

SHIPS' PAINTS

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Introduction

Paints for ships are very old, as old as ships themselves, and many changes have taken place since the earliest recorded times, both in ships and in the means of decorating and protecting them.

An account of ships' paints can cover a wide field, but it is intended in this paper to deal mainly with those paints used in H.M. ships. Warships as a separate entity did not come into being until Charles II took over the sizeable fleet built up by Cromwell, and called it the Royal Navy—ironically, Charles was the first British monarch who did not personally own his Navy!

The types of paint used over the years changed very little until the wooden vessel was replaced by the first of the ironclads late in the 19th Century. With the advent of the iron and steel ship, shipbuilders were faced with the new problem of corrosion and this gave considerable impetus to the marine paint trade, as paint was soon found to be the simplest and most effective means of protecting steel under marine conditions. The decorative properties of paint, then, took second place.

Developments in ships' paints since the days of the early wooden vessels can be divided into four eras as follows :—

- (i) Up to 1810 : Wooden ships. Simple oil paints for decoration above water—tar and copper metal sheathing below water.
- (ii) 1810 to 1939 : Iron and steel ships. Red lead, white lead, zinc oxide, etc., in linseed oil. Proprietary anti-corrosive and anti-fouling paints.
- (iii) 1939 to 1958 : Titanium dioxide, etc., in oil-modified synthetic resins (alkyds, penolics, etc.). Admar and Pocoptic underwater.
- (iv) 1958 to date : Improved modified alkyds, etc., for general protection. Increasing use of catalyst-cured coatings (epoxys, etc.).

In considering paints for H.M. ships, there is a tendency to concentrate not only on protective paints, but on protective paints for the underwater areas of the ships. This is natural as the operational efficiency of a warship is largely dependent on the condition of the underwater hull, that is, on the performance of the outer bottom coatings applied. Other ship paints, therefore, can be regarded as of secondary importance in comparison.

To illustrate the importance of protecting ships' plating, it has been stated⁽¹⁾ that if a ship was under weigh at 20 knots for six months in each year, an unpainted plate in the outer bottom would lose about 60 mil. thickness per year. Put another way, in modern naval frigates where 10 lb ($\frac{1}{4}$ in. thick) shell plating is used, an unprotected plate would require renewal after 12 months' service, and if not renewed would be holed in two years. Local pitting in areas of high turbulence could cause even greater rapidity of breakdown.

As a preface to an account of paints for naval vessels, it is important to emphasize one or two essential differences between ships of the Navy and

Merchant Fleet and to bear these points in mind when considering the various types of paint used :

- (i) H.M. ships are truly global—they have to be ready to operate in any part of the world at short notice. Merchant ships usually have regular well-defined routes.
- (ii) In peace-time, H.M. ships spend a lot of time at anchor. Merchant ships normally have a quick turn-round and spend most of their time at sea.
- (iii) At sea, H.M. ships operate at varying speeds, according to operational requirements. Merchant ships operate at economic speeds, to a timetable.
- (iv) With H.M. ships, maintenance of operational (i.e. fighting) efficiency takes priority over all other requirements.
- (v) As H.M. ships do not have to show a profit on their operations, it is often possible to use higher grade paints than on merchant vessels, where the profit motive is paramount.

It is clear, therefore, that H.M. ships present their own peculiar problems which cannot necessarily be solved by comparison with commercial ships. It also shows why a separate organization of scientists and technologists is essential to deal with these problems.

Surface Preparation

No discussion on ships' paints can ignore the subject of surface preparation. The use of higher grade paints has focused attention on the need for proper surface preparation if these paints are to give maximum performance.

For years steel used in H.M. ships has been pickled in cold 5 per cent inhibited hydrochloric acid for 24 hours to remove the mill scale, rinsed with fresh water and then put in open racks to weather. When required for use, the loose rust is removed by wirebrushing. The surface so produced is reasonably satisfactory for coating with the normal underwater paints and has given good results above water with oil-based paints. It is not, however, good enough for the modern coating systems, and there is no doubt that the widespread desire to take advantage of the improved protection offered by modern coating materials has hastened the introduction of grit blasting methods into dockyards and shipyards.

Grit blasting has, however, brought its own problems—the type of abrasive to use, its size and shape and consequently the physical characteristics of the surface produced by the process. As to type of abrasive, the Admiralty uses crushed steel grit in a closed vacuum process (Vacu Blast) and a silica-free slag in an open-blast process for ships' bottoms. The standard of surface preparation given by the Vacu Blast is shown in FIG. 1.

A number of shipyards have installed descaling and cleaning machines using steel shot, which is thrown from an impeller wheel on to the surface being cleaned.

