawing of a screw dated September 18th 1873 (Fig. 5) while V.M. Hovey in a paper on the history of extrusion equipment[20] has adduced strong circumstantial evidence supporting the contention that a Mr.A.G. De Wolfe was insulating wire, with a composition dubbed Kerite, by means of a screw extruder some time in the 1860's, possibly 1866.

It may be helpful in following the ensuing discussion if, at this point, the salient features of thermoplastic extrusion and extruders are briefly elucidated. The object of the operation is to continuously convert plastics in granule form into a given shape, for example a rod or tube or profile of less regular or simple shape. Thus the granules are fed through the hopper into the flights of an archimedian screw which fits fairly closely into the barrel The latter has a number of collar heating bands which control its temperature and thus give rise to several temperature zones along the length of the barrel. The plastic material is forced forward by the rotating screw and as it moves forward it is softened by the frictional heat developed through the shearing action of the screw on the polymer, supplemented by the heat conducted from the barrel wall. By the time it reaches the end of the screw the material is molten and in this state it is forced through the die whose configuration it takes up. The extrudate is then cooled as it is hauled off.

As the diagram (Fig. 6) shows, a breaker plate and screen pack are normal parts of a plastics extruder. The plate is a sturdy steel disc drilled with a number of holes (about a quarter inch in diameter) and it supports the screen pack which generally consists of several wire gauzes varying in

PHOTOGRAPH C

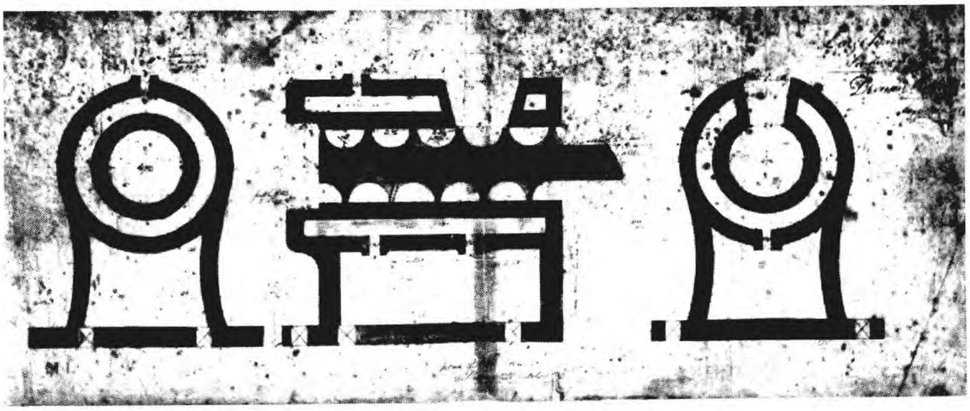
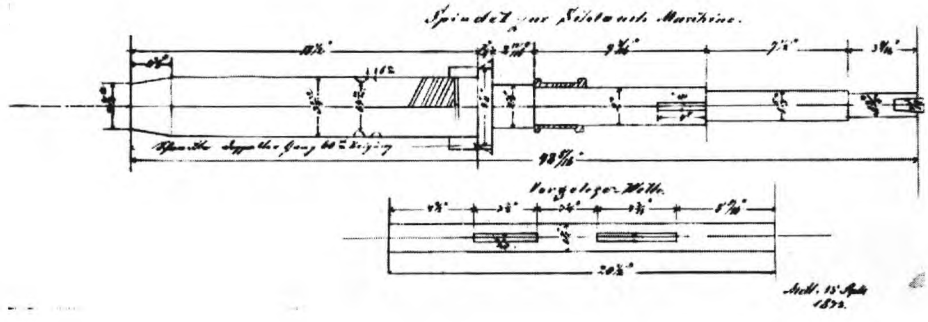


Fig. 5



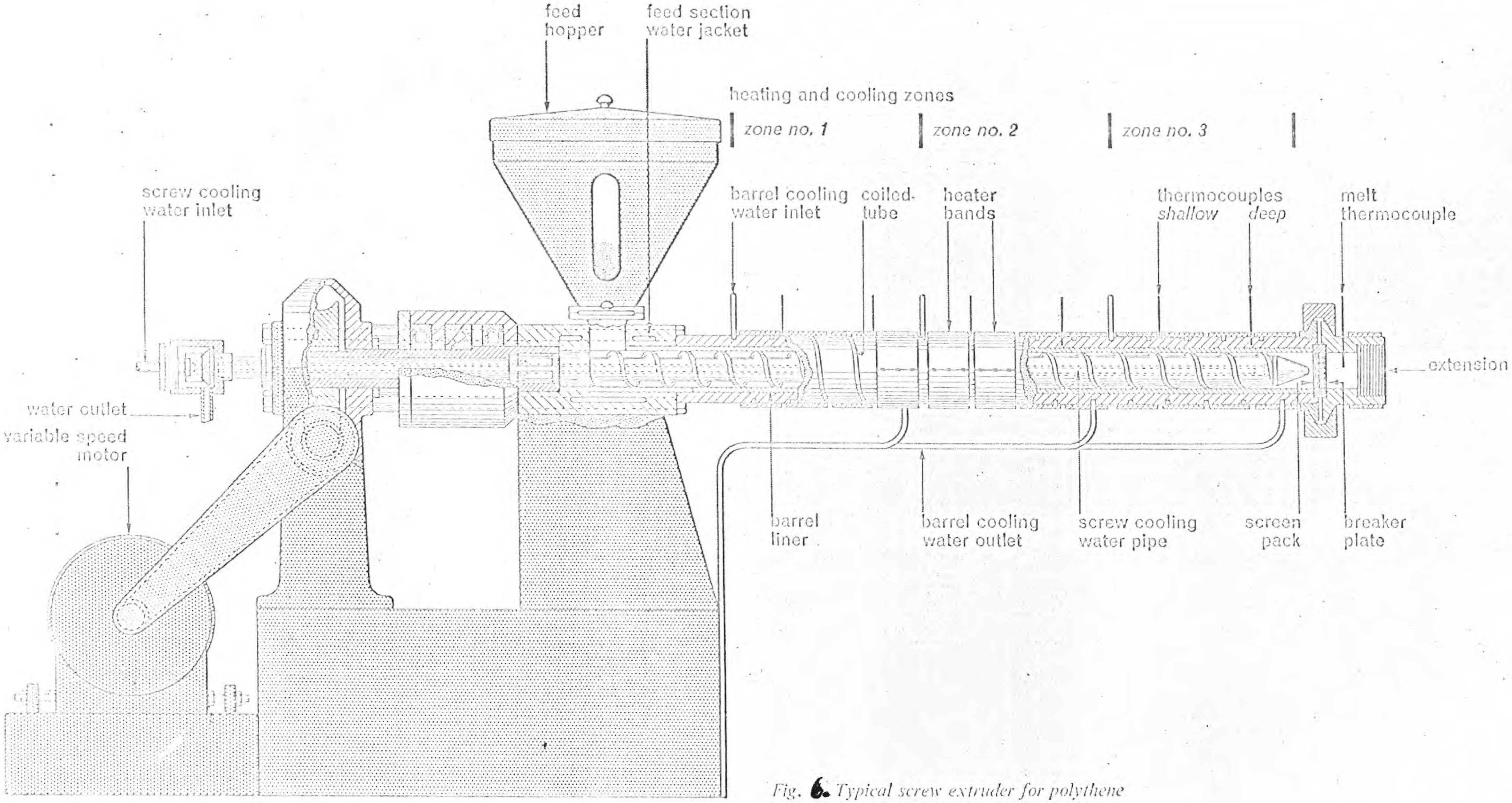


Fig. 6. Typical screw extruder for polythene

mesh size. This assembly prevents grosser contamination from coming through to the die and it ensures the arrival of a more uniform plastic melt. In addition its presence creates an obstruction to the flow of material which raises its back pressure in the barrels of the extruder and so increases the shearing action, or working, to which the plastic is exposed.

In these circumstances a considerable source of power must be made available not only to drive the material forward but also to develop the heat, which is a basic requirement of the process. Thus a motor of about 7 horse power is required for an extruder with a 30mm diameter screw and this goes up to about 75 h.p. when the screw reaches 120mm. A domestic vacuum cleaner takes a ½ h.p. motor.

A careful examination of the screw in the diagram will indicate that this is not the simplest item of the extruder but we shall consider its evolution in due course.

To date, Gray's patent remains the first clear exposition of this type of machine, the object of which, he said, was to "supply india rubber, gutta percha and similar plastic compounds to moulding or shaping dies, free of air, comparatively free of moisture and that at a uniform or unvarying pressure".

To do this he used "the arrangement of machinery shown in the accompanying drawing (Fig. 7) for feeding plastic compound to the die box.

"A is the ordinary cylinder which carries at one end the die box B and is closed by a cover at its other end. In this cylinder is mounted a propelling screw C for forcing the plastic material through the die". Here was the crux of the invention and the basis upon which future extruder designers built. Gray also incorporated a pair of heated

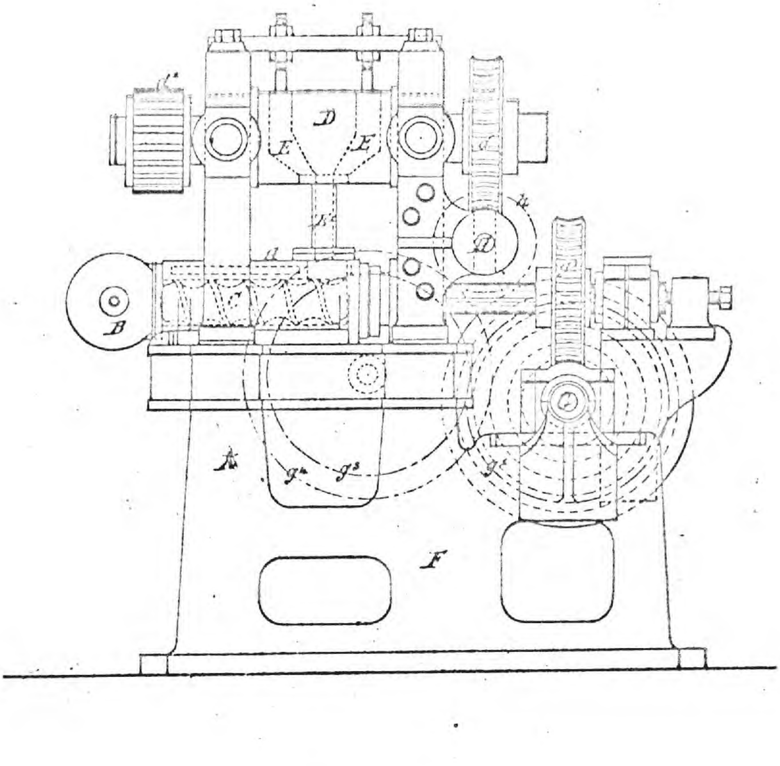
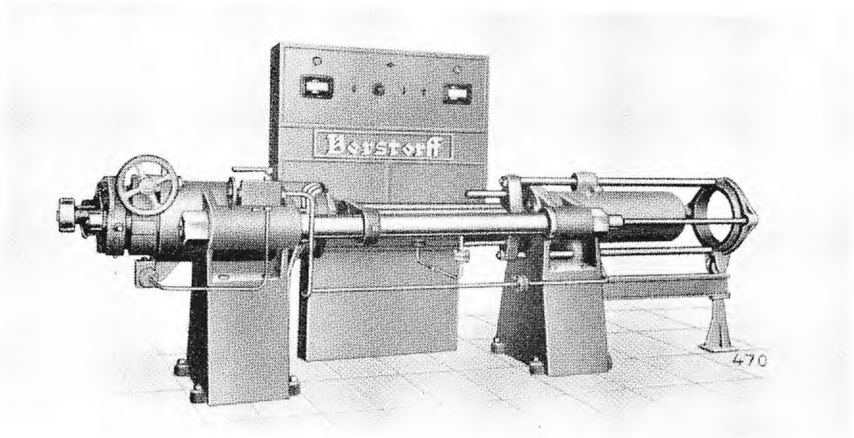


Fig. 7



PHOTOGRAPH d

not suitable for larger bore tubes (say above 10mm)[21].

The 250mm "presses" each produced a total pressure of 100 tonnes, equivalent to 20 kg/cm.^{2} The barrel, made from ordinary steel, was electrically heated to keep the pvc at 150-160°C, while the die was maintained at 210-230°C. A 20kg billet of pvc was loaded into the barrel and after extrusion at the rate of about 2 metres per minute, gave a length of tube which depended on its wall thickness. The largest pipes produced were 15 cm (o.d.). The extruder had to be cleaned after each batch and all in all each cycle required thirty to forty minutes.

At Deutsche Celluloid Fabrik at Eilenburg six similar machines were steam heated (even more like the original celluloid equipment) and they worked at a barrel temperature of 160°C and a die temperature of 170°C. Their largest pipe was 16 mm in diameter with 8 mm walls and was extruded at 4-5m per minute.

However such ram extruders, or "stuffing presses", as they were sometimes called, suffered the limitation associated with intermittent working whether they were processing gutta percha, celluloid or pvc and so appear historically as a <u>cul de sac</u> in the evolution of pvc processing methods.

Plasticised pvc is a rubbery sort of material and so the other obvious approach to extrusion was on the screw extruder. Those workers who regarded pvc as a substitute rubber began their experiments on rubber extruders in the early or middle 1930's, coincidentally with their more celluloid orientated colleagues. They found that pvc could be extruded on these machines, in fact it was so processed on a limited scale for a number of years before and during the war. But rubber extruders were designed to extrude rubber whose flow behaviour, amongst other things, is very different from that of pvc and whose processing circumstances in general are so much at variance from the newer material.

E.G. Fisher in his book on the "Extrusion of Plastics" has explained so well how the characteristics of a rubber extruder stem from the needs of the process that I can do no better than quote the relevant paragraphs. "The first screw machines were produced for the processing of rubber and were intended to receive hot stock in strip form directly from a two-roll mill. The extrusion machine therefore had little to contribute to the stock by way of heat and was looked upon merely as a means of masticating it and continuously shaping an already heated material by forcing it through a die... The barrel and die were heated chiefly to avoid the lowering of stock temperature by radiation losses.

"In order to satisfy these requirements, the following features were necessary:-

a) a feed port, placed tangentially to the screw and a driven feed roll to facilitate hot strip feed;

b) a screw and barrel just long enough to compact the material and force it through the breaker plate [on the infrequent occasions when it was present] and the die;

c) the barrel to be heated to a relatively low temperature - usually by steam - in order to conserve heat in the material;

d) a water-cooled feed port and screw to prevent sticking and precuring of the stock respectively;

e) the feed screw to be deeply cut in order to accept a large volume of material and designed with decreasing pitch to give a compression ratio without unduly increasing the amount of shear;

f) the screw to be driven at a relatively low rotational speed in order to avoid excessive frictional heat;

g) as a result of the above points, the machine need not be particularly robust in its construction and thrust bearing arrangements and the drive motor can be relatively small".

The story of the emergence of machines well suited to extrude pvc, and other themoplastics for that matter, is in fact the history of the gradual modification of rubber extruders as described in the preceding paragrph.

Mr. Fisher's first point was concerned with the extruder arrangement to receive the supply of rubber in the form of a hot strip. This arose naturally from the preceding rubber process which consisted of the preparation of the rubber compound in an internal mixer, followed by a sheeting operation on a hot two roll mill, followed by the cutting of the sheet into strips. These were then fed hot, as they came off the mill, into the extruder.

To begin with pvc was treated in the same way. Dr. Raalf of Dynamit Nobel has described how gloved workers moved pvc strips from preheating ovens to the extruder. The pvc which was imported from another factory, unlike the rubber which was normally compounded on the spot, had to be specially preheated.

Telcon in Britain, which had developed in the gutta percha tradition, asked the David Bridge Co. to put feed rolls on the rubber extruder to force the pvc into the barrel. This was a reversion in 1936, or thereabouts, to the original Gray arrangement of 1879 but Telcon preferred this to preheating pvc strips in ovens or on hot plates, their first method of feeding the new compound.

Herr Theysohn of Troester told me that cold feed first appeared in Germany in 1939. The shift from the use of hot compound occurred because pvc did not in the nature of things arrive at the extruder while hot, as did rubber. A second important reason was the variation in the temperature of the material arriving in the barrel. It took at least some minutes to feed in a length of strip and in this time cooling brought about a temperature change within the feed. This in turn led to variation in behaviour inside the barrel and variable pressures at the die orifice.

The alternative to hot strip feed was the supply of pvc in granules. It was supplied by the manufacturers in this way and loaded from bags into a hopper which was situated at one end of the barrel; a method, incidentally, which had already been applied in injection moulding.

A further modification of the rubber extruder arose from the need for higher processing temperatures required for pvc. It appears that the first electrically heated machines were introduced by Horst Heidrich, an electrotechnician in Germany, on small versions of up to 30-35 mm diameter. He first made them some time before 1933 because Mr. Hornung who left Germany for England ("on the day after the Nazi stormtroopers' torchlight procession at the Brandenburger Tor") in that year established Suflex Ltd, to continue his insulated electrical wiring business and managed to transfer some of his Heidrich extruders to this country. At least one of them is still operational although it is difficult to say whether its present form incorporates any significant modifications.

The first systematic approach to the problem of plastics extruders seems to have come from Paul Troester who, in response to stimulation from I.G. Farben, built small laboratory machines. The polymer producers asked for longer screws and higher temperatures and the Type HLSFE was the Troester solution in 1935. The barrel was heated by high-pressure steam and the die was electrically heated. They made four or five such machines in that year[22].

A "root and branch" attack, rather than piecemeal change of the rubber extruder had to wait until 1937 when Colin Ratcliffe, chief engineer of the Francis Shaw company, decided that pvc was quite a different material from rubber and hence needed an extruder of correspondingly different design. The company had become familiar with pvc following its production of the first U.K. made injection moulding machine in 1931. The advent of this machine had brought Mr. Frank Shaw, Chairman of the company, into contact with Mr. Peter Delafield, who was later responsible for sales of I.G. Farben pvc in Britain. The latter so convinced the Chairman of the bright new future for this new material, in spite of the wall of apathy and even hostility which it was then meeting, that Shaw decided to proceed with the production of an extruder designed specifically for pvc. It was even called the "Mipolam Extruder" for a while.

There were three major departures in the new design, as compared with the machines that were then in use. The first was electrical heating. Although this was not a pioneering effort, as we have just seen, it contrasted with contemporary practice and confirmed the Heidrich development. The second feature took into account the thermal instability of pvc and the consequent evolution of hydrochloric acid by building the barrel and screw from Nitralloy, a hardened and corrosion resistant steel. The use of special steels for barrel lines and screws became normal practice thereafter.

The final major innovation in the Shaw pvc extruder was the increase in length to diameter (L/D) ratio of the screw.

In many respects this component constitutes the heart of the extruder and its design is of crucial importance. As has already been pointed out, the length of a rubber barrel and screw has to be sufficient merely to compact the rubber strip and force it through the die, that is to change its shape. Furthermore, since the rubber is normally fed hot, there is no need to add heat to the mass other than to compensate for radiation losses. Thus the rubber screw had, and indeed has, an L/D ratio of about 3-4 to 1. But it soon became evident that this was quite inadequate for a cold granular feed of pvc. The material was simply not hot and fluid enough by the time it reached the die and therefore did not emerge as a uniform smooth extrudate.

Various ad hoc remedies were applied and rejected or developed as experience dictated. The difficulty was to find a solution between the scylla of inadequate plasticising and the charybdis of overheating and decomposition. Merely raising the temperature of the barrel or gas heating the die, for example, would increase the quantity of heat passing into the pvc but with the distinct danger of local overheating. Another method of coping with the situation was to increase the residence time of the polymer in the barrel by slowing down the rate of movement.

This last sentence does not put the problem quite as the workers then saw it. To put it in more realistic and immediate terms, they were conscious of the fact that putting pvc through a rubber extruder allowed of adequate quality extrudate only at very low rates of output and they had to raise productivity to make the new material viable, competitive and attractive.

Preheating the feed obviously contributed to the heat content of the pvc in the extruder and was helpful, from this point of view. Some workers tried preheating granular feed, as an advance on pvc in strip form but the practice was rejected for the reasons already discussed.

Lengthening the screw and barrel as proposed in 1937 from an L/D ratio of 3 to 1 to about 8 to 1 offered a way out of the difficulty. A longer barrel allowed more heat to flow into the polymer without raising the temperature but equally important, a longer screw exposed the pvc to more shear, or working, and hence the greater generation of heat within the mass of material. The proportion of frictional heat was growing and this was good because the conduction of heat from the barrel is slow and inhibited by the thermal insulating properties of the material.

For the same reason the depth of the flight of the rubber extruder was reduced. A shallower flight increases the shearing action on the pvc granules and produces more heat but this point had to be watched very carefully because too much working leads to thermal decomposition of the material.

To increase the work done on the polymer the rubber extruder was further modified by the insertion of a breaker plate and screen pack (that is a fine screen, see Fig. 6). One cannot ascribe a precise date to the introduction of this feature of the plastics extruder, since it was used from time to time in rubber processing to prevent contamination from reaching the die. In carrying out this function the breaker plate was not allowed to seriously impede the flow of rubber. For pvc extrusion however it was found to be a positive advantage to place such a restriction across the flow of the material, not only to ensure a clean extrudate but to build-up the back pressure inside the barrel and so increase the generation of heat and thus produce a more uniform polymer melt.

The screw L/D ratio did not long remain at 8 to 1. After the war it continued to grow. By 1945 11 to 1 was common[23] and at present it seems to have reached equilibrium at about 20 to 1.

Screw design responded in another way to the change from rubber strip feed to pvc granules. For rubber the function of the screw was simply to deliver the rubber to the die for reshaping. It was therefore simple and uniform in design or at most with a constantly decreasing pitch along its length towards the die. The depth of the flight of the screw was as big as practical so as to give as big a volumetric capacity as possible. With granular pvc, account had to be taken of the fact that the bulk density of the feed was lower (that is unit mass occupied a greater volume) than strip rubber. Hence there was a greater compression on plasticisation which had to be reflected in the ratio of the volumetric capacity of the flight at the feed end to that of the die end. This was the origin of the characterstically three zoned screw of the plastics extruder. The feed zone relatively deeply cut with a large pitch followed by the compression zone designed to compact the material as the polymer changes from a solid to a molten condition and finally the metering zone arranged to deliver the melt to the die at constant volume and pressure.

Screws of many designs have been produced and their performance examined with the whole range of polymers. Many contradictory recommendations have been published as to the most effective screw for a given polymer, which suggests that even now we cannot be sure about the best design for pvc, rigid or plasticised. Tracing the development of the screw in this respect is therefore difficult but it is interesting to observe that in an article on "The Extrusion of Plasticised

PVC Compositions" published in 1945, the author in discussing the "design of the worm" spoke only in terms of variation of the pitch of the screw[23]. Another author writing in 1948 discussed not only the pitch but also the depth of flight but he did not yet refer to the three zones[24]. It was only after 1950 that the value of metering zones ~~were~~ was recognised[25].

The use of cold feed and the thermal instability of pvc as compared with rubber imposed further modifications on the extruder. Whereas until the advent of pvc temperature control was of no great concern to the processor, he more or less hoped it was within the range required, this casual attitude was not possible with pvc.

The point was made with great force by E.L. Midwinter in his paper in 1945 on "The Extrusion of Plasticised PVC Compositions"[26]. "Correct gradation of temperature at different parts of the machine is exceedingly important. The degree of softness of the plastic must increase as it approaches the die and for this reason temperatures of the barrel, head and die should increase in that order. Higher temperatures in the barrel than the head cause a back flow since the viscosity of the material in the head is higher than that in the barrel. Thus production rates are reduced with the attendant risks of decomposition of plastic due to prolonged exposure to high temperatures.

"Local hot or cold spots also disrupt flow by causing back flow and turbulence".

The author went on to consider three aspects of temperature control which demand close attention: the effects of machine design, the efficiency of heating systems and temperature measurement. We have already considered aspects of the first two and on the third point the author said "Temperature measuring points should be as near the plastic stream as possible and not on the outside of the machine ... The most convenient arrangement is to have all thermocouples linked up to one control board ... For conventional machines the temperature should be recorded at the hopper and head extremes of the barrel, one or two points along the head run depending on length, and at the die as near the orifice as possible".

The article makes it clear that in 1945, while those 'skilled in the art' of pvc extrusion were already aware of the qualitative change in the nature and sophistication of the extrusion process being ushered in by pvc, many extruders of this material were still blissfully ignorant of these vital considerations.

Writing for an American readership W.F. Hemperly was saying much the same thing. (It is interesting to note in passing that both he and Midwinter were working for polymer manufacturers who found it essential to educate their customers in the handling of their materials, in order to create a market for the new polymers). Hemperly also had a word for the machinery manufacturers in pointing out that the thermal sensitivity of pvc demanded "thorough streamlining of all internal parts of the extruder and the elimination of all pockets where the material might stagnate ... Open joints between fitting members, abrupt shoulders in the path of resin flow, particularly in the head and die will cause stagnation of small quantities of materials which will in turn result in decomposition".

Concerned with the possibility of thermal breakdown he went on to say that "it is for this same reason that the use of breaker plates and screens which are difficult to streamline properly is not recommended for the extrusion of rigid type vinyl resin compounds although their use is desirable when plasticised compound is extruded".

The modifications of the rubber extruder to fit it for the processing of pvc, and other plastics, pointed in one direction, at least in so far as size was concerned. The screw and barrel were longer and stouter, the motor to drive the screw against considerably increased resistance had to be much more powerful, the bearings had to be correspondingly more substantial. Altogether pvc extruders came over a period to assume the robustness characteristics of plastics machines as compared with their rubber counterparts.

Before leaving the subject of extruders, a very brief reference will be made to the twin-screw variety. Its origin is generally ascribed to Roberto Colombo in his Italian patent of 1937[28]. The Germans were quickly interested in its possibilities and experimented during the war with Colombo machines and Eckert and Ziegler modifications of them[29]. Dynamit Nobel at Troisdorf installed six Italian twin screw extruders early in the war for polystyrene and pvc and used one of them for unplasticised pvc.

Judging from the length and detail of the description of this type of extruder in the B.I.O.S. report, the machine seems to have been new to the British investigators and was worthy of "evacuation" to England for more study.

Such study resulted in further development of the twin screw machine, not only in England, though it has not achieved the ubiquity of the simpler single screw version.

Calendering

Like extrusion, calendering is a process which is very simple in concept. It involves the passage of a suitable material between heated rollers to form sheeting of required width and thickness. But simple though the concept be, its achievement in practice has proved to be no easy matter.

It all started with the machine first built by Edwin

Marcus Chaffee of Roxbury, Mass. U.S.A., whose contributions to the foundation of rubber industry have received less than their due. In 1835 he patented the two roll mill, or "preparing machine" as he called it, in which the rubber stock was compressed and mixed with other ingredients between two steam heated iron rolls. In the next year he developed the calender from this and patented both machines in 1836[2].

His main intention was to eliminate the use of solvents in the application of rubber to fabric, or any other base. From 1832, the year in which his Company, the Roxbury India Rubber Factory, was established "for the purpose of manufacturing ... india rubber cloth and leather and other india rubber goods", his process consisted of the application of a solution of rubber in turpentine. In 1835 he proposed to his fellow directors the use of a new machine which could save the Company the $50,000 per year it spent on solvent and speed up operations as well. Notwithstanding the enormous cost of the proposed calender, $30,000, the idea was approved and Chaffee's "Monster" saw the light in the following year.

The diagram of the machine (Fig. 8) is taken from Chaffee's patent specification in the London Patent Office, but as there is no text available in the London records the following description has been culled from Henry C. Pearson's book on Rubber Machinery (1920)[30].

"It had four steam-heated rolls, A, B, C and D. The rolls A and D were 18 inches in diameter while the other two were 12 inches in diameter. Roll B was geared to move slower than the others, providing friction between A and B and also B and C. Where it was desired to use only three rolls, the upper one was disengaged and cloth passed into the machine between B and C. This cloth on a roller E was passed around

E. M. CHAFFEE.

Making Rubber Fabrics.

Patented Aug. 31, 1836.

Fig. 1.

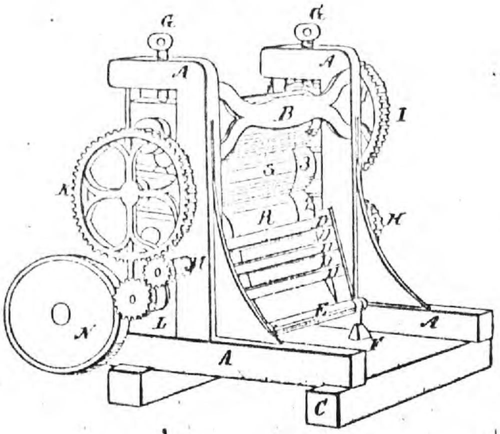


Fig. 3.

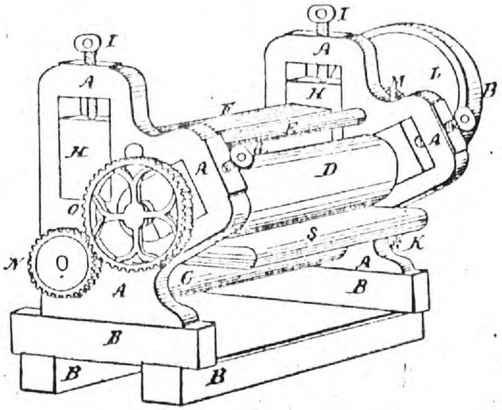


Fig. 2.

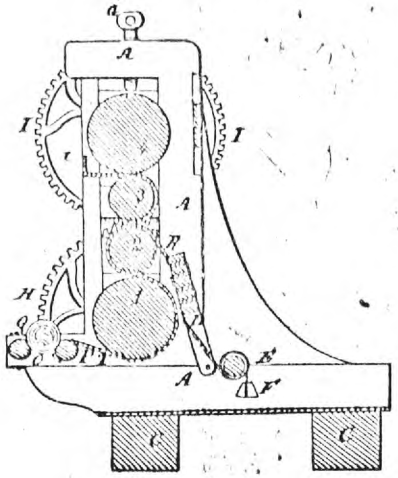


Fig. 4.

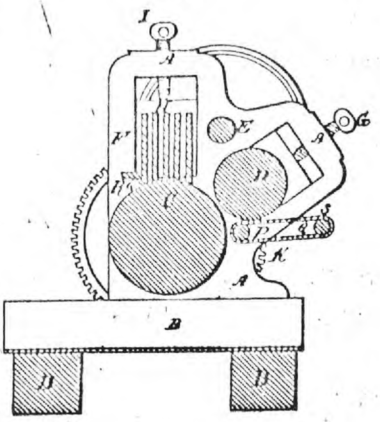


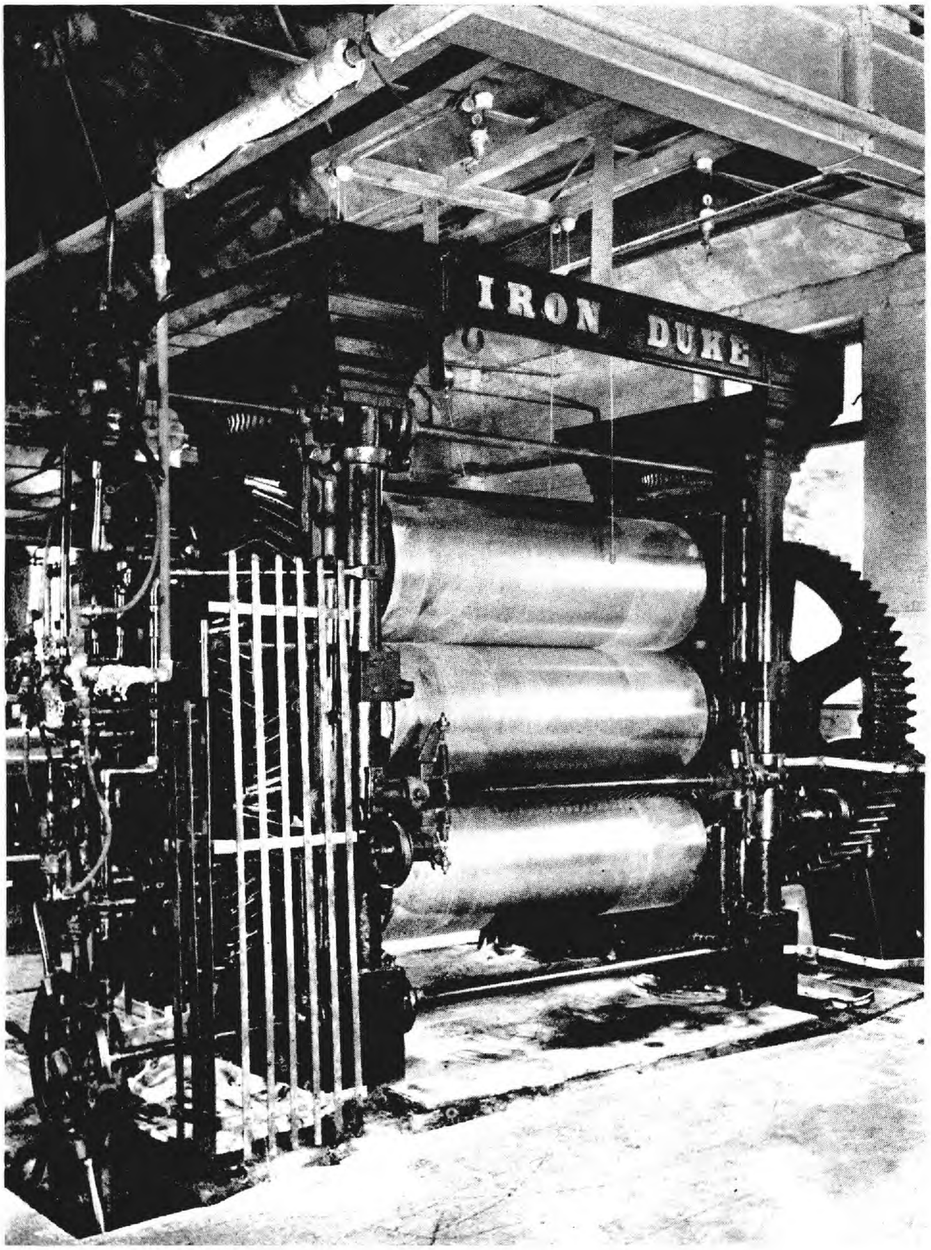
Fig. 8

a number of bars, F, to provide tension. The rubber was fed between A and B, passing around B and coming in contact with the cloth between B and C, where it was pressed into the fabric. The double sheet then passed around C and D and was wound up on roller G".

Charles Goodyear, the discoverer of vulcanisation of rubber was immensely impressed with the Chaffee calender. In his book, Gum Elastic published in 1855, he expressed his admiration of the calender and the two roll mill in the following eulogy "It is now generally agreed by manufacturers in this business that the machinery or at least the principle of it, is perfect. It is hazardous to express an opinion in this age of improvement that any machinery or thing is perfect; but the reason for believing that this machinery does not admit of further improvement in principle is that no complaint is made of it. It is of the simplest kind, doing the work with greater rapidity, although it requires great mechanical power owing to the toughness and tenacity of the gum"[31].

In England the first calender was built around 1840 and was still in operation in 1954, while the "Iron Duke", a three roll calender whose rolls were all about 26 inches in diameter, was made in 1849 and it too is still in use in the works of G. Spencer, Moulton and Co. Ltd. at Bradford-on-Avon. These were made with a view to manufacturing rubber sheeting as well as rubberized fabric. (Photograph (e)).

Pearson, writing his description of Chaffee's calender in 1920, said that "it differs very little in principle from the machine manufactured today" and H. Willshaw in his book on "Calenders for Rubber Processing", published thirty six years later echoed the thought in his observation that "there are probably many other calenders now approaching an age of 100 years ... the basic design having changed but little during that time"[32].



PHOTOGRAPH e

Notwithstanding Goodyear's views on the perfection of the calender it might be a worthwhile study to consider how, in a progressive industry, a processing machine could remain viable and economic after 100 years. Whatever the reasons, it seems that significant developments in design of calenders coincide with and were in fact stimulated by the desire to make pvc sheet. Indeed Mr. Ryding, Chief Engineer of Iddon Bros. of Leyland, made the interesting and historically very significant comment that his company came into the plastics business through the complaints of some of their customers who used Iddon machines, designed for rubber, to calender pvc.

Calendering pvc really became feasible when Wick in Germany and Semon in the U.S.A. discovered that it gelled at a temperature of about 150°C or more. This indicated that for successful processing, rubber calenders would have to be modified at least with respect to the upper temperature limits of the machine. In 1935, the year of Wick's discovery, workers at the Deutsche Celluloidfabrik, Eilenburg, had successfully made pvc sheeting on the calender at about 180°C, that is at least 60° above normal rubber calendering temperatures[33]. In the following year, 1936, Fikentscher and his colleagues (H. Jacqué in particular) at Ludwigshafen began their investigations into the dependence of the mechanical properties of pvc upon K-value and processing temperature and from that emerged the calendering technique used in the production of so-called <u>Luvitherm</u> a form of pvc sheeting which was especially strong.[34]

Development of the calender and calendering techniques for pvc also occurred in the U.S.A. and to judge by its leading position in that field after the war progress must have been marked and interesting between 1935 and 1945. But as with other aspects of this study, it has been difficult to piece together a coherent picture from this side of the Atlantic, so that I shall confine myself to European, and in the main German progress.

PVC was calendered in several forms from 1935 onwards. At Dynamit Nobel, for example, they made calendered sheet from Hard Mipolam (unplasticised pvc) which they sold as Vinidur. They also manufactured plasticised pvc sheet, as well as material made from vinyl chloride copolymers[35]. Manufacturing conditions varied only marginally however in operating temperatures and in calendering speeds. The differences certainly did not require changes in calender design. Even Luvitherm manufacture, which involved a considerable departure from normal practice by calendering at low temperature then passing the mechanically weak film over a roll at very high temperature (over 200°) and finally stretching it both in the direction of and at right angles to the length of the sheet[36,37,38], even this process did not impose any changes on the design of the calender itself, though it did, of course, call for a special stretching device.

But calendering pvc differed substantially from the rubber process and that became obvious from the beginning. PVC processing was more demanding in at least three respects. I have already referred to the higher operating temperatures. The second feature was the need for a much closer control of the thickness, or gauge, of the film. G.V. Kullgren described the situation clearly in a paper read in 1949[39]. He said "... such a machine, in the hands of a skilled and experienced operator and under favourable conditions, can produce rubber sheeting within a thickness tolerance of ± 0.0005inch. Most production tolerances, however, are greater than that, usually in the order of ± 0.001 or 0,002 inch. One common method of checking thickness is to weigh each roll of sheeting as it is removed from the calender against a corresponding weight tolerance. This method does not tell you that any particular section of the material is within tolerances ... further it does not compare the thickness of the edge and centre of the sheet.

"A modern calender now in production 24 hours per day and seven days per week produces sheeting which must be held within a tolerance of ± 0.0002 inch".

The third way in which pvc calendering marked an advance on its rubber analogue was in the speed of operation, the rate of production in yards per minute.

Throughout this discussion it must be borne in mind that we are dealing in the main with the production of thin gauged sheeting, the commonest form of calendered pvc. This was, and is, the process which is most rigorous in its requirements and is thus the pace-setter for calendering generally. But only part of the calendered rubber output is in this form and the bigger proportion goes into coated fabric for tyres and belting, thick sheeting for shoe soles and chemical lining among other uses.

Several firms in Germany accepted the challenge of the new pvc technology and set out to make calenders specifically designed to deal with it. Outstanding were the firms Joseph Eck und Söhne, Paul Troester and Hermann Berstorff.

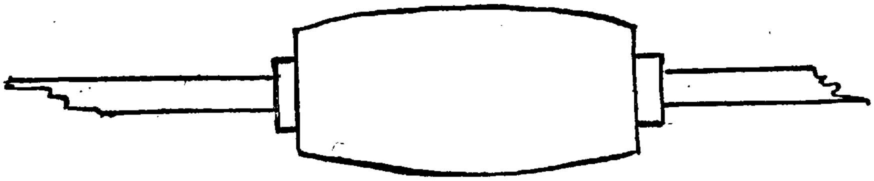
Eck's major contribution was the application of the principle of Schrägstellung, known in English as cross-axis alignment. It was applied to compensate for the roll bending which occurred, with consequent variation in film thickness across its width. In other words they developed, or more accurately, adapted, a technique for gauge control. The problem and its attempted solution might be described in this way.

The calender is a machine which basically consists of a number of cylindrical rolls mounted at their extremities in a frame. These rolls are generally several feet in length and just like a beam supported at both ends, they are subject to deflection under load, which increases as does the distance from the supports. Consequently when a charge of rubber or pvc is fed into the calender nip, bowing of the rolls leads to a sheet of non-uniform section, which at its simplest (and rather exaggerated) looks like this:

Fig. 9.

One way of dealing with the problem, long used by the rubber industry, has been to camber, or contour, the rolls so that they deviate in their outline from true cylinders to compensate for the non-uniform deflection. For example a roll might be given a convex outline in section, with a camber of several thousandths of an inch:

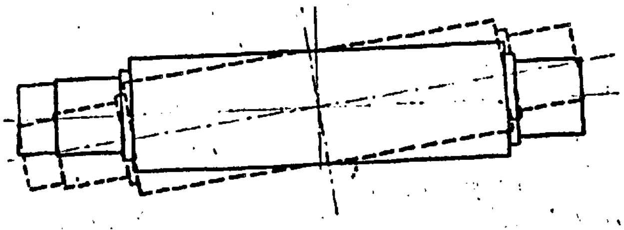
Fig. 10.



But although this is a satisfactory solution for a given set of conditions of temperature, speed and material, a change in one or more of these variables leads to a corresponding alteration of load and then the cambering is no longer correct.

This was the situation for which Eck offered their cross-axis alignment. The principle which had been used in the manufacture of mill and fibre board, involved an axial movement of one or more rolls of the calender so that adjacent rolls were no longer parallel in one plane. The diagram below (Fig. 11) shows one roll behind the other with the axis of the far one crossing that of the near roll. In this way the nip opening is greater at the ends than it is at the centre and this can compensate for roll deflection. Since the displacement, or swivelling, of the roll can be regulated, their relative positions can be varied to meet particular circumstances.

Fig. 11.



In theory this procedure is straightforward but in practice there were many engineering difficulties. Dr. R. Röhm, who directed pvc operations at Dynamit Nobel before and during the war, became well aware of them at Troisdorf. His company persuaded of the plausibility of the design, bought a four-roll Eck calender. But they were disappointed by its performance. A post-war allied investigator summarised their experience thus: "The skew-setting had been found in practice to be 'spongy' so that it was impossible to skew the rolls to a definite amount or keep the amount of skew fixed. Eventually the rolls had been set back with their axes parallel and the machine used as a conventional calender.

Despite this unsatisfactory experience, Dr. Röhm was still of the opinion that skew-setting was basically sound and should give good results once the mechanics of skewing had been put right. The Eck calender delivered to Troisdorf was of wartime manufacture and the workmanship and materials in the bearings was poor"[40]. J. Brown discussing the same problem in 1951 confirmed Röhm's view of the shortcomings of cross-alignment at that time and also justified his assessment of its potentialities. Said Mr. Brown "Devices are established by which a gauge correction by mechanical means can be obtained by cross-alignment of the rolls.

"In the past most of the devices for this purpose were considered clumsy and were seldom used by calender operators after the first setting by the engineers. The performance of the latest equipment for this purpose, operating on fine gauge plastic film, is successful and can be instantly adjusted by the calender operator with push button control during the production running of the calender"[41].

That was in 1951 and if it might give the over-optimistic impression that cross-alignment is now the complete answer to gauge uniformity, it still remains true that this principle is incorporated in the design of most modern calenders.

The Troester Company of Hanover in Germany was set up in 1892 to manufacture rubber machinery, I have already briefly discussed its contribution to extruder design and must now turn to its part in calender development.

Their experience in the years leading up to the second World War was distilled in a booklet written by their Designer, Dr. H. Decker, and published by the company in 1943, "Kalender für Gummi und thermoplastische Massen". In his forword the author said "The processing of Buna (synthetic rubber) and the new thermoplastics, predominantly pvc, has been called for in growing measure since the proclamation of the Four Year Plan and with this development new calender requirements are becoming manifest. These stem from the need for a general purpose machine which can be used for various materials and working conditions. Above all the temperature range, which is relatively limited in the processing of natural rubber, must be substantially increased.

"Working temperatures up to 250°C are necessary for thermoplastics, while Buna must be processed at about 100°C ... to be able to achieve economic speeds.

"... Further, greater claims are made on the accuracy of the rolls which must accommodate various materials of widely differing toughness and produce a range of sheet thicknesses right down to the finest film whose gauge tolerance across its width must not exceed 5 - 10μ. Detailed consideration must be given to the forces at the nip and the various factors upon which they depend, on the requisite rigidity of the rolls and appropriate cambering and all these lead to new design concepts".

Dr. Decker summarised here the "growing points" of progress in calender design as he saw them in 1943 and later in the book described the "Modern Universal Calender" which Troester put on the market to meet the new desiderata[42]. This machine was subsequently encountered and reported upon by an Allied investigating team[43].

It will be appreciated that the Troester calender incorporated many new engineering features and variants of older practice but there were several points of especial interest when tracing the historical development of calenders which will be discussed here.

The machine was of the vertical four roll type and each roll was 1200 x 500 mm. Each roll was driven by a separate regulable D.C. motor through an epicyclic gear box, the motor unit being mounted in the end of the roll. This was in contrast to the then conventional arrangement in which the calender was driven by a single motor geared to the rolls by spur gears or end wheels. The advanced nature of the Troester arrangement can be gauged from the observation of H. Willshaw in his book on calendering in 1956 that "Up to the present a single large motor has been used to drive the rolls but the latest development in this connection is to use a single motor for each roll drawing through an epicyclic reduction gear train ..."[44].

This independent motor system conferred a greater flexibility on the machine.

A second feature of this calender was the elimination of roll cambering and its replacement by cross-axis alignment. Troester used this technique under licence from Eck but modified the engineering so that adjustment could be made while the machine was running. Eck's design necessitated a shut-down of the calender to permit any adjustment. Cross-alignment was applied to one of the rolls by moving its two bearings forwards and backwards respectively in horizontal slides. The movement was effected electrically and at its maximum gave a difference in separation of the rolls of 0.5 mm between the middle and ends.

No independent comment was available on the performance of the Troester modification of the Eck design, or indeed of the calender generally. The B.I.O.S. investigator saw it in the early stages of erection at Chemische Werke Hüls before anybody had had a chance to work on it. It is quite likely however, that some company in England might have some views on its behaviour as the investigators reported that "the calender and its associated gear was the subject of an application for evacuation dated 25th September 1945". I have not been able to trace its final resting place[45].

A third noteworthy feature of the calender was the roll heating arrangement. By means of high pressure steam 200°C was attainable, and together with this relatively high temperature went a sophisticated regulating system which aimed to maintain a uniform heat history of the pvc in the calender. The regulators were actuated by temperature differences between the inside and outside of the rolls.

The path of the circulating steam is illustrated in Fig. 12 which can be compared with an earlier and cruder design (Fig. 13) and a more modern arrangement in which the heating elements are brought much closer to the surface of the roll (Fig. 14).

Fig. 12.

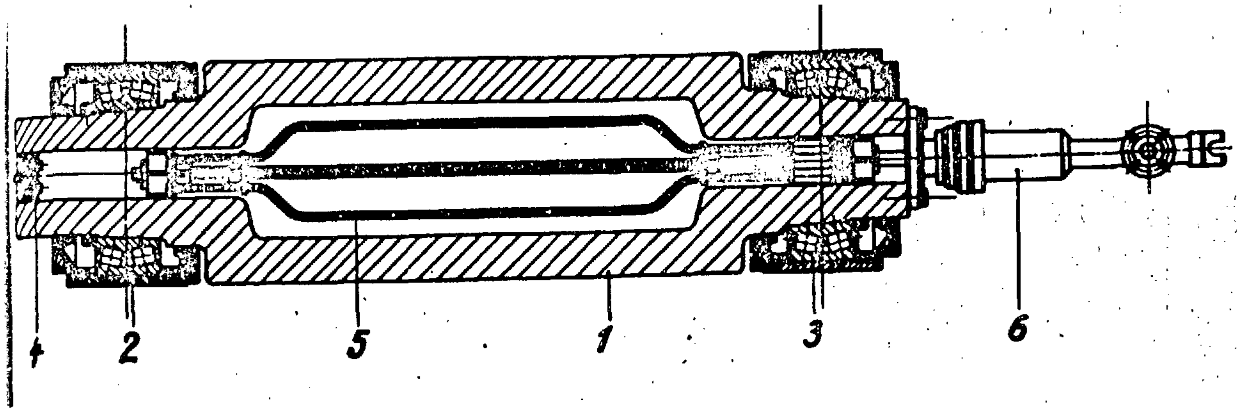
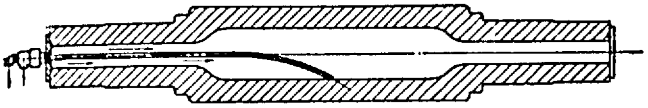
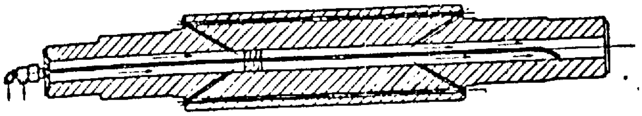


Fig. 13.



CONVENTIONAL CHAMBERED ROLL

Fig. 14.



DRILLED ROLL

A final point for comment on the Troester Universal Calender relates to the bearing lubrication system. Running at about 200°C and at a high speed the older cruder methods of lubrication were becoming quite inadequate. In these conditions the oil began to break down and was not doing its job. In this machine the roller bearings were flooded with lubrication oil by circulating copious quantities in an enclosed system. The oil was kept moving through the bearings by an electrically driven pump and then through a sump at the foot of the calender where it was filtered and cooled before being returned to tanks at the top of the calender and thence back to the bearings.

The advantages of this sytem were several. It provided adequate lubrication, it helped control the bearing temperature and it led to an appreciable saving in oil consumption. The sealed bearings in this sytem had of necessity to be effective and this gave rise to an incidental bonus; it very successfully reduced contamination of the calendered product by leaking oil.

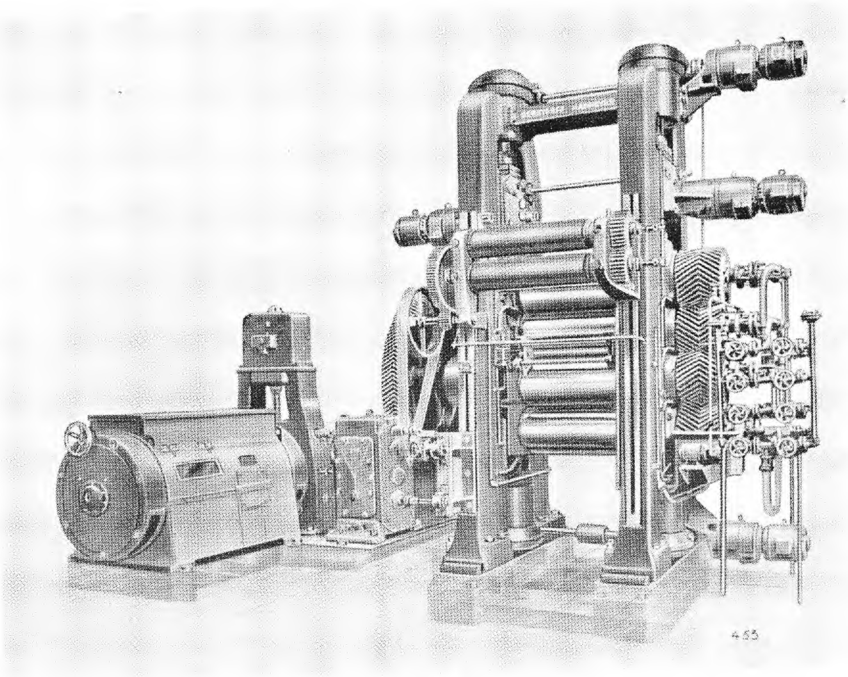
It may be of interest to note that the price quoted for the calender was RM 138,240 and complete with take-off accessories this rose to RM 165,440 (about £14,000).

The Hermann Berstorff Company, also of Hannover, was very active in the field of calender manufacture. It must have been the first firm to make such a machine specifically for pvc. Mr. Szczesny, the Managing Director, told me in an interview that they made a three roll calender in 1934 for Dynamit Nobel. The process for making pvc sheet at that time still bore resemblances to the celluloid technique in that it required calendering followed by "pressing the sheet between plates while applying heat"[46]. That machine was followed by another in 1936 and in all Berstorff had made ten machines for pvc by 1941.

One four roll calender made in 1939 incorporated oil circulation and another made for the Deutsche Celluloidfabrik at about the same time used the Eck cross-alignment principle. Berstorff did this under licence from Eck. It will be observed that both Troester and Berstorff had this arrangement with Eck, who claimed that the former had the right to use it in small laboratory machines while Berstorff could make the larger versions. Troester's Universal calender for Chemische Werke Hüls was therefore the subject of some legal disputation[47].

Berstorff used one motor for driving the rolls, with end-couplings, as will be evident from the photograph taken from a contemporary catalogue. (Photograph (f)).

This description of the calender design situation gives a fair picture of the limits of advance up to and including



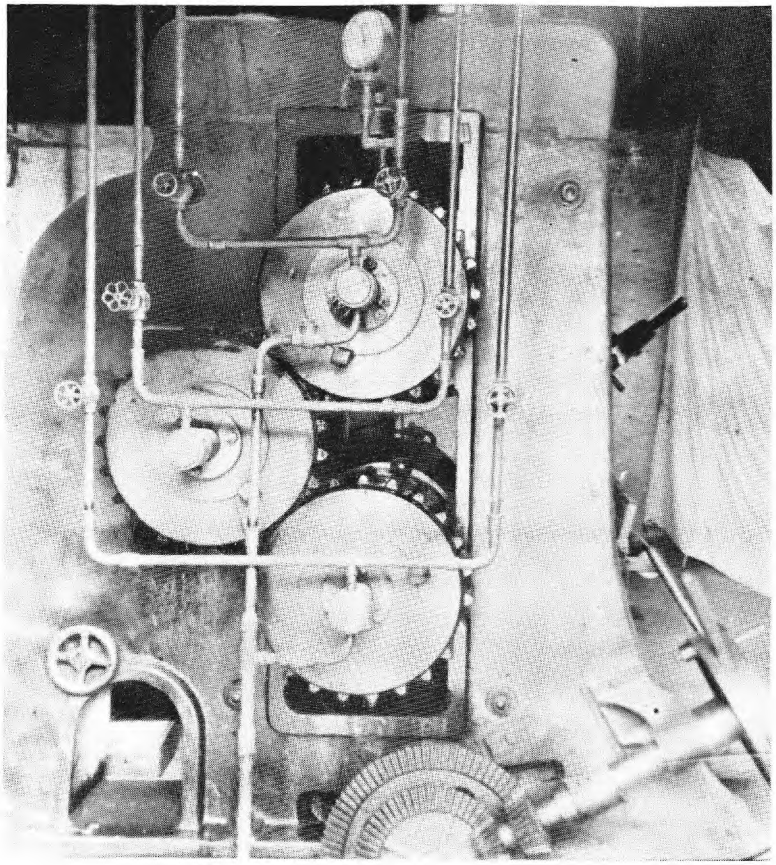
PHOTOGRAPH *f*

the beginning of the war; at least in Europe. This is not to equate the most progressive developments with those dominating the scene. At that time the old fashioned rubber calenders were still very widespread, as one might have anticipated from the small amount of pvc then being processed.

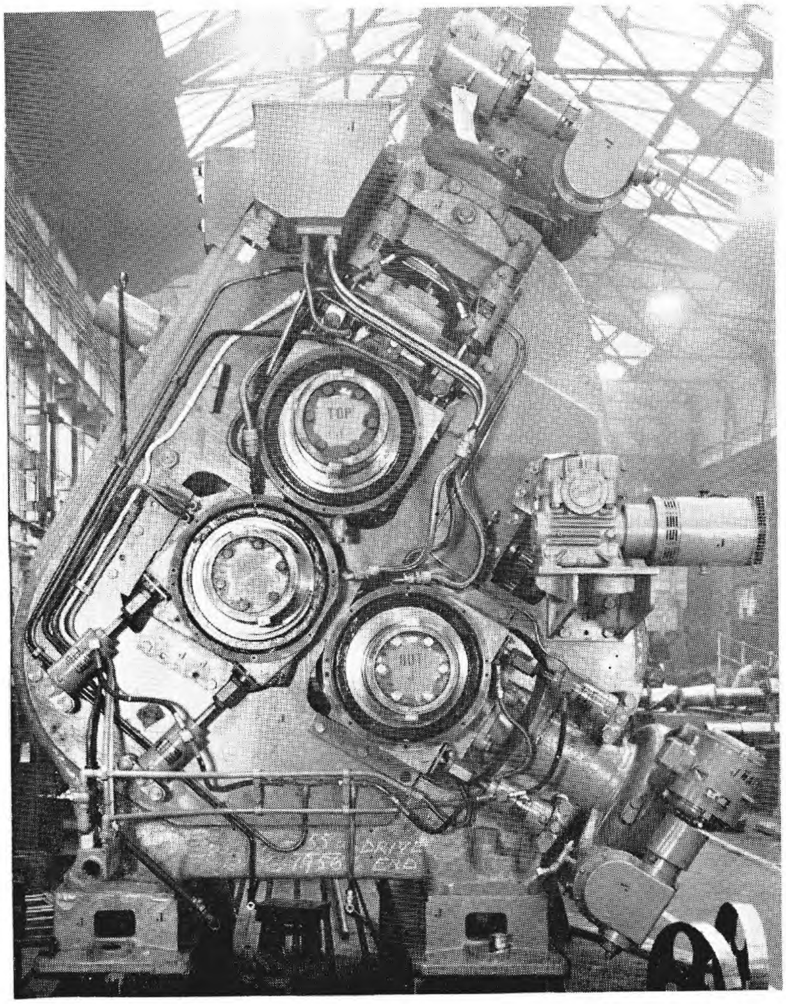
Calenders were, of course, made during the war but, as Mr. Szczesny told me, there were no significant changes in calender design between 1939 and the end of the war.

Many features of the modern calender emerged in the early 1950's and mainly from the U.S.A. Thus alternative ways of arranging the rolls were introduced. In addition to the vertical configuration of three or four rolls there came the "L", the inverted "L", the "Z" and the triangular configuration. The last variant however was not altogether new. David Bridge & Co. made one as shown in the photograph in 1908, though it must be conceded that it looks rather crude when compared with a modern triangular calender made by the same company. (Photographs (g) and (h)).

Peripherally drilled rolls, as illustrated in Fig. 14 to obtain more accurate temperature control of the roll surface and a faster response to the need to raise or lower the temperature, preloading of rolls to obtain uniform pressure at the nip, roll bending as an alternative means of compensating for roll bowing, sophisticated radiation techniques for measuring film gauge and automatically adjusting the nip to obtain the desired thickness, all these features, and others, so well known to those "skilled in the art" of calendering, all were incorporated in the calender and its ancillaries fairly recently and so hardly qualify for discussion in this historical account of the development of machines used in the processing of pvc.



PHOTOGRAPH 8



PHOTOGRAPH h

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Chapter 8

Early Applications of PVC

"There is nothing like wood" shouted the advertisements in the Underground trains to the hurrying Londoners, some time ago, as they were carried from one part of the city to another. The object of the message was to counter the inroads which new materials were making into some of the traditional applications of wood. The appeal was based on the unthinking inate conservatism that resides in most of us.

New materials have commonly faced an initial prejudice which has often been supported by the apparent superiority of the older and established incumbent, tempered and modified as it has been by the years of experience in use, as compared with the untried fledgling product still bearing all the shortcomings of an incompletely developed material. Older people well remember - and connoisseurs of oriental rugs all learn - the superiority of vegetable dyes over the synthetic variety. The old craftsman looked back with regret to hand-made steel and every bibliophile knows that rag-paper is preferable to wood-pulp. When a new material seeks to compete not only with traditional ones but with materials specially selected by the customers for their aesthetic qualities, "feel", and personal satisfaction, it inevitably encounters a subjective resistance which is very deeply based. When, moreover, the replacement is dictated by necessity in a time of shortages, dislike for the innovation is intense and persistent.

Such factors have been conspicuous in the reception of plastics and pvc in particular. Arriving as they did in both World Wars under the general description of ersatz - a term of opprobrium in several languages - it has taken a long time for the virtues of these materials to penetrate the public attitude of hostility. The conviction that plastics are somehow "cheap and nasty", an attitude, at times, explicitly stated and more often expressed by a passive resistance, has been buttressed by an igmorance of the facts of life in this fast changing technology.

The reluctant acceptance of pvc by both the general public and industry provides an interesting illustration of my contention. Notwithstanding some obviously advantageous properties which emerged even in its early days, pvc had to battle against a hostile world. In Germany and Britain it was foisted on unwilling recepients not because of its advantages over traditional materials but primarily because national shortages dictated the use of substitutes.

The Germans had vivid memories of the ersatz which the Allied blockade had forced upon them in the First World War, and in their minds pvc was associated with the privations and shambles of the Second. In Britain the immediate post-war period saw a tremendous scarcity when pvc was pressed into service for many applications irrespective of whether it was suitable or adequate. The net result of these experiences was an antipathy to pvc which has dogged producers and converters until quite recently and still finds an echo even today.

The first suggestion for possible applications of pvc was made by Klatte in one of his group patents discussed at length in Chapter 2. The purpose of DRP 281,877, was to protect for the Griesheim Elektron Co. a series of uses of the polymer which he had recently synthesised. Nor was the patent an essay in the obvious, as so many are. It drew attention "to the surprising fact that one can convert the so far worthless materials, without modification of their chemical structure into technically valuable products".

All sorts of things could be made from pvc; substitutes for horn, films, artificial fibres, lacquers, etc. In fact most of the articles made in celluloid, it said, might equally well be made from pvc, with the added advantage that they would not burn with the ferocity of things made from celluloid.

The fact that Klatte's patent led to no applications for at least twenty years and that pvc did not, in any serious way, encroach upon the traditional markets of celluloid is of significance in this research into the application of pvc. It illustrates a serious difficulty in recreating the pattern of its uses, particularly before any statistics on the subject were available. Klatte's patent is an early example of the torrent which followed, all proposing that the material was ideally suited to this or that application. In some cases events have proved them right, but ultimately the patent literature in this field is more reliable as a testimony to the imagination and ingenuity of patentees than it is a guide to the significant and fruitful uses of the material. For this reason, in this chapter I have had little recourse to this body of literature, which is so useful elsewhere.

For somewhat different reasons the journals have to be used with circumspection. Technical investigations reported in reputable journals can generally be relied upon and taken at their face value but when one reads articles on particular applications or surveys of applications, it is not irrelevant to remember that they were, and are for that matter, often written by people who were knowledgeable precisely because they had an interest in extending these applications. It is therefore not altogether surprising that hopes were sometimes confused with achievements, and accounts were sometimes not altogether balanced or entirely objective.

The hard facts of the situation are often in the archives of the companies that were involved in the making and selling of pvc and articles from it and these, apart from some pre-war and wartime records of German activities, are not readily available.

The point might be illustrated in this way. In the latter years of the 1930 decade the U.S. Journal "Modern Plastics" was wont to review the annual progress of plastics under various headings. Under "pvc" and "vinyl chloride-vinyl acetate copolymers" it listed the attractive properties of these materials and discussed their applications. In 1936, for example, it said "vinyl resins [meaning the copolymer] have found wide usage in dentures. This exacting application requires strong tough material that is tasteless, odourless, resistant to mouth acids and non-irritating to mouth tissues. All of these properties are found in these resins which also permit the reproduction of the delicate pink shades required"[1]. In 1937 and 1938 it repeated the claim that "these excellent properties in a single resin make it desirable for many industrial applications such as : dentures ...[2,3]. An earlier paper on "Applications of Vinyl Resins" by Davidson and McClure described how "after several years of effort a type of pure vinyl resin ... has been produced that is eminently satisfactory for dentures. The material has been placed on the market within the last six months by two of the large dental manufacturing companies and their experience has fully justified its use"[4]. Yet in a list of typical applications of this material in 1939, dentures were nowhere to be found.

Reminiscing some twenty years later the same Joseph G. Davidson explained the puzzle when he said "... for a time we supplied Vinylite resin [Carbide and Carbon Vinyl chloride-vinyl acetate copolymers] plaques for the manufacture of dentures for false teeth. This was excellent business, for although the volume was small the price was good, something like $5 a lb. But here again we ran into difficulties.

"In 95% of the cases vinyl dentures worked out perfectly and were far superior to the materials that had been used previously but in the case of people who had a high roof to their mouths (a high palatal surface) the vinyl dentures would flex a little at each closing of the jaws and finally, through fatigue, would crack down the middle. Fortunately during this time new uses began to develop in other directions"[5]

The early hopes for the use of the copolymer in dentures were obviously, for the most part, quite soundly based, but one weakness ruled it out. The facts of this situation, however, would not emerge from any reading of the Journals.

A study of the same journals would lead one to believe that toothbrush handles were a significant and growing outlet for these materials, but Mr. Davidson in his more detached account painted the picture rather differently. "About that time somebody had the bright idea of moulding toothbrush handles from it, so we bought a few injection moulding machines and moulded thousands of toothbrush handles. Here we were within fingertip reach of success but the toothbrush handles were found to be lacking in one respect. Tufts of bristles are inserted as part of a high speed drilling operation and the Vinylite resin softened to the point where it gummed up the drills and slowed down production; therefore Vinylite was unacceptable because it took longer to process even though when finished a good toothbrush handle was obtained"[5].

There must be many other stories of "the one that got away" locked away in the memories of workers of that time and in the archives, but these remain inaccessible. A point that would probably emerge from most of them, however, would be the fact that the early attempts to use the properties of pvc were frequently efforts to substitute it for established plastics.

J.G. Davidson described one aspect of this process rather well. "As often happens we tried to substitute it for known resins, Bakelite phenolics for example, but in comparison with these it was no good. We sent a sample of it to the Bakelite Company ... and they returned it with a notation that it was of no interest because on boiling in water it was reduced to a gummy mess. It had no dimensional rigidity under stress and generally was not like the Bakelite phenolic resins; therefore obviously no good. Its properties were not similar to the other two resins available then; namely cellulose nitrate and cellulose acetate and we became quite discouraged"[5].

But Davidson was speaking here of what must have been the first attempts of his company to find outlets for pvc; of the time when "a white plaque of vinylite put on the roof and exposed to the sun would turn jet black in an hour or so and become as brittle as a thin piece of charcoal"[5].

The Americans, like the Germans, required some experience before they learned how to incorporate plasticisers into pvc and to make commercially interesting copolymer. Although, according to promotional literature of Carbide and Carbon Corporation, Vinylite was first produced at South Charleston, W. Virginia, in 1927, the first comprehensive plastics exhibition in the U.S. in November 1934 did not include anything in pvc. At any rate a contemporary account made no mention of it[6]:

In the next couple of years however things began to move and according to one estimate, made in 1938[7], 450 tons of pvc were made in the U,S.A. in 1935 and 900 tons in 1936.

Parallel developments were taking place in Germany. Up to 1935 a number of establishments of I.G. Farben were independently concerned with the applications of plastics that they were developing. But in that year the Kunststofftechnischen Kommission (Kuteko) was established to co-ordinate all this work. At a meeting, held at Ludwigshafen at the end of September it was decided to pool information on pvc, copolymers and post-chlorinated pvc and a month later at Frankfurt progress reports were presented by representatives from Bitterfeld, Wolfen and Ludwigshafen on various applications.

The minutes of that meeting[8] provide a succint summary of the situation. Bitterfeld listed the following fields of application for PVC and PC.

"1. Cable insulation because of its good water resistance and lack of ageing.
2. Moulding material for cups, tubes: high softening point. Battery boxes: resistant to sulphuric acid. Records, high surface hardness.
3. Leather and rubber sustitutes: no ageing.
4. Insulation films: good electrical properties, cold and water resistant.
5. Adhesive films for wood: higher softening point and waterproof.
6. Films in general for the coating of paper, wood and other material and as a substitute for celluloid: tough and waterproof.
7. Tar refinement."

Ludwigshafen submitted a detailed report on vinyl chloride copolymers and classified applications as follows:

"A. Without Solvent

I Without plasticiser

- a) Moulded articles: combs, toothbrush-handles, spectacle frames, saucers, battery boxes, dentures, etc.
- b) Surface lamination (paper, cork, wood etc.) with thin films, cards, lampshades, washable curtains etc.
- c) Drawn articles: bowls, spectacle cases, brushbacks, etc.
- d) Blow articles: figures, dolls, etc.
- e) Insulating films: for electrotechnology.

II With plasticiser

- a) Artificial leather, still in the experimental stage.
- b) Cable: detonation cord and low-tension cable, using tricresyl phosphate or Palatinol as plasticiser. High-tension cable using electrically superior plasticiser e.g. Vulkanol B and Clophen A.60.

  Substitute for lead sheathing used for the mechanical protection of cable with plasticisers as in detonator cord, and the simultaneous addition of much filler.

  About 10 tons of copolymer per month goes to the cable industry.
- c) Soft rubber: tubes and soft rubber articles. Copolymer appears to be too dear so far, as leather and soft rubber substitutes.

B. With Solvents

- a) Adhesives: Investigations in collaboration with the Uerdingen works were indicated.

b) Lacquer binders: It was reported that parallel investigations were being carried out at Ludwigshafen."

To this list was added another from Troisdorf. They reported the following applications for

"PVC

a) Battery box separators

b) Records

c) Cap peaks

d) Pipes for warm water transport

PVC or Copolymers

a) Detonator wire insulation

b) Low tension wire insulation

Copolymers

a) Combs

b) Manometer-windows

c) Films for laminating with cards etc.

A comparison of this summary of the applications of pvc contemplated by the Germans in 1935 with analagous U.S. reviews[1,2,3] shows how similar were the two approaches in the search for uses for this new material and how much the emerging patterns resembled one another. Looking back with the benefit of more than thirty years of hindsight, one can also observe the same mixture of the trivial and the origins of very significant developments.

In view of the intense concern today with the rational extension of the uses of pvc in various aspects of building, the early recognition and exploitation of some of these possibilities is interesting.

Already in 1933 the Carbide and Carbon Chemical Corporation had completed a commercial research project, the object of which was to develop "the application of modern materials to the construction of homes"[4]. The initial intention was to satisfy a requirement for a "light-weight, smooth-surfaced fireproof door" and "a sectional wall panel". The company was so encouraged by the success of the exercise in which Vinylite was used to make these two components that it extended the project to the design of a three-roomed apartment utilising Vinylite wherever possible.

"The walls in all cases were built of the large panels ... three Vinylite doors were moulded in the same general way ... the lighting arrangements were quite unique. No direct lights were in evidence and all of the illumination was transmitted through transulcent sheets of Vinylite which have a transmission efficiency of more than 90% ... various towel racks and grab bars in the bathroom were sections of the same material of proper design and cross-section. Vinylite was also used to mould the toilet seat, toothbrushes, cosmetic jars ... door knobs ... Even the windows were sheets of translucent Vinylite - they could have been transparent had the view warranted it".

Enthusiasm was unbounded. And while the authors were prepared to admit that "initially this apartment was built solely as a means of demonstrating the possibility of using this resin for architectural construction with no attention at this moment to the economic problems involved", they had to state now that "the more the project is studied the more feasible it becomes from this standpoint".

In the event, most of the applications were then unsuitable or uneconomic, but one was outstandingly successful and is now just an accepted item in domestic building, namely "vinyl" flooring. "The complete apartment was floored with Vinylite tiles ... To indicate the range of colours the tiles in the living room are alternately green and yellow with a dark green border, whereas those in the kitchen are black and grey with a black border, in the bathroom the colour scheme is coral and blue with black border".

In Germany work on vinyl floor tiles was proceeding along similar lines and by the Kuteko meeting of March 1937 it was confidently reported that the processing of pvc for this purpose jad been firmly established[9]. In that same year the millions of visitors to the National Exhibition in Düsseldorf, dubbed "The Creative Nation" (<u>Schaffendes Volk</u>) to the greater glory of Hitler's campaign for a self-sufficient German war economy, walked on a pvc floor "without leaving a trace of wear "[10]. Such was its abrasion resistance. In the paper from which this last quotation was culled, "PVC floor covering: Properties and Laying Thereof" the author reported that "equally favourable results have been obtained by the shipping companies". He attributed its success to "its complete resistance to ageing, it suffers no permanent change under the influence of light, heat and oxygen and does not become brittle with time ... As compared with rubber floor-covering it does not loose its elasticity and noise absorbing properties. In addition it is non-flammable, quite odourless and resistant to chemicals".

Once more the enthusiasm of the author made his description rather less than objective, but a number of photographs of pvc floors in dining rooms, foyers, cafés etc. bore testimony to the widespread use of pvc floors and time, after all, has vindicated his and many other people's expectations.

The Germans were as interested as the Americans in the possibilities of pvc in wall panelling and just as Carbide and Carbon were experimenting with their Vinylite, so Dynamit Nobel of Troisdorf were developing wall covering from their vinyl chloride copolymer which they called "Astralon".

Another field in which it soon emerged that pvc had much to offer was that of electrical wiring and cable manufacture. The interest was two-fold. In the first place it seemed that pvc constituted satisfactory ersatz for natural rubber and secondly it possessed some genuine technical advantages as compared with the natural product.

Both factors were important but there is no doubt that the first was the dominant consideration in Germany while the second probably carried more weight in the USA. For some time, between 1936 and 1940, neither consideration could seduce the decisive people in this field in Britain from their attachment to natural rubber. Why should they succumb to the attractions of pvc? The British had ready access to natural rubber grown in British owned plantations in the Far East. The price of pvc was several times as high as rubber and furthermore the cable industry was technically geared to the processing of rubber and was not disposed to accept the inevitable problems associated with a change of insulating material.

The German cable manufacturers were not enthusiastic either but they had to contend with pressures which were not yet felt abroad. In 1935, as I have already indicated[8], cable insulation was high on Bitterfeld's list of applications and at the December meeting of Kuteko a planned campaign of visits to cable manufacturers was put in hand. Three months later at a further meeting it was reported that "a keen interest in pvc and vinyl chloride copolymers was envinced by the cable-makers", and a still growing enthusiasm was minuted in the meeting of March 1937[9]. Attention was drawn to the point that "the search for usable plasticisers is important". All this led to an estimate that the amount of pvc required in 1938 for cable manufacture would be as much as 150 tons per month.

Why did pvc commend itself technically for application in this field? An answer was given by R.G.N. Hamilton, an electrotechnologist, in a paper which he read to the Plastics Institute in London in 1937[12]. In it he compared the performance of a number of thermoplastics with rubber whose "outstanding advantages are flexibility, elasticity, resistance to abrasion and to moderate temperature ... The main disadvantages of the rubber are that it oxidises and ages with time, is attacked by a variety of materials, the most serious of which is oil, it is inflammable and not as resistant to moisture as might be desired. In addition the dielectric losses are so great at high frequencies as to render the material unsuitable for use".

As an alternative to rubber "the material which so far appears to promise best is polyvinyl chloride. It possesses all the desirable properties, except that of heat resistance ..." Nevertheless, he warned that there were disadvantages. While the electrical insulating properties of the polymer itself were good, the admixture of the necessary plasticisers brought about deterioration. "Accordingly it is often advantageous to employ mixed plasticisers so as to strike a satisfactory balance between the various desired properties, (e.g. ageing, oil resistance, low temperature and flexibility). This in general will mean that the material will have slightly inferior electrical properties when compared with rubber and it becomes of interest to see why a material several times the price of rubber can be of any interest".

The reasons, the author said, were various and sometimes complex but in brief they included its non-flammability, resistance to oil, freedom from corrosive effect on copper, [because of the absence of the sulphur present in vulcanised rubber] , good water resistance and, even at that time, a faster rate of extrusion as compared with rubber.

In assessing the net result of the interplay of all these factors the author came to the conclusion that pvc "will take its place as an insulating covering where operating conditions, except temperature, are especially severe and cannot be met by rubber". His reading of the situation is somewhat unexpected because it does not seem to flow altogether from his detailed consideration. In spite of awarding good marks to pvc as a rubber alternative, his conclusion was that pvc had a future as a specialist material, not in competition with natural rubber.

Four months after Hamilton's paper, two workers of a German cable manufacturing company wrote a paper, in Kunststoffe, on the same subject, namely "Synthetic High Polymers as Materials for Cable and Electrical Wire Manufacture"[13]. They were very conscious of the temperature dependence of many of the properties of pvc and they drew attention to the facts that "even if the tensile and impact strengths of thermoplastics are only marginally inferior to those of rubber compounds the changes of these properties with temperature require especial consideration. At low temperatures the tensile strength increases while at the same time the toughness declines and finally falls below an acceptable minimum. Simultaneously the mass becomes brittle ... On the other hand, raising the temperature causes softening ... In addition to all this there must be added the deterioration of dielectric properties".

These facts led the authors to the same conclusion as Mr. Hamilton, "This behaviour shows that it is not possible in cable and electrical wire manufacture simply to replace rubber with pvc. The applicability of this material depends on its particular properties". There were, they thought, many situations in which these could be put to good account.

In 1939 workers of the B.F. Goodrich Company in America who had developed plasticised pvc under their trade name "Koroseal", expressed the same sort of reservations about the effect of changing temperature and of incorrect formulation on its electrical use. They nevertheless felt that "in the electrical wire and cable industries, Koroseal is ideally suited to many applications for use as insulation or sheathing. For such uses as insulation on apparatus and machinery wire, switchboard and station control cable for light and power services and building wire the material is finding increasing applications"[14].

This was confirmed, partially at any rate, at the Schaffendes Volk Exhibition at Düsseldorf, on the stand of the AEG Co., which displayed a number of cables insulated or sheathed with pvc[15].

These extracts from the historical record show quite clearly that pvc was seen to be a significant new material for cable manufacture but not so outstanding in its properties that everyone was immediately convinced that it ought to be adopted in place of rubber. Even in Germany, where governmental pressure for such a change was at its most intense, manufacturers tended to cling to the traditional material and processes associated with it. Dr. Illoff, who in 1938 was charged by I.G. Farben with the task of selling pvc to the cable-makers, has told me in private conversation, that he had great difficulty in disposing of Bitterfeld production at that time. As he recalls, there was about 1000 tons in store just before the outbreak of war. This was predictably taken up very quickly when supplies of natural rubber were suddenly cut off as the struggle was joined.

Unplasticised, i.e. rigid, pvc was a material whose interesting and useful properties the German recognised quickly. Its mechanical properties were adequate for a range of applications. Its resistance to many chemicals made it a "corrosion resistant" substance and the ease with which it could be worked and shaped increased its usefulness. Above all it could replace metals which had to be imported and paid for in foreign currency.

The last consideration was the one which most clearly distinguished the German attitude from the American and accounted for the determination with which the Germans sought to overcome the difficulties associated with the processing of rigid pvc. It explained why they were better at handling the material and maybe even today retain an edge over their rivals in this field.

Dr. Georg Wick, the leader of the I.G. Farben team in Bitterfeld, has told me that late in the 1930 decade rigid pvc accounted for about one third of all the pvc made there. Processing relatively large quantities of a material requiring new techniques and craft skills posed a problem which the Germans were quick to appreciate and one which others have yet to recognise. This was the need to establish adequate training facilities to produce a core of workers capable of manipulating sheets, panels and tubes of rigid pvc and converting them to all manner of useful shapes.

I.G. Farben established schools in Halle, Vienna and Bitterfeld which ran courses every month, catering for about forty people, designed to teach the skills involved in welding, lining, machining and so on. Dr. Wick thought this investment paid handsome dividends and doubtless contributed to the commanding lead which the Germans achieved.

In 1935 rigid pvc was being produced in semi-finished form at the Deutsche Celluloid Fabrik in Eilenburg, at Troisdorf and at Bitterfeld. To rationalise the marketing of these products I.G. Farben set up the Verkaufsgesellschaft Kunststofferzeugnis (VKE) at Eilenburg, which thereafter sold them under the trade name of Vinidur. By 1938-9 the VKE was delivering 110 tons per month and of this 80 tons went to the chemical industry, 20 tons to the manufacture of batteries and 10 tons for gramophone records[16].

I.G. Farben was itself a considerable consumer of pvc in its own chemical plant. In its 1938 extension of pvc plant capacity, storage tanks for pvc emulsion were lined with sheets of the polymer to inhibit its coagulation. Other parts of the plant were similarly lined and the whole piping system and valving consisted of pvc[17]. Subsequent examination of the equipment in 1946 showed that all were in good condition.

PVC piping was used before and during the war for the transport of a large variety of fluids. For example, since it is highly resistant to sulphuric acid in dilute and concentrated form, it replaced lead in contact with this acid. It was also used to contain nitric acid, alkalis, sodium bisulphite among other things and in the process sometimes replaced rubber. Its physiological inertness and freedom from tates and smell permitted its use as piping in the transport of water, milk, fruit juices and beer.[18]

Such piping systems required good welding techniques for joining lengths together, for setting "T" and other joints in the system and for incorporating "windows" of clear, transparent vinyl chloride copolymers, Astralon, or Vindur from time to time. Quite sophisticated and entirely adequate techniques were evolved before the war, inspired very largely by Dr. A. Henning[19].

Perhaps some of the most interesting and impressive examples of the art of rigid pvc working and welding came in the shape of valves for various situations in chemical plant. A paper by H. Klant, published in 1942 illustrates a range of types which he considered as steps in the as yet incomplete development of pvc valves[20].

The reasons for the use of 20 tons per month of pvc in 1938-9 in accumulators were persuasively discussed by Dr. Hauffe in 1937 when he was selling the idea of batteries made from pvc on behalf of the Deutsche Celluloidfabrik[21]. He put it thus: "If the fundamental construction of an accumulator has changed little in the last ten years, the designer has at least tried to improve and change those parts not involved in charging and discharging; to save weight, to increase strength etc.

"Thus, for many years there have been attempts to replace the heavy, breakable, glass vessel with lighter materials. At that time these were hard rubber and celluloid ... while celluloid has found application only in smaller accumulators, hard rubber has been introduced in large quantities particularly on account of its cheapness and easy workability. If today renewed attempts are being made to produce safe though transparent containers then one is inescapably led to the new plastics ...

"It is not especially surprising that vinyl polymers have been proposed for the purpose. Many such polymers are chemically resistant, extremely stable to acids and alkalis, non-flammable, transparent and have good mechanical properties. Further, all have the characteristic of becoming plastic when heated which is significant insofar as it makes it possible to mould transparent, acid and alkalis resistant containers.

"Amongst other parts required in the accumulator one can name separators, locking plugs, degassing tubes and others and for all of these vinyl polymers can be used with advantage. These parts can be made without difficulty in all shapes by moulding, drawing, punching, sheets, rods and tubes or direct pressing of moulding powder".

Dr. Hauffe's points were not just sales talk. In the conditions of pre-war and wartime Germany they made good sense.

In 1938-9 the residue of the 110 tons per month of Vinidur, after the chemical industry and accumulator manufacture claimed 100 tons, went into gramophone records. These were made from vinyl chloride-vinyl acetate copolymer as well and in the U.S.A. simultaneous efforts were being made to popularise this material as a replacement for the old established shellac record.

As early as 1935 Dynamit Nobel reported to Kuteko on their experience in using pvc for the master from which the records were made. Later they went on to make the records themselves from the material. In a lecture given in Berlin in April 1941 on "The Application of Newer Plastics", Dr. Röhm spoke of the use of a 50/50 vinyl chloride-vinyl acetate copolymer for this purpose. "The total content of polymer in the record is barely 20%. The rest consists of pitch and fillers. Such record compounds, which can be processed in exactly the same way as shellac, are in no way inferior to it, so that at an equivalent price their future is assured". The composition of modern long playing records is hardly as rich in pitch but Dr. Röhm's prediction as to the future of pvc records looks quite conservative when viewed from today's world of shellac-less records.

But today's world does not rely solely on these records for sound reproduction. Tape recording based on plastic film is equally popular. Such magnetic tape had its origin in the period just before the war. "In 1938 realisation of the disadvantages of steel recording tape, including demagnetisation on standing, led to the trial of magnetite in a plastic tape. The theory was that isolation of the magnetic particles from one another (by the plastic) would lead to a less rapid demagnetisation. Iron powder was not suitable because of its tendency to oxidation. A.E.G. found that ferric oxide (Fe_3O_4) was better in respect of retention of magnetisation."[22]

A number of plastic tapes were tried and the most successful type was made from <u>Luvitherm</u>; calendered and biaxially orientated pvc sheet. When Allied investigators looked for samples of this recording tape in the German plant making it, they found that all of it had been requisitioned to record the proceedings of the trials of the War Criminals at Nuremberg.

Such then were the major applications of unplasticised pvc as developed almost exclusively in Germany before and during the war, stimulated as it was by a shortage of foreign raw materials and foreign currency.

In discussing the uses to which pvc was put in its early days, I have tried to highlight applications which subsequently turned out to be of special interest or to indicate some reasons for failure to capture certain markets or to draw attention to particular circumstances which influenced the people responsible for finding outlets for the new material. I have not discussed many early applications firstly because there were quite a number of fertile imaginations conceiving possible uses and secondly because there is such a paucity of available information on the subject. I have no doubt however, that given the will, time and co-operation of the companies involved, research workers have a rich mine of social, technological and economic history awaiting their attention.

The application of vinyl chloride copolymers as surface coatings, particularly in the U.S.A., is a typical example. The early tentative attempts to use pvc in clothing: in shoes, rainwear and starchless collars, is another. I have indicated in my discussion of pvc pastes something of the beginnings of pvc as a leather substitute. Many of these explorations have borne fruit and are now an accepted part of life in technically developing societies. Others sank without a ripple ...

Today the production and processing of pvc is carried out by a powerful world-wide industry disposing of several million tons per year. There is every indication that this output will be increased several-fold before it achieves an equilibriu within the spectrum of materials used to satisfy man's needs.

Liebig, in his devotion to the idea of chemistry in the service of man, would doubtless be overjoyed at this outcome of his speculations in 1835. Klatte would probably be astonished that the subject of his lapsed patent of 1912 had become such big business today; as would most of the workers whose imagination and inventiveness have been described in these pages. How much greater would be their surprise if they could see the pvc industry of the future.

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