THE CHEMIST IN THE SHIPYARD

By Dr. G. E. Gale, Scientific Adviser (Navy), New Delhi

ABSTRACT

This paper is intended to illustrate the role that the chemist has to play in the maintenance of ships, and the scope of the work that a Dockyard Laboratory has to carry out. A number of specific problems are discussed and certain modern laboratory techniques are outlined.

If one takes a slight liberty and includes the metallurgical chemist under the generic term " chemist " then one may fairly say that a chemist is intimately concerned with a ship from the moment it is born, because nothing can be made out of steel or any other metal until the chemists and metallurgists have done their work. After the ship has been launched, chemists are involved in a number of different aspects of its running and maintenance; and it can be argued that they are involved in the death of ships, too, because when a ship is at last sold and broken up for scrap metal chemists analyse the scrap and say for what purpose it can be used.

Steel is of course the main structural material for ship building. One takes it so much for granted that ships are made of steel that one tends to overlook the fact that there is hardly a practicable alternative material to use. Wood is the only other material that has ever been used to any extent for making ships; but ships of the size that we know today would be literally impossible if they had to be constructed out of timber; a wooden ship three hundred feet long —not very large by our standards—would sag about four feet at the bow and stern when riding over a large wave; with consequences that can be left to the imagination.

Light Alloys

The only metal that shows any sign at present of replacing steel for shipbuilding purposes is aluminium, or rather certain alloys of that metal. Aluminium is not nearly so strong mechanically as steel. The main advantages that it has over steel are its lightness— the magnesium/aluminium alloys for example weigh only about 170 lbs. per cubic foot as against about 490 lbs. per cubic foot for steel— and the fact that some of its alloys are highly resistant to corrosion. The use of aluminium alloys in shipbuilding does, however, introduce a number of complications.

In the first place the mechanical properties of aluminium and its alloys vary very considerably according to their composition and the treatment that they receive. In some cases these variations are produced by cold working—that is, by subjecting the metal to mechanical strains such as those which result from hammering it or from rolling it; this is because the crystal grains, which are large in the original alloy as cast, become modified in shape as a result of the work done on them. In other cases the variations in mechanical properties result from heat-treatment. The range of variations that may be encountered is illustrated in the table.

Typical Aluminium Alloys

Class of alloy.	Ultimate tensile strength tons/ squ. in.	Elongation on 2 ins. (%)	Brinell Hardness No.
1. Aluminium (99·99%) (" soft ")	3·9—4·1	50—55	14—16
2. Aluminium (99·99%) (" hard ")	5·5—7 5	15	30
3. Aluminium/magnesium (3·5%) (" soft ")	15—16	22—26	55—60
4. Aluminium/magnesium (3·5%) (" hard ")	23—24	3·5—4·0	95—100
5. Aluminium/magnesium (5%) (" soft ")	18—20	15—25	45—65
6. Aluminium/magnesium (5%) (" hard ")	26—28	2—5	100—120
7. Aluminium/magnesium (7%) (" soft ")	21—23	18—20	55—60
8. Aluminium/magnesium (7 %) (" half hard ")	24—26	6—10	95
9. Aluminium/magnesium silicide (1·8%) (" solution treated ")	16—18	18—22	65—70
10. Aluminium/magnesium silicide (1·8%) (" fully heat treated ").	20—23	10—14	70
11. Aluminium/copper/magnesium, Duralumin type, ("sollution treated ").	26—28	8—15	100—120
12. Aluminium/copper/magnesium, Duralumin type. ("fully heat treated ").	29—32	8—15	..
13. Mild Steel (B.S. No. 548—1934)	37—43	14—18	..

Notes :(a) The hardening shewn in the case of Nos. 1 to 8 is mainly due to cold work (rolling drawing, etc.)

(b) " Solution treated " means that the metal has been rapidly quenched in water or oil from about 500°C.

(c) " Fully heat treated " means that the metal has been re-heated to 150°—200° for several hours after it has been solution treated.

In the case of alloys which are to be put to marine use, corrosion resistance is highly important. Once again the alloys shew wide variation in this respect. The magnesium alloys are in general the best, provided that the magnesium content is not over about 5·5 per cent. ; in the 7 per cent. alloy, for example, an intermetallic compound may be precipitated at the grain boundaries, leading to rapid corrosion, especially if the alloy is under mechanical strain. This undesirable change is greatly accelerated if the metal is heated to about 75°C. Another alloy whose corrosion-resistance is affected by heat is the aluminium/magnesium silicide alloy ; the solution-treated metal has superior properties to the fully heat-treated material. Heat sensitivity of this sort is undesirable in alloys for marine use since they cannot be welded, for example, without losing one of their more important characteristics.

Some aluminium alloys possessing very good mechanical properties, such as the Duralumin types, have relatively poor resistance

to corrosion, a failing which they share with copper-containing alumi-
nium alloys in general. The most generally useful alloys for marine
purposes are the 3·5 per cent. and 5 per cent. magnesium alloys, or
possibly variations thereof incorporating a proportion of manganese.

Another peculiarity possessed by some of these alloys is that of
" age-hardening "; that is, the alloy spontaneously becomes harder
and stronger, but less ductile, on standing at room temperature after
it has been quenched from a high temperature. In some cases this
hardening takes place in as little as 20 minutes ; but it can be delayed
greatly by cooling to temperatures below zero. Certain alloys of this
type are popular for making rivets because it is very useful to have
a material which, whilst being initially soft enough to be suitable for
rivetting, later develops considerable strength automatically and with-
out further treatment. Since they would be too hard to drive in the
hardened state, it is common practice to place these rivets in a refri-
gerator immediately after quenching and to store them there until
required. Age-hardening takes place because these alloys, when
quenched, are substantially in the condition of a uniform solid solu-
tion ; but afterwards the alloying elements more or less rapidly preci-
pitate out in accordance with their true solubilities. A typical alloy of
this type contains 4·5 per cent. copper, 0·6 per cent. manganese and
1·5 per cent. magnesium.

Aluminium is sometimes used in shipbuilding as an insulating
material, in the form of thin foil ; its effectiveness partly arises from
the fact that its heat-reflectivity is high, a property not possessed by
more conventional insulating materials such as asbestos or cork.

Small boats and canoes have been successfully constructed from
aluminium alloys, and were much used during the war. The largest
all-aluminium craft that I have seen described in the technical press
is a 60 ft. survey launch built recently in England for the Pakistan
Government. The main application of these alloys in large ships is
at present for replacing the steelwork of the superstructure, the
funnels, bridge, upper decks and so on. The liner " United States "
contains 2000 tons of aluminium in its upper parts, producing a saving
of 2500 tons weight. This saving is not in direct ratio to the density
of the alloys because owing to their low-strength greater thicknesses
have to be used than in the case of steel ; but it is a very considerable
saving nevertheless. Almost more important is the fact that the
saving is in the top of the ship, leading to an increase in stability. The
saving of weight also means that an equivalent amount of additional
cargo can be carried for the same engine power.

Failure of Metals

Much of the work of a metallurgical chemist in a dockyard is
concerned with investigations into the causes of failure of metal com-
ponents. Failure may arise from so many causes, and may be accele-
rated by so many chance factors, that the subject is almost incapable
of being summarised. Broadly, however, failure may be due to :—

  i. The use of the wrong type of metal or alloy.

  ii. Bad design, leading to excessive stresses in the metal.

  iii. Fatigue accelerated by corrosion.

  iv. Incorrect metallurgical handling, for example the metal
      may have been wrongly heat-treated so that it does not
      possess the correct crystal structure or grain size.

v. Corrosion.

vi. The existence of hidden cracks or flaws, porosity, or even actual cavities.

The above list is far from complete. All problems such as these ultimately find their way to the dockyard laboratory for solution. Sometimes they are very complicated, especially in cases where there has been more than one factor involved in the failure. Each type of failure usually has its own characteristic symptoms when one has learned to recognise them. Chemical analysis will reveal whether the composition was correct or not. Microscopic examination of the polished and etched specimen will tell us what we want to know about the crystal structure and grain size. The determination of mechanical properties such as tensile strength, impact resistance, hardness and extensibility, will also afford many useful clues. Corrosion will usually manifest itself quite clearly by discoloration or the presence of solid residues of corrosion product. It need hardly be said that in addition to the required technical information the metallurgical chemist must be in full possession of all facts relating to the conditions under which metals are employed in ships, the working stresses to which they are normally subject, and the corrosive and other influences to which they are likely to be exposed.

The detection of cracks and flaws in metal components can be carried out in various ways :—magnetically ; by the use of fluorescent solutions ; by X-rays or gamma radiation ; acoustically ; and by other physical processes.

Magnetic crack detection consists essentially of magnetising the piece of steel or iron and covering the surface of the metal with a thin fluid, usually a light mineral oil containing suspended particles of magnetic material such as magnetic iron oxide, known as " magnetic ink ". Surface cracks and discontinuities possess a lower magnetic permeability than the iron or steel surrounding them, thus distorting the field and producing local poles to which the particles in the fluid are attracted and around which they align themselves. This gives a clear visible indication of the defect. Cracks that would not otherwise be apparent can be easily detected by this technique. Although the method is really intended only for cracks which emerge in the surface of the metal, imperfections just below the surface will sometimes distort the field sufficiently for their presence to be revealed.

The magnetic flux can be applied by means of a permanent magnet, and small portable sets are commercially available. In the case of larger objects, however, it is necessary to employ electromagnets ; these are usually fitted with hinged pole pieces to enable them to fit over curved surfaces. In all cases it is important that the magnetic flux should run across, and not parallel to, the crack. In order to increase the visibility of the particles in the magnetic ink it may be desirable to coat the article with a quick drying white paint : a mixture of zinc oxide and a cellulose varnish is eminently suitable for the purpose.

It should be noted that residual magnetism is often left in articles which have been examined by this technique and that it may be necessary to remove this subsequently by suitable electrical treatment.

Fluorescent methods can be used for non-magnetic materials and even for non-metallic substances. A solution containing, for example, fluorescein, is applied to the surface of the metal and the excess is wiped off. The fluorescent solution that has penetrated into pores and surface cracks is not removed by simple wiping and the points at which it has been retained in the metal become immediately and brilliantly visible on examining the specimen under ultra-violet light. The method is quite sensitive, and is capable of revealing defects which cannot be seen with the unaided eye. It is often used for detecting porosity in castings. In the case of hollow articles it is sometimes useful to apply internal hydraulic pressure in order to force the fluorescent solution out of fine pores. The technique will not, of course, reveal flaws which do not emerge at the surface.

Cavities, cracks and flaws which are entirely below the surface can be detected by X-rays and recorded photographically. When a beam of X-rays traverses a piece of metal the absorption increases with the atomic number of the absorbing atoms, the number of atoms, and the wave length of the radiation which is being used. Consequently a piece of steel that contains a cavity will absorb less than a sound piece of steel, and the cavity will appear as a dark patch on the final negative. The angle at which the cavity is traversed has an obvious bearing on the intensity of the image, so that it is usual to take radiographs of a suspected area from several different directions, the objective being to ensure that in one photograph at least the beam will have passed through the cavity along its greatest length. X-rays of varying degrees of hardness are of course available, and the type to be used is selected according to the thickness of the metal to be tested, soft rays being used on thin sections, hard rays on thicker specimens. Thicknesses ranging from about one quarter inch up to two inches of steel can be examined in this way.

Gamma radiation is coming increasingly into use in place of X-rays. The principles are the same as for ordinary X-radiography. Radioactive isotopes, which are now readily available, are used as the source. Cobalt 60 is widely utilised for general purposes and is capable of being employed for the examination of castings up to about 11 inches thick. Unfortunately the radiation is too hard for use on thin sections. Iridium 192 is a rather softer source, and is used on thinner specimens than Cobalt 60, but even so it is too hard for many purposes. The discovery of a source comparable to very soft X-rays would be most helpful to workers in this field. Cobalt 60 has a half life of 5 years or so but Iridium 192 has a half life of only 70 days which makes it rather inconvenient to use unless the laboratory is near an atomic pile.

The relative merits of X and gamma-radiography could be argued at some length ; suffice it to say that gamma-radiography is much cheaper and is simpler in operation and can deal with considerably greater thickness of metal, whilst X-radiography is better for thin specimens, and is considerably faster. For general utility on board ships, however, there is no doubt that gamma radiography possesses great advantages ; the equipment is small and portable, and no power-supply is needed.

These techniques are widely used in the examination of welds ; if unskilfully performed, welding may suffer from a considerable

number of defects such as cavities, porosity, shrinkage, cracks and so on. Weakness in a welded joint may be of very serious consequence, especially in large structural work such as ship-building, and in boilers and pressure vessels. Radiography is thus a most valuable tool for ensuring the soundness of welded metal structures. It has been stated that all the many, many miles of welding in the liner "United States" were radiographed. Radiography is also invaluable in the case of large castings, propeller shafts, and so on.

Radiography is extremely valuable in training welders. Welding is an extremely important operation in ship-building and repair-work, and its correct performance requires considerable skill and experience. In order to attain high standards of workmanship, small test-welds made by welding trainees are radiographed so that the men can see for themselves the defects in the work they have done. It has been found that workmen often take a keen interest in these radiographs and are anxious to obtain good "pictures". The strength of test-welds is also determined, and in this way the ability of individual workmen can be accurately assessed. In some shipyards it is the custom to make all welders submit a test-weld to the laboratory once every six months.

Acoustic methods of testing are based on the transmission of supersonic vibrations through the metal. The waves are interrupted whenever they meet a discontinuity, even if this is very thin; and they are reflected from areas where there is an abrupt change of density or elasticity. The time of flight of the wave front is of course proportional to the distance traversed; and the attenuation, that is, the loss of amplitude with distance travelled, depends on the grain size of the metal and on its composition. All these relationships are utilised in supersonic testing which, theoretically at any rate, is an extremely versatile tool in the hands of a skilled operator. It can be used to detect laminations in rolled steel sheet,—a thing difficult to do by any other technique—and to measure the thickness of metal in cases where one side of the piece is inaccessible, as for example when it is desired to know the thickness of the plating on the hull of a ship in order to see if it requires renewal. The technique can also be adapted for assessing the average grain size of metals.

The supersonic vibrations are generated and detected by means of piezo-electric crystals, usually quartz, which are placed on the oiled surface of the test piece. The crystals are usually mounted on wedges so that the beam will enter the metal at an angle to the surface. Alternatively the sending and receiving crystals may be immersed in water, the object under inspection being submerged in the path of the sound beam. Sometimes a continuous stream of waves is propagated, whilst the receiving crystal is used to explore the far side of the test-piece in order to detect sound shadows cast by large flaws; alternatively a brief transmission can be made and the echoes reflected by small flaws observed; in both cases the energy picked up by the receiving probe is arranged to give an indication on a cathode ray oscillograph. The precise depth of a flaw below the surface can often be worked out, as can the thickness of the metal itself. The beam can be arranged to penetrate as much as 20 feet. A spherical cavity 0·2 inches in diameter is detectable at 10 feet : and a similar cavity of diameter 0·02 inches can be revealed at a depth of a few inches. Under favourable conditions holes as small as 0·001 inches have been

detected. The interpretation of results is often, however, complicated by the occurrence of false echoes. Frequencies as high as 5,000,000 cycles per second are sometimes used. The frequency must, however, be adjusted to the size of the crack or defect, so that specimens have to be tested over a wide range of frequencies.

Probably the most useful application of ultrasonic testing in a shipyard is the measurement of the thickness of metal. In the absence of such equipment the only practicable alternative of estimating the thickness of the plating on, for example, the hull of a ship is to bore a hole through it. The equipment can also be adapted for measuring the thickness of pipes ; curved vibrators are available for use on the bends.

Magnetic sorting equipment, of the type known as the " Cyclograph," has shewn itself to be of tremendous value for the rapid identification of specimens of different metals which have become mixed in storage, or of a series of specimens of the same material which shew variations in properties amongst themselves. The instrument is based on the principle that when a metal core is introduced into the high frequency field of a coil, energy losses will result. The coil is part of a tuned circuit and controls the operating frequency of an oscillator. Core losses occurring in the field of the coil decrease the output of the oscillator. The oscillator output is viewed on a cathode ray tube, where the variations become immediately apparent.

At frequencies ranging from 2 Kc to 10 Kc, core losses are mainly governed by the magnetic properties of the metal inserted in the field of the coil. The magnetic properties are in turn correlated with the chemical composition and the structure of the metal. At higher frequencies core losses consist mainly of eddy current losses, and the magnetic properties exert relatively little effect. Lastly at very high frequencies the flux in the test coil confines itself to the surface layers of the metal sample.

By selecting the appropriate frequency range it is possible to detect variations in the composition of both magnetic and non-magnetic metals and in surface conditions such as the thickness of plating which has been applied, surface stresses and imperfections, depth of carburization, and so on.

Typical examples of the work that such apparatus can do are :— the sorting of bullet cores according to hardness ; the detection of abnormal stresses in individual specimens from a series of repetition production items ; the detection of irregularities in metal bands, and so on. The most likely use for this equipment in a shipyard is for the rapid sorting of mixed metal stocks, thus saving lengthy analytical work.

This account does not exhaust the possible methods of detecting flaws in metal but it does give an adequate idea of the resources available to the metallurgical chemist. One important point to be noted is that none of these methods involves damage to, or destruction of, the specimen which is being examined, unlike processes such as analysis or metallographic examination.

A well-equipped shipyard laboratory should possess magnetic crack-detecting equipment, gamma-ray and light X-ray kit, a supersonic thickness meter, and if possible some form of Cyclograph.

Fluorescent testing does not require elaborate equipment other than a source of ultra-violet light. In general, magnetic methods are the most valuable ; they are reliable for detecting surface cracks, which are in practice the defects which it is most important to reveal. A good general rule is, however, to utilise all the resources at one's disposal when tackling a particular problem.

Micro-analytical Methods

The chemist in a shipyard will normally have a good deal of analytical work to perform in connection with metals. I have no intention of discussing analytical methods, but I should like to emphasize the advantages to be derived from adopting modern techniques in metal analysis, especially those involving a photoelectric finish, such as is provided by the well-known Spekker instrument. These methods are not only very fast, and as accurate as the classical methods for routine purposes, but the saving in cost of chemicals is also very great. For example, consider the amounts involved in analysing 100 samples of steel for the four elements manganese, molybdenum, chromium, and vanadium by the Spekker method. For an additional expenditure of 200 mls. of phosphoric acid, 50 gms of urea, 20 gms of silver nitrate and 250 gms of ammonium persulphate one can save 1.1 litres of concentrated sulphuric acid, 4 litres of concentrated nitric acid, 660 mls. of concentrated hydrochloric acid, 750 gms of stannous chloride, 50 gms. of sodium thiosulphate, 4 litres of butyl acetate and 100 gms. of sodium bismuthate. This is *without* adopting a microchemical approach. Spekker methods are capable of being adopted to micro-quantities ; when this is done the consumption of chemicals becomes reduced to a very much greater extent still ; it is in fact divided by about ten. In a country like India where chemicals are rather scarce and very expensive it is most important that all chemical laboratories should make the maximum possible use of modern microchemical techniques.

Boiler Corrosion

The corrosion of boilers is often a problem on board ship, and the corrosion that occurs can take several distinct forms. One type of internal boiler corrosion is known as " air bubble " pitting, and as the name implies is associated with bubbles of oxygen adhering to metal surfaces. There is little risk of such bubbles collecting whilst the boiler is steaming, owing to the violent agitation which occurs, but they can collect fairly easily when the boiler is shut down and may form pockets in the tops of steam and water drums, and around nuts, boiler fittings, and the like. Once the bubble has settled in contact with the metal of the boiler the course of the corrosion reaction is entirely electrochemical, the e.m.f. involved originating in the fact that a piece of steel which is well aerated is cathodic to one which is less well aerated. This is known as the differential aeration effect. The metal against which the bubble rests is thus cathodic to the surrounding areas, which are anodic, and on which corrosion then begins to take place. The iron which is lost at the anode becomes converted ultimately to the ferric condition at points round the edges of the bubble, and often forms a skin over it. This skin permits the passage of ions but restricts the access of more oxygen. When the oxygen in the bubble has been all used up in feeding the cathodic reaction and in oxidising iron to the ferric condition, the situation becomes reversed. The area which was at first cathodic because it

was oxygen-rich has now become oxygen-poor, and hence behaves as an anode instead of a cathode. Thus all the subsequent corrosion is concentrated at one point beneath the site of the original bubble, leading to deep pitting. This type of corrosion can be reduced by adding a little sulphite to the feed water to remove oxygen.

External corrosion often occurs in marine boilers, most commonly beneath deposits of soot which collect in the more inaccessible portions of the heating system. Fuel oils often contain appreciable amounts of sulphur—possibly as much as 3%. This of course becomes oxidised during the burning of the fuel oil, and sometimes as much as 2% of free sulphuric acid may be found in the deposits to which I have referred. This leads to serious wastage of the external boiler components. So far a really practicable answer to this problem has not been evolved. As a matter of interest it may be mentioned that appreciable quantities of vanadium, derived from some types of oil fuel, may be found in the external deposits in boilers, and in times of extreme shortage it might well be worthwhile to organise the systematic collection of these deposits.

Another type of corrosion, internal this time, which frequently gives rise to trouble is the so-called deposit attack, and it is very frequent in the condenser tubes of boilers. These are usually made of various types of cuprous alloy such as cupronickel, aluminium bronze or even alpha brass. Deposit attack mainly occurs on the cold water side of the tubes : sea-water is of course the cooling agent. The cause of deposit attack is the lodgement upon the tubes of debris of almost any sort—sand, mud, sea shells or small sea-weeds which have not been filtered off ; corrosion then occurring as the result of differential aeration effects, the part beneath the deposit being anodic to the remainder of the metal and thus suffering concentrated attack.

Hull Corrosion

The portion of a ship which is most exposed to corrosive influences is of course the hull. A ship is in fact a highly corrodible mass of metal half-immersed in a highly corrosive medium.

There are a number of factors which do, or which can, govern the amount of corrosion that occurs below the water line. Stray leakages of direct current from ship' electrical machinery may make a serious contribution to corrosion ; and in particular currents arising from certain types of welding operation in which the ship's hull is used as the earth may lead to very intense local attack. In such cases the attack becomes focussed upon points where the coating of protective paint has been scratched or damaged and very deep pits may be produced at such places. Potential differences also arise wherever dissimilar metals are in contact ; although most of the hull is of steel, there are certain fittings which are not, the propellers for example ; these are usually made of bronze or other cuprous alloy. Potential differences can also arise between adjacent areas on the same piece of metal. An instructive example of this can easily be demonstrated in the laboratory. Take a piece of copper about $2'' \times 3''$ and clean the surface thoroughly, either by sand-blasting or by rubbing it with sand-paper, and then place it in a neutral solution of sodium chloride containing a little phenolphthalein. Do not stir the solution ; leave the piece of copper quite still. You will find

that almost at once an alkaline reaction will develop over a considerable area of the metal. This is due to the fact that part of the surface is reacting cathodically to the remainder. The reaction ceases after a while, but is usually strongly marked during the first few minutes. In the instance quoted the potential differences undoubtedly originate in differential surface strains introduced during the vigorous abrasive process that was applied. Such strains arise very easily in the case of large metal plates such as those on the hull of a ship; they are introduced during welding or rivetting, and in the case of curved plates, during bending; and they also arise in consequence of the heaving and straining to which the ship is subjected when at sea. If some form of heat treatment has been applied to one part and not to another, as in welding, the heated area will shew a different potential form that of parts not so heated. Rust-spots will react differently from unrusted steel, and millscale, if still present on the plates, will do so also. Temperature differences between various parts of the hull will also lead to the setting up of potential gradients with a corresponding movement of current. Differential aeration, too, makes a considerable contribution. It is hardly too much to say that the hull of a ship behaves in practice like a mass of anodes and cathodes all in metallic contact with each other. Though in many cases the actual potential differences are small, nevertheless there is a continual flow of current from one part of the hull to another, and a corresponding amount of corrosion. The hull is normally protected by painting with paints specially designed for the purpose. Detailed discussion of these paints would take too long; suffice it to say that in the main these paints were developed on an empirical basis, and that it is only in quite recent years that a scientific approach to the problem has been made. This can be illustrated by one novel material which has been proposed recently, the so-called cementiferous paints. These, as the name implies, are more like cements than paints. The cement used is an oxychloride type, rather like the Sorel cements often used for floorings in houses, but a high proportion of zinc or magnesium dust is mixed in with the cement—a sufficiently high proportion for the metallic particles to be in contact with each other throughout the coating. The mixture can be applied by brush and, a great advantage in shipyard practice, it can if necessary be applied to damp surfaces. Ship's plates coated with these paints are protected in much the same way as if they were galvanised; the zinc particles are not only in contact with each other but with the steel of the plating as well. Zinc is of course strongly anodic to steel, and all the corrosion that occurs takes place in the zinc—an example of what is sometimes known as "sacrificial corrosion". The function of the oxychloride cement is merely to hold the metallic dust in position on the hull. These paints give excellent protection, not merely to the metal beneath them but to bare patches on the hull, which remain quite bright and untarnished after long immersion in the sea.

Another application of the principle of sacrificial corrosion that has received a great deal of attention recently is the process known as cathodic protection. This is applied to ships which are expected to lie in harbour for long periods. The ships are connected electrically to large anodes of highly pure magnesium which are hung in the sea over the side of the ship, and the ships then form the cathode of a shorted electrical cell. The anodes used may contain as much as 100 lbs of

magnesium and may last for about a year. The potential difference between the anode and the ship must be kept at a level sufficient to mask all the corrosion currents, such as I described earlier, which normally flow from one part of the hull to another. This is checked by periodic measurements of the ship's potential against a standard electrode ; a potential of about 0.8 volt relative to a silver/silver chloride electrode is adequate. When in that state the ship should remain free from corrosion even if there is no paint on the bottom at all. This process 'will of course not protect the vessel against ordinary atmospheric corrosion which takes place above the water-line.

One paint that is never used below the water-line on a ship, although its protective qualities are excellent in almost all other situations, is red lead. This pigment is sometimes reduced to metallic lead at localised points if used on a ship's bottom ; bacteriological action has been suspected in some cases, though the true explanation is not entirely clear. When this does happen the results are disastrous. The lead and the steel in contact with it now form an electrical cell in which the steel is the anode— a situation the exact reverse of cathodic protection. Cases have been known where in consequence of this action steel plates have been completely perforated in a short space of time.

Antifouling Paints

Antifouling paints form another class of interesting materials. Fouling is the term used to describe the mass of shell fish and sea weeds which accumulates on the hull of a ship. The increased frictional drag which is caused by this is so serious that it has been estimated that 20 per cent. of all fuel consumed by a ship for purposes of propulsion is used entirely in overcoming this increased resistance to movement. It has long been known that fouling could be prevented, or at any rate greatly reduced, if the hull were coated with certain special paints containing poisonous compounds of copper or mercury. Typical toxins used are cuprous oxide, mercuric oxide, and mercuric thiocyanate. An essential feature of such paints is that the binding medium should contain materials like rosin or shellac, which are slightly acid in nature and in consequence will slowly dissolve in a faintly alkaline medium such as sea-water. The effect is that the slow dissolution of the binding medium continually exposes fresh particles of the toxic pigment to the solvent action of the sea. Within the last few years investigations have been carried out to determine the minimum amount of toxin which must be dissolved out of the paint film per day if the ship is to remain free from fouling organisms. The result was most surprising. All that is necessary to prevent fouling is that the paint film should release into the sea 10 microgrammes—not milligrammes, microgrammes—of copper per sq. cm. per 24 hours. When these minute amounts are considered in relation to the vast volume of sea water that surrounds a ship it seems almost incredible that they should suffice to kill off the spores or larvae of sea-weeds and shell-fish, but the finding has been confirmed beyond doubt. What then is the precise mode of action ? One explanation is that the toxin liberated from the paint does not diffuse away into the sea, but remains trapped as it were within the layer of sub-laminar flow—a thin film of liquid which is theoretically not in motion relative to the ship even when it is moving. There is a little evidence in support of this, but not much.

On the other hand it is of course known that colonies of young algae growing in a laboratory tank can be killed by merely dipping a copper coin into the water. But even so the most probable explanation seems to be that the toxin exerts a repelling effect upon the spores and larvae rather than that it kills them.

Fire Retardant Paints

A good deal of attention is paid to the fireproofing of materials that are to be used in ships, which may be illustrated by one example.

At first sight there would not seem to be much danger of fire in a ship made largely of metal, but there is of course always a considerable amount of inflammable material on board of one sort or another. The potential danger in petrol tankers does not in any case need any emphasis. There do not seem to have been any serious fires in passenger ships recently but there were several major disasters about twenty years ago; on one occasion a big French liner, whilst still being built, was completely burnt out. Investigations into this and other instances shewed that the paint used for interior decoration often played quite a large part in causing the fire to spread from one part of the ship to another. In one case a nitrocellulose finish had been used throughout the ship, and once a small fire had started at one point the nitrocellulose burnt very violently, the flames extending sideways over the surface in a very short time, so that the conflagration soon travelled over the entire ship. The lessons of that disaster were of course taken to heart and the more inflammable types of paint were thereafter avoided but even so it was found desirable during the war, when fires were a not infrequent occurrence, to carry the development of fire-resisting paints a stage further. It was found that even in the case of paints which did not shew any signs of permitting the flames to extend sideways over the surface it was still possible for a fire to be transmitted from one compartment to another. This happens as follows : suppose there is a fire in one compartment. The steel walls will get very hot, of course, and the paint on the side of the wall remote from the original fire will start to decompose. The decomposition will necessarily begin on the under-side of the film, the part of the film in immediate contact with the hot wall undergoing what is in effect a destructive distillation in the absence of air. The vapours produced are unable to escape because there is a film of intact paint above them. The result is the production of large bubbles, sometimes several inches across and perhaps an inch deep, full of highly inflammable vapour. Ultimately, of course, the bubble bursts and emits jets of hot gas which may spontaneously ignite and form tongues of flame several inches long. These will set fire to anything inflammable within their reach, thus causing the spread of fire from one compartment to another despite the existence of steel fireproof walls between them.

The objective was therefore to produce a paint which on heating the dry film did not produce inflammable vapour. One way to secure this would seem to lie in the provision of supplies of oxygen in the paint film itself so that when subjected to strong heating there would be adequate amounts available to oxidise the carbonaceous matter present. The paint film should then, theoretically at any rate, emit carbon dioxide and water rather than oily vapours.

This can be done by incorporating easily-reducible oxides in the paint. It happens that many common paint pigments are oxides, for example zinc oxide, titanium oxide, antimony oxide, iron oxide, and so on, although not all of those are easily reducible. The effectiveness of a number of oxides was investigated and it was found that in general those with a higher heat of formation than carbon dioxide were useless for the purpose whilst those with lower heats of formation were fairly good. Thus aluminium oxide, iron oxide, silica and titanium dioxide were ineffective whilst zinc oxide, copper oxide and some others showed considerable promise. The curious thing is that the most effective oxide was antimony trioxide, although its heat of formation would put it in the ineffective category. It would appear that this oxide catalyses the oxidation of organic matter in an unexplained manner, or else that some side reaction occurs which does not take place with other oxides, except arsenious oxide (which though of course unsuitable as a paint pigment, behaves even more effectively than antimony trioxide). The matter seems to merit further detailed investigation since it might have considerable relevance to the fireproofing of materials other than paint.

It should be pointed out that the fireproofing of paint does not mean that the paint is unaffected by heat or fire ; actually the paints described above are *more* sensitive to heat than ordinary paints ; the essential thing is that they decompose in a safe and not a dangerous manner. This same principle is involved in some other forms of fireproofing ; certain textiles, for example.

The possibility of producing an entirely fireproof paint that is quite unaffected by heat exists in the organic compounds of silicon such as ethyl silicate, which when painted out in the form of a solution slowly hydrolyses under the influence of atmospheric moisture and leaves behind it a film of cross-linked silica. Paints of this type are available commercially though they suffer at present from certain disadvantages which have prevented them from coming into wide use. Silicone resins, which are polymers of organo-silicon compounds possessing a cross-linked ether type of structure, are also available, although very expensive at present, and these too offer the possibility of making paint films which are largely inorganic in nature ; silicone paints are however of the stoving type. It is interesting to note that titanium analogues of silicon ester such as butyl titanate are also available commercially and may ultimately find an application in this field. Incidentally a kind of rubber can be made from the silicones.

Oil Fuel

Ships cannot of course move without fuel of some sort and there are a number of problems which arise in this connection, especially with present day fuel oil. Furnace fuel oil is a residue from the distillation of petroleum and the ever-increasing demands for aviation spirit in recent years have led to the situation where more and more of the lighter fractions are nowadays distilled off from the residues than was the case before the war. The requirements for jet fuel have in particular affected the type and quality of petroleum residues. Jet fuel is much heavier in nature than

petrol or aviation spirit and in order to obtain adequate supplies it has been necessary to take the distillation process far beyond what was a satisfactory stage in the pre-jet era, when the fractions now required were not in great demand. The consequence is that the furnace fuel oil of today is a much thicker and heavier product than before ; so thick in fact that it is often very viscous and is sometimes difficult to pump. An even worse feature is that many present-day oil fuels shew a strongly marked ability to emulsify with sea water. In some cases you can put the two together in a beaker, stir them briefly with a rod, and find that the mixture is completely uniform.

In practice it is difficult to avoid oil fuel coming into contact with sea water. Quite apart from the question of leaky tanks, it is common practice, especially in warships, to replace fuel oil pumped out and consumed in the furnaces by pumping in an equivalent amount of sea water in order to maintain the stability and trim of the ship. The rocking of the ship in rough seas may be quite sufficient to cause a great deal of sea water to become emulsified with the oil. It is possible for an emulsion containing 26 per cent. of oil and 74 per cent. of sea water to be formed. The tendency to emulsification appears to be due to the presence of compounds of high molecular weight of the asphalt type in fuel oils that have been distilled at a high temperature and have undergone a considerable amount of thermal decomposition. The emulsions are of the water-in-oil variety, oil forming the continuous phase. One consequence of this is that if further quantities of fresh fuel oil are added to an existing emulsion, mixture can take place quite freely. Some emulsions are so thick as to be incapable of being pumped.

The effects of using fuel oil containing sea water are most undesirable. When such oil is burnt in a furnace the salts derived from the sea water are transformed into minute molten particles which are carried forward by the gas stream. Interaction with sulphur dioxide in the presence of hot steam leads to the formation of sodium sulphate from sodium chloride. These salts become ultimately deposited in liquid form on the brickwork which lines the furnace. At the high temperatures involved the refractories react with the molten salts to produce a glassy low-melting slag which runs down thus exposing fresh surfaces of brickwork to further attack. If the oil fuel contains vanadium, as some do, this greatly assists in the process. Ultimately the brickwork may become completely ruined and the furnace will have to be re-lined if the boiler is to continue in operation. Another consequence equally objectionable in its way is that when these molten salts collect on the boiler tubes they rapidly pick up particles of dust, grit, metallic oxides derived from the fuel, and so on, so that the gas spaces between the tubes may become blocked, thus preventing proper heat exchange and ultimately making it impossible to maintain steam pressure in the boiler.

Fortunately methods of removing sea-water from the emulsions with fuel oil are available. The addition of quite small amounts of the well-known commercial wetting agent Teepol will suffice to break the emulsion completely, after which the oil and water can be separated mechanically in various ways. The breaking action of the Teepol is so pronounced that an unpumpable emulsion of the type referred to above can be rendered pumpable by merely spraying a solution of Teepol on to it.

Explosions and Toxic Hazards

The above account by no means exhausts the matters with which a chemist may find himself involved in a shipyard or in connection with the operation of ships. It may be of interest to mention one lesser type of activity which the dockyard chemist is often expected to undertake. That is the investigation of possible hazards of explosion and of poisoning by abnormal atmospheres. The former danger arises mainly when a fuel tank or a petrol tank has to be opened up for repairs, especially if the repairs involve welding. There is of course also a toxicity hazard in entering an apparently empty petrol tank since petrol vapour is actually very poisonous; 0.1 per cent. of petrol vapour in air will speedily cause dizziness, and anaesthesia and death are rapid in an atmosphere containing 2.5 per cent. A number of satisfactory instruments are available for testing such atmospheres; they usually depend on the principle of burning a sample of the air-petrol vapour mixture in a closed chamber by means of a hot wire, and measuring the pressure difference which results; or alternatively the instrument can be arranged to detect changes of resistance in the hot wire, which will occur if combustion takes place on its surface, leading to additional heating; this alteration of resistance can be calibrated in terms of petrol vapour concentrations.

Miscellaneous

In addition to work in the above fields, the shipyard chemist will find himself concerned in a number of other activities. General foundry work, for instance, is a never-ending commitment, involving the testing of moulding sands, pyrometry, the provision of advice on the heat-treatment of metal and the normalising of castings, and the like. The control of boiler-water in steam installations will also require his attention; and he may perhaps also be required to supervise such processes as the kiln-drying of timber and the rot-proofing of rope.

Quite apart from actual laboratory work he will of course be expected to provide technical advice upon materials of all sorts, upon their properties and correct method of use; and he will be called upon to explain cases of the failure or erratic behaviour of those materials in service. In order to do this he must not only be well-informed in the chemical sense; he must also have knowledge and experience of the actual conditions which the materials of ship have to face in practice, and must keep in close contact with ship-designers and ship-builders and with the engineers and others who maintain and use the ship when it has been built.

Much of the work of a shipyard chemist in this country will inevitably be concerned with the supremely important question of indigenous production. This problem looms so large before us that in the present writer's considered view it is the most important single aspect of the work of the defence scientist at the moment. Not only must indigenous production be stimulated in order to strengthen the economic condition of the country, it must be encouraged in order to safeguard the requirements of the Navy and Mercantile Marine in time of war, when overseas sources of supply might be cut off; even if India remained neutral, a global war would deprive her of many raw materials and much manufactured equip-

ment, spares, and so on. From the point of view of the research defence scientist as such, the situation is that he will remain to some extent limited in his scope in a country whose industrialisation is incomplete, because it is obviously of little use for him to develop new types of equipment or armaments if there is no possibility of producing these items on a large scale. It is his responsibility therefore to do everything in his power to find substitutes for those materials which are in short supply, to advise upon the stockpiling of raw materials against an emergency, and to give freely of his specialised knowledge in assisting the development of those industries upon which the services depend.

The responsibility of the chemist in this connection is, if anything, higher than that of any of his scientific colleagues, since good material is the basis of all types of Service equipment, from bayonets to asdic sets. So important is chemistry as the foundation for industry that it has sometimes been said that the real strength of Germany in the last two Wars lay not so much in her land, sea and air forces as in the great chemical combine, the I. G. Farbenindustrie. This is, of course, a large overstatement; but there is nevertheless a great deal of truth in it.

From the Indian Navy's point of view, particular importance attaches to the production of high grade steel and of non-ferrous alloys in general; and to the development of light alloys of a type suitable for constructing small craft. Such alloys can also be used to replace many fittings at present made out of various types of yellow metal. A certain quantity of special alloys for limited but highly critical purposes is also required, mu-metal being a good example. Rubber is an extremely important material, whose performance often leaves a very great deal to be desired. Corrosion is the eternal enemy of steel ships, and the provision of a wide range of efficient protective paints is essential. Antifouling compositions are a type of paint whose importance can hardly be exaggerated since they have a direct bearing upon operational efficiency in that they affect speed, fuel consumption, and the length of time between dockings. Insulating varnishes, fire retarding paints, deck paints and non-slip deck coverings are also materials which are in great demand but whose commercial production is anything but simple. The foregoing list is far from exhaustive, but it will suffice to provide some idea of the scope for chemical and metallurgical work in connection with the indigenous production of naval requirements.

Author's Note.—Since the above was drafted, further information relating to radioactive isotopes has become available :—

Thulium 170 is now obtainable, having a half-life of 127 days; it can be used for many purposes for which iridium 192 is used. This thulium isotope is essential for work on light alloys. Caesium 137 is likely to be available soon; it has a half-life of about 25 years, and is useful for intermediate thicknesses.

A Cobalt 60 source of about 250 mC, with caesium 137 and thulium 170 should enable one to tackle all radiographic problems connected with steel 2½" thick down to 1/32" (or ¼" in the case of aluminium). Greater thicknesses of steel than the above can be dealt with using cobalt 60, but sources of much higher activity than 250 mC are needed; with a source whose activity is of the order of 1250. mC it claimed that thicknesses of 8" to 11" of steel can be radiographed.

A source is, of course, still capable of being used even after its half-life has been exceeded; but the length of exposure has to be correspondingly increased.