At the present time, the steel grit being used in the Vacu Blast process is between 18 and 24 B.S. mesh. This gives a surface roughness or profile on mild steel of 2 to 3 mil. Surface profile is measured by three separate methods :

- (a) Vertical measurement using the microscope
- (b) Sectioning and taking a photomicrograph
- (c) The Talysurf Surface Measuring Instrument, which traces the profile of surface irregularities and records them on either :
 - (i) A graph recorder giving a representation of the surface irregularities ; or

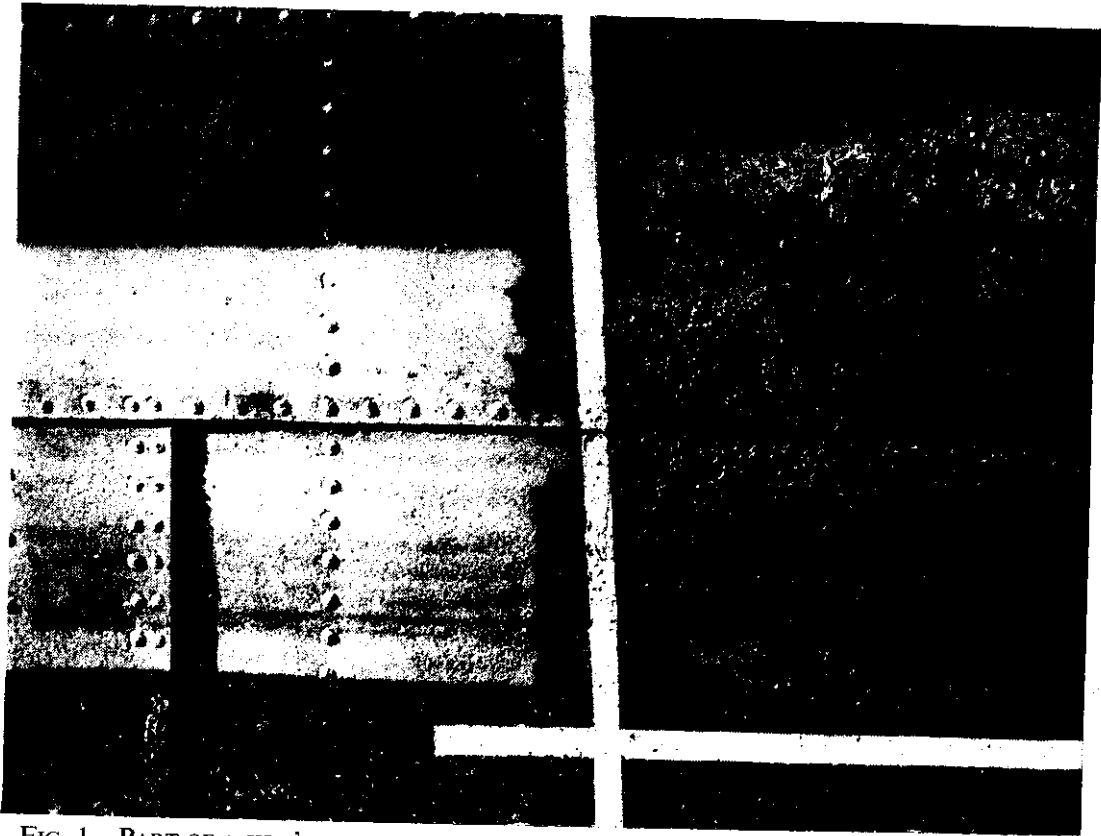


FIG. 1—PART OF A SHIP'S OUTER BOTTOM PLATING CLEANED BY THE 'VACU BLAST' PROCESS

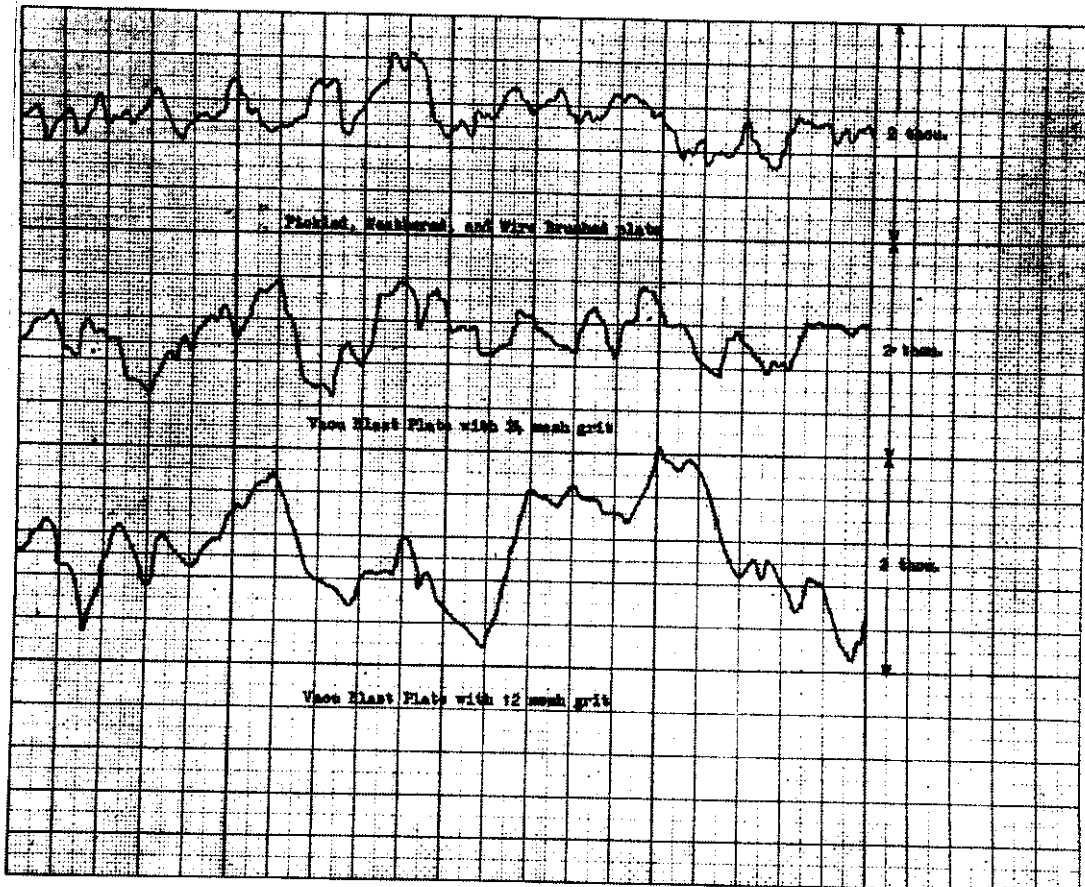


FIG. 2—SURFACE PROFILES OF PICKLED, WEATHERED, WIRE-BRUSHED AND GRIT-BLASTED (VACU BLAST) MILD STEEL PLATE

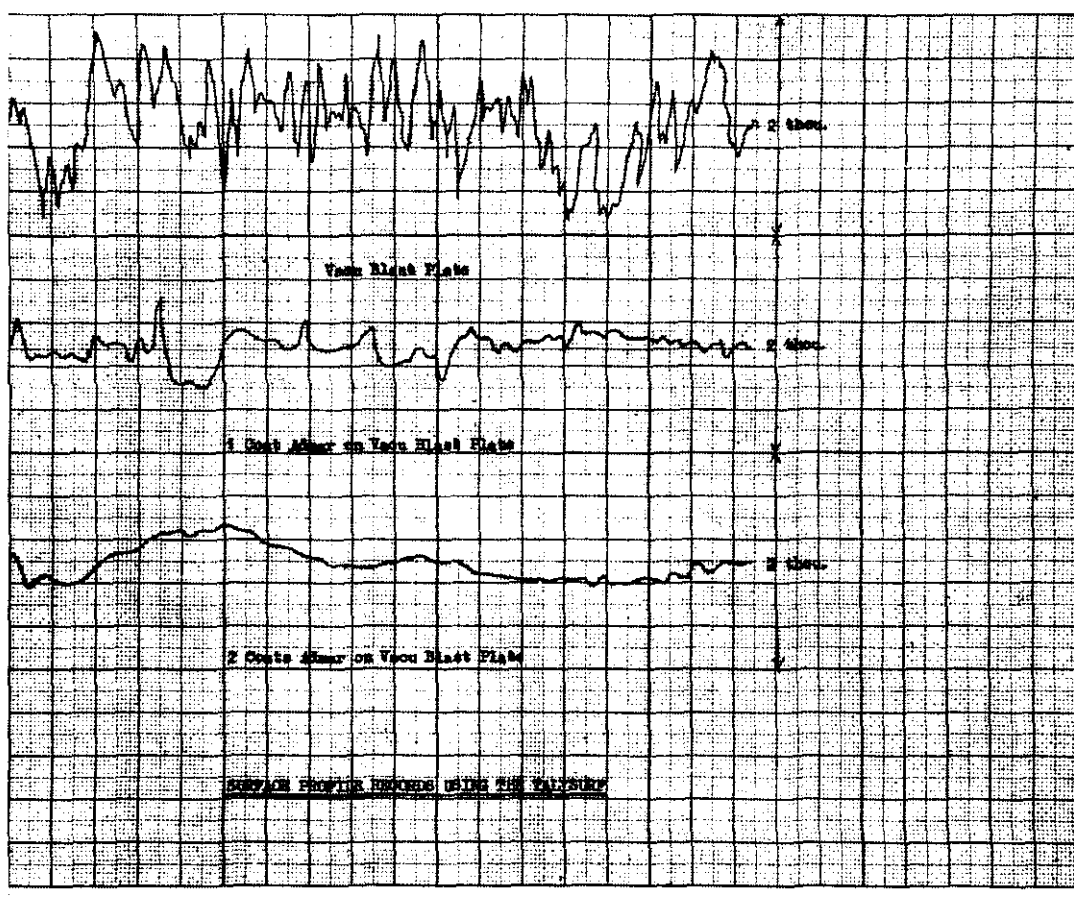


FIG. 3—SURFACE PROFILE OF GRIT-BLASTED PLATE BEFORE AND AFTER COATING WITH ONE AND TWO COATS OF ADMAR

- (ii) An Average Meter, which shows the centre-line average (C.L.A.) index of all irregularities coming within a prescribed length of surface.

Profiles of typical surfaces obtained by pickling, weathering and wirebrushing compared with grit-blasting are shown in FIG. 2.

The importance of controlling surface profile is shown by an early experience in which the outer bottom of a frigate was gritblasted using the open-blast process and given two coats of A.C.655 protective paint before undocking. Within weeks the outer bottom was severely rust-spotted. The reason was that blasting had been done using a coarse grit giving a surface profile on the plating of 7 to 8 mil. Two coats of A.C.655 give a thickness of 2 to 3 mil. dry film, so it is not surprising that some high spots remained uncoated. The recommendation that final paint thickness should be three times the maximum surface profile may be a little generous but is a good rule to follow—this implies a total coating thickness of 6 to 9 mil. on the outer bottom. On H.M. ships for new construction, or any new plating, adequate thickness is obtained by five coats of A.C.655 and one coat of anti-fouling paint, which gives a total coating thickness approaching 9 mil.

Measurement of surface roughness is important for another reason. Recent emphasis on smaller ships and higher speeds has made it imperative that friction losses on the underwater parts of a ship be reduced to a minimum. Apart from factors such as fouling, shape and positioning of any cathodic protection anodes and other fittings, the smoothness of the paint coating is of considerable importance. Some simple tests were carried out to see how many

TABLE I—*Formulation of Admar and A.C.655*

	<i>Admar (Red)</i>	<i>A.C.655 (Red)</i>
Basic lead Sulphate	26.7	20.0
White lead	13.3	—
Aluminium Powder (non-leafing)	—	10.0
Iron Oxide	13.3	10.0
Barytes	13.3	10.0
Phenolic Resin	5.3	9.
Phenolic resin	5.3	8.0
Linseed stand oil	10.7	8.0
Tung oil	—	8.0
White Spittit	10.00	17.0
Naphtha	6.5	8.0
Lead naphthenate	} To satisfy drying requirements	
Cobalt naphthenate		
Manganese naphthenate		

coats of Admar were required to produce a smooth finish over a correctly grit-blasted surface. It appears that two coats are effective, as shown in FIG. 3.

On a ship scale some important trials have been carried out by the British Shipbuilding Research Association⁽²⁾ on two sister ships of 18,000 tons d.w. to determine to what extent the original trial performance deteriorated with time in service. Neither ship was grit-blasted before painting and the results showed that after 3½ years one ship had deteriorated to the extent of 40 per cent in s.h.p., and even after docking, cleaning and repainting was still 32 per cent above the original trial performance. The second ship gave similar results. It seems fairly clear that this residual loss of performance was caused mainly by roughening of the hull due to corrosion, and points to the value of thorough initial surface preparation.

Underwater Paints

A ship can be regarded as a very corrodible body partly immersed in a very corrosive liquid. Long experience has shown that paint coatings are effective means of preventing this corrodible body from disintegrating.

An underwater paint system has to meet two basic requirements :

- (i) To protect the steel surface against corrosion ; and
- (ii) To prevent the attachment of fouling organisms.

Underwater corrosion is now accepted as being an electrolytic process, in which anodes and cathodes are present to form a cell with the water as the electrolyte. Anodes and cathodes can occur in a single metal such as steel, due to lack of homogeneity. When the steel is immersed in water a current will flow removing Fe ions from the anodes and depositing rust—in other words,

corrosion always occurs at the anodes. The pattern of the anodic and cathodic areas depends on many factors, such as variations in composition of the metal, variations of salt and oxygen concentration in the water, and so on.

Paints can control the corrosion of steel in water in two ways : by forming a physical barrier between the corrosive salts and the steel surface ; and by incorporating inhibitive pigments which stifle the corrosion reactions at the metal surface. This concept has been the guiding principle in the development of modern anti-corrosive paints.

Up to the early part of the last war, all underwater paints for H.M. ships were purchased from the trade. In the early years of the last war collaboration with the British Iron and Steel Research Association (B.I.S.R.A.) resulted in the selection by the Admiralty of Formulation No. 173 for extended trials as an anti-corrosive paint. It was first manufactured as Pomar at Portsmouth in 1945 and ship trials were carried out over-coating it with Pocompt anti-fouling, quartered against proprietary systems. As a result of these trials, Pomar was adopted for Service use. Later it was governed by a Specification and given the name 'Admar', supplies being obtained from the trade. It is a good general protective paint and has given good results in service. It became clear, however, that a paint based on a more water-resistant medium and less liable to blistering would be an advantage. Investigations carried out by B.I.S.R.A., with Admiralty collaboration, showed that this could be achieved by incorporating some tung oil in the medium and aluminium powder in place of white lead in the pigment, which led to the adoption of A.C.655.

The formulae for Admar and A.C.655 are compared in TABLE I.

On clean steel, A.C.655 gives a smooth coating with good protection against corrosion. It meets the needs of the Navy for application to clean steel, but is not suitable for maintenance purposes. While superior to Admar on bare steel, it shows signs of stripping from old paintwork. The explanation is fairly simple. The old coating of anti-corrosive and residual anti-fouling may appear dry but in reality is carrying absorbed water. 655 is sufficiently water-resistant to be unable to take up any of this absorbed water, so in time the film is pushed off. Admar, on the other hand, either takes up this water or allows it to pass through the film more easily, thus relieving any stresses formed. In common with merchant vessels, a separate maintenance coating is now used on naval ships. At present 655 is used on new construction or ships cleaned to bare steel, while Admar is used as the maintenance paint over old paintwork.

The statement that 655 is used on bare steel requires qualification. The procedure is that after grit-blasting, a coat of pretreatment primer is applied followed by five coats of 655 on the outer-bottom and six coats on the boot-top area. This use of pretreatment primer is in line with the recommendations of a recent B.I.S.R.A.⁽³⁾ report with which Admiralty was closely associated. It appears to be effective in passivating the surface, which immediately after blasting is in a very active condition, and in improving the adhesion of paints such as Admar and A.C.655.

A.C.655 is certainly a good paint for underwater protection under normal conditions and the formulation is widely used in the paint trade. A new demand, however, has been made on underwater paints in the past few years—resistance to cathodic protection current. Fairly comprehensive trials by many authorities, including the U.S. Navy and the Admiralty, have shown that the types of paint most resistant to cathodic protection conditions are those based on non-saponifiable materials. The conditions at the surface of a cathodically protected ship's bottom are alkaline and this alkali reacts with paint coatings based on oils or oleoresinous media containing fatty acids to form the corresponding soaps. This action going on in the paint film softens it and leads to its disinte-

gration. Straight linseed oil paints, like red lead, are rapidly attacked, but Admar and 655, containing very little free oil are only slowly attacked. They, however, are not as resistant as paints which contain no saponifiable constituents—the best being vinyls, epoxys and polyurethanes, closely followed by neoprenes, chlorinated rubbers and bitumens.

Epoxy paints include the solvent-free types, cold-cured solvent type epoxys and coal tar epoxys. The latter have aroused considerable interest in recent years as promising marine coatings, but there are a number of problems associated with their use. In common with all amine adduct and polyamide-cured epoxys they do not cure below 50 degrees F and seem slow to cure below 70 degrees F. This means that during the winter months in this country, coal-tar epoxys cannot be applied successfully to exterior ship surfaces. This comment appears to apply to all epoxys and is possibly delaying their wider use for external conditions.

Difficulties in application have also occurred. Since the trend among manufacturers seems to be toward thicker coats, difficulties have been experienced in applying coal-tar epoxys under normal dock conditions in cold weather. Possibly it will be necessary for marine use to specify spreading rates and film thickness for each material. In other words, a balance must be achieved between the ease of application of a thinner coat against the practical advantages of reducing the number of coats required by applying a fairly thick film per coat. An alternative colour to black would be an advantage, so that with multicoat systems a continuous coating without holidays could be ensured by alternating black with a coating of another colour.

It is normally recommended that successive coats be applied within seven days, i.e. before complete cure, in order to ensure satisfactory inter-coat adhesion. A longer interval may result in stripping of the top coat. This requirement is not easy to fit into normal shipyard practice. If a ship is being grit-blasted, followed by a coat of a coal-tar epoxy, it may be more than seven days before a second coat can be applied. Also associated with application is the question of pot life ; a satisfactory pot life in this country may be very short in the tropics.

For underwater protection, the final coat is anti-fouling. With the limited experience to date no troubles with adhesion of the normal anti-fouling paints to coal-tar epoxys have been encountered. Difficulties may arise, however, in recoating. The normal practice is to wash off and touch-up the old coating and apply a coat of anti-corrosive and finally anti-fouling paint. The application of an epoxy-based paint over a water-soaked surface, which is virtually what the residual coating will be, is likely to lead to stripping. A maintenance coating is obviously required and at present a paint of the aluminium bitumen type is under trial.

It appears that the time has arrived for a measure of standardization of coal-tar epoxy paints. If possible, the grade and type of tar used should be controlled, and it should be specified that the tar should contain certain compounds, such as coumarone, in order to achieve proper cross linkage with the epoxy resin. If not, the result is a mixture and will not have the desired properties. To ensure that cross-linking compounds are present, a test for cure and resistance to solvents and oils may be necessary. Also the proportions of base and hardener should be standardized and possibly a choice between amine adducts and polyamide curing agents indicated.

These are some of the problems which must be overcome before coal-tar epoxy paints can become more widely used on H.M. ships. Our knowledge of this type of modification of an epoxy resin is still very limited, but such materials have considerable promise as marine protective coatings.

Many of the points which have been considered apply to other cold-cured

solvent type epoxy coatings, which are being used to an increasing extent in H.M. ships, but not so far for underwater applications. They are used mainly for coating fuel tanks in submarines.

Paints for Boot-Tops and Stern Fittings

The boot-topping or waterline area is the most abused portion of the ship's hull. It is neither totally submerged nor totally out of the water, but is continually subjected to alternate wetting and drying. Also, there is considerable water friction and the risk of mechanical damage at the waterline.

The practice for many years on H.M. ships has been to carry the outerbottom coatings up over the boot-topping area and to apply an extra coat of protective paint. This, however, has never given satisfactory results. Modern resin coatings appear to provide the answer. Trials have been carried out on solvent-free epoxy coatings and the results are promising. Coal-tar epoxys, solvent type pigmented epoxys and polyurethanes might also be used and would appear to have advantages in application, while coatings based on resins such as butyl methacrylate cannot be ignored.

Severe erosive conditions due mainly to water turbulence also occur around stern fittings such as rudders and shaft brackets. There is, in addition, the risk of corrosion occurring due to the proximity of the bronze propellers. Again, it has been found that the normal outerbottom coatings are not satisfactory and many alternatives have been tested. One of the most promising is neoprene, but results have been variable. Due to the very great cohesion of a neoprene film, usually much higher than its adhesion to most metal surfaces, when adhesion fails the film detaches in sheets, leaving large areas of metal unprotected, and this has happened more than once in practice. The secret appears to be in the use of the correct primer, which should be controllable, and correct surface conditions for application, which are not always controllable in a dry dock.

Although unsatisfactory on rudders, neoprene coatings have been more successful on the underwater inlets and discharges and are at present the approved coating.

The most promising materials so far for rudders and shaft brackets are the solvent-free epoxies. Applied over a grit-blasted surface to build up a coating thickness of 10 to 15 mil., very good results have been obtained. No primer is required, no corrosion inhibition is provided—protection is obtained by ensuring adhesion of a thick film almost completely impermeable to water.

Antifouling Paints

Before considering anti-fouling paints, a word about fouling itself, the serious effects of which are often not sufficiently appreciated. The Germans came to realize the importance of the problem during the last war, even though a little late. In a letter to Professor Hammerlung on 23rd March, 1943, Professor Wettstein said : ' The great practical importance of preventing growth formation over a considerable period in war, and later in peace-time in merchant ships, requires no further stressing. The speed of a vessel can be reduced by 35 per cent ; millions must be spent yearly on docking and painting. According to a confidential communication, the loss of the *Graf Spee* is to be ascribed to a reduction in speed resulting from growth.'

The following are some of the effects of fouling :—

- (i) Fouling increases the roughness of the hull and propellers, leading to a reduction in speed, an increased consumption of fuel and losses in time and money in applying remedial measures. This would be expected with a ship in the condition shown in FIG. 4.



FIG. 4—FOULING ON A PROPELLER AND PARTS OF THE STERN AREA OF ONE OF H.M. SHIPS AFTER A PERIOD IN RESERVE

- (ii) It can contribute to hull corrosion by accelerating the breakdown of protective coatings. Species vary in their destructive powers, the most serious probably being the barnacle, which if it settles on a fairly soft coating such as bitumen will cut through the film as its shell grows. Other species, like the calcareous tube worm are so adherent that they cannot be removed at dockings without damaging the paint film, resulting in the necessary repainting being further increased.
- (iii) It can directly cause corrosion due to the intermittent occurrence of fouling setting up local variations in oxygen concentration causing galvanic corrosion effects or by producing acidic conditions that assist pitting.
- (iv) It can block seawater inlets and fire mains.
- (v) It can impair the performance of sonic detection equipment by fouling the sound transmitting and receiving surfaces.

Many methods of preventing fouling have been tried from time to time, but experience has shown that success is only assured by those which provide a poison in solution at the hull surface. The most effective poisons are salts of certain heavy metals, particularly copper and mercury, which are lethal to fouling organisms and are commonly used in anti-fouling paints. These paints are so formulated that the poison will gradually leach out. In recent years, investigators in this country and the U.S.A. independently arrived at a definite relationship between the leaching rate of a paint and its anti-fouling properties. The minimum rates, expressed as the metal, to prevent fouling are

Copper	..	10 $\mu\text{g}/\text{cm}^2/\text{day}$
Mercury	..	2 $\mu\text{g}/\text{cm}^2/\text{day}$

and if at any stage leaching rates fall below these figures, fouling may occur.

There are two types of anti-fouling paint—the soluble matrix type and the contact leaching type. Soluble matrix type paints normally comprise poisons and pigments in a matrix of rosin and suitable plasticisers, the paints being so formulated that on immersion in sea-water the poisons are released by combined dissolution of both poison and matrix. Most commercial anti-fouling paints are of this type—as is also Picoptic, used by the Navy. These paints are designed to give protection against fouling for the period between dry dockings of H.M. ships, which can vary between 9 and 15 months according

TABLE II—*Difference in composition between a soluble matrix type and a vinyl type of anti-fouling paint*

	<i>COLD PLASTIC U.S.N. Formula No. 143 (per cent by wt. dry film)</i>	<i>VINYL U.S. Formulation No. 121 (per cent by wt. dry film)</i>
Cuprous oxide	41.0	80.0
Resin	34.0	8.0
Phenolic condensate	17.2	—
Vinylite	—	8.0
Chlorinated rubber	0.9	—
Tritolyl phosphate	6.9	4.0

to the class of ship. Pocoptic meets this requirement and is in fact a reasonably economical paint.

Contact leaching anti-fouling paints have a much higher poison content bound in an insoluble matrix. The principle is that each poison particle is in intimate contact with its neighbour in the dry film, so that as each is dissolved another is exposed and the poison is thus gradually extracted from the matrix solution.

The best known contact leaching paints are the vinyls, in which cuprous oxide is the sole poison and the matrix is rosin and a PVC/PVA copolymer. This gives a very hard, smooth film and if a film thickness of 3 to 4 mil. is applied, a life of up to two years can be obtained on a ship. In actual fact, it is doubtful if the vinyl anti-fouling paints are true 'contact leachers', but they certainly approximate to it. Probably the only true contact leaching paints are the copper metal types used mainly on wooden vessels and yachts.

The difference in composition between a soluble matrix paint and a vinyl type is shown in TABLE II ⁽⁴⁾.

The leaching rate characteristics of the vinyl and soluble matrix types of paint are quite different. In tests carried out with each type of paint, the leaching rates of all the vinyl formulations were initially high, but fell steadily during prolonged sea exposures. The time elapsing before the leaching rate fell below $10 \mu\text{g}/\text{cm}^2/\text{day}$ decreased regularly as the percentage of copper in the paint became smaller, being six months for a paint containing 90 per cent cuprous oxide, compared to two weeks for the paint containing 60 per cent.

With paints based on a cold plastic matrix, leaching rates were also initially high, but fell more steadily during the two months of soaking and attained fairly steady values which were maintained for the duration of the experiment. The steady-state values for paints containing 20 per cent and 40 per cent cuprous oxide were adequate, but for anything less than 20 per cent were inadequate. Cold matrix type paints are clearly more economical in their use of copper poison.

Contact leaching paints of the vinyl type are little used on commercial vessels, but are quite widely used on ships of many navies of the world, including the U.S.N. and the Royal Australian Navy. Vinyl paint systems must be applied to a grit- or sand-blasted surface during dry and warm weather. They are very

sensitive to poor weather conditions during application and must not be applied to damp surfaces. Failure to realize this has led to some serious stripping failures in practice. They have, however, two great advantages—they give hard, smooth films and are resistant to cathodic protection.

The British Navy is rather a law unto itself concerning anti-fouling paints and has for many years made its own, a soluble matrix type based on the U.S. Cold Plastic Formulation, Mare Island 143E. This paint, somewhat modified in composition and manufacturing technique, was given the name Picoptic ('Po' from Portsmouth, 'co' from cold, and 'ptic' from plastic) and is still used on H.M. ships. All the paint is made in one plant and there is such good control at all stages that there is little variation from batch to batch. Picoptic is compatible with Admar and A.C.655 anti-corrosives.

The position is, of course, not static and investigations continue with the object of improving anti-fouling paints and suitable methods of evaluating them. The ideal anti-fouling paint should give complete protection against fouling for a long period—two years is the Admiralty's goal—must resist erosion, maintain a smooth surface and adhere firmly to the anti-corrosive coating. There is no doubt that paints are now available which approach this ideal. The Central Dockyard Laboratory, in particular, has produced several promising paints giving freedom from fouling under raft conditions of over four years. The best of these is being introduced into the Service and it is believed that multiple coats of this paint will give good results on ships for periods of up to two years.

Improved anti-fouling paints for submarines and the boot-top area of surface ships have also been developed. These paints must be black, and to this end salts of mercury as well as copper are incorporated to obtain the desirable properties. Carbon black is required to obtain the black colour, but formulations based on copper sulphide have been tried with reduced amounts of carbon black.

Mention has already been made of the general rule that for copper type anti-fouling paints, fouling usually occurred if the leaching rate fell below $10 \mu\text{g}/\text{cm}^2/\text{day}$. Some years ago it looked as if the exception to this rule had been found—paints containing cupric hydroxide gave quite promising results at a copper leaching rate of 2 to $3 \mu\text{g}/\text{cm}^2/\text{day}$. Further investigation, including tests on plates attached to the keel of a ship and removed at intervals for chemical examination, showed the initial claims to be unfounded. One of the difficulties encountered was that differences were found in stability and reproducibility of different samples of cupric hydroxide. It was concluded that paints incorporating cupric hydroxide might confer a certain degree of anti-fouling protection, but were unreliable, their copper utilization being less economical than that of cuprous oxide paints.

In recent years, trials have been carried out of a number of anti-fouling paints in conjunction with cathodic protection. Results so far have shown that when applied over sufficiently alkali-resistant protective paints, the normal type of anti-fouling paint is satisfactory, though some combinations show some loss of adhesion. During this trial, the idea was put forward that the alkalinity produced by the cathodic protection current might accelerate the solution of the rosin medium and so stimulate the leaching rate of a low-leaching paint. There appeared to be no noticeable effect, however, in practice.

Another problem peculiar to warships is the effect of fouling on underwater sonar equipment. If detection devices are to function satisfactorily, they must be kept free from fouling; many ideas have been tried, but recourse has been made again to anti-fouling paints. Quite satisfactory protection is obtained using a coat of pretreatment primer and a single coat of anti-fouling paint giving a total film thickness of about $1\frac{1}{2}$ mil. At this thickness there is no

serious interference with sound transmission. Thick coatings, like the U.S. Hot Plastic Antifouling Composition, can reduce the transmission by over 90 per cent. This is attributed to the presence of air occluded in the coating⁽⁵⁾. Fouling on the equipment causes loss of transmission by reflection, scattering and absorption. The effectiveness of the sound gear is also decreased by increasing cavitation noise due to fouling.

For testing anti-fouling paints, there are at present only two methods available, the laboratory leaching rate test and the raft trial, i.e. immersion in the sea.

The leaching rate test has been of great value, not only for assessing the potentialities of a paint, but in formulating new paints. It is the only test capable, after suitable correlation, of giving exact and fairly rapid information regarding the effect of any modification of a formulation. The test is now so well known that details are unnecessary. In brief, panels coated with the paint under test are leached at regular intervals in a known quantity of sea-water under controlled conditions. As the majority of paints rely on copper poisons, the most frequent analysis is to determine the copper content of the leachates. This is performed by forming the yellow diethyl dithiocarbamate complex, in the presence of other reagents, to suppress interference by other ions, extracting the complex with carbon tetrachloride and determining its absorbance in an abridged spectrophotometer. From the copper content the leaching rate is calculated, expressed in micrograms/sq cm of paint per day. This technique is applied to other poisons and methods have been worked out for mercury, zinc, diphenylamine and chlorarsine. The test can, in fact, be applied to any soluble constituent of the paint, provided that a sufficiently specific and sensitive micro method can be devised. The test has so far only been applied to poisons ; it would be of particular interest to follow the breakdown of the medium by this means. A possible method has been found for estimating the solution of rosin from the medium in sea-water. If this method can be perfected, we shall have a measure of the solution of the one component which appears to control the rate of solution of the poison.

The leaching rate test has the obvious limitation—it is not an accelerated test. Emphasis has been laid, therefore, on developing such a test. Since chemically accelerated tests have not proved satisfactory, attention has been devoted to developing a laboratory test simulating the flow conditions on a ship. There are two methods of approach, one is to move the paint surface through the sea, the other is to move the sea past the static paint surface. The first experiments involved rotating paint cylinders in a sea-water tank, but difficulty was found in creating turbulent surface conditions. The second method studied involves passing sea-water through a tube with the painted surface suitably located within. Turbulent conditions can be created and a speed of 20 knots of sea-water can be achieved. The aim is a five- or six-fold acceleration of the normal leaching rate.

Techniques for preventing fouling not requiring anti-fouling paint have been tried from time to time. Recently a toxic dispersion system which ejects a kerosene solution of an organic poison from a pipe system located along the ship's bottom has attracted much attention and a number of ships are being fitted with it. There is insufficient evidence so far to suggest that it is a serious rival to the traditional anti-fouling paint.

The emphasis so far has been on underwater paints, and no mention has been made of those used above the waterline, both outside and inside the ship. For each particular requirement there is a paint system specified—a position which is never reached, however, without surmounting a few obstacles. To give a more balanced picture of ships' paints, one or two of these specific problems are considered, albeit somewhat sketchily.

TABLE III

	<i>Linseed Oil</i>	<i>Soya Bean Oil</i>	<i>Tobacco Seed Oil</i>
Saturated acids	8.7—11.3	11.5—14.3	7.9
Oleic acid	4.8—18.8	25.9—33.7	16.2
Linoleic acid	23.2—62.3	52.0—58.8	70.4
Linolenic acid	24.2—50.2	2.1— 5.8	—

Exterior Paints

Red lead in a linseed oil medium has long been used as the primer for the exterior parts of H.M. ships above the waterline. It is unsurpassed in its anti-corrosive properties, but has a number of disadvantages, the chief being its slow drying and its comparatively poor brush-out properties. After considering various modifications, a red lead graphite primer based on a modified phenol formaldehyde linseed tung oil medium is now being introduced which dries overnight to a smooth film, with adequate anti-corrosive properties.

Other types of primer, including those based on micronized lead and calcium plumbate, as well as zinc-based paints, are being evaluated.

Zinc chromate, used for years on aluminium surfaces, continues to give generally satisfactory results.

For some time, the undercoat and topcoats have been based on alkyd resins. Alkyd resin based paints came into use for the above-water areas of H.M. ships during the last war. The formulation decided on after consultation and trials was a long oil linseed modified alkyd resin pigmented with equal parts of titanium oxide and antimony oxide with suitable extenders, and, of course, tinting agents to produce the familiar Admiralty light grey. Though this has given much better performance than the previously used white lead/linseed oil paints, eventual experience showed it to have two faults: (1) poor colour stability; and (2) poor adhesion under water-soaked conditions.

Colour Stability

Colour instability has taken the familiar form of yellowing on exposure—a defect which becomes very obvious when touching-up takes place. Much work has been devoted to the fundamental cause of yellowing. It appears that there are a number of contributory factors, and these include the effect of light, the effect of type and amount of unsaturation, and so on. Now this paint, to Admiralty Specification DNC/M/73, is based on a linseed oil modified alkyd and it has been observed with linseed oil that little or no yellowing occurs when the film is exposed to direct sunlight or to a source of ultra violet radiation. Some yellowing, however, occurs in diffused light, but severe yellowing occurs in the absence of light. This is in line with the experience on H.M. ships where yellowing of interior paints for submarines has been as serious as that experienced with exterior paints. Yellowing is also accelerated by temperatures above normal and by high humidity. This behaviour suggests that the reactions which are promoted by sunlight prevent the formation of the chromophoric groups necessary for colour. Evidence regarding the production of chromophoric groups is obtained from the type of unsaturation required to produce maximum yellowing. Linseed oil films yellow badly and contain an average of 42 per cent linoleic and 37 per cent linolenic acid. Tobacco seed oil, which shows practically no yellowing, has, according to some

TABLE IV

	<i>Old (DNC/M/73)</i>	<i>New (DNC/M/80)</i>
Resin medium	Alkyd or phenolic alkyd	Alkyd
Modifying oil Linseed	70 per cent	High linoleic veg. oil (60— 70 per cent fatty acid)
Tung	Permitted up to 100 per cent as replacement	—
Pigment		
Antimony oxide	37.5 per cent (min.)	—
Rutile titanium dioxide	37.5 per cent (min.)	80 per cent (min.)
Zinc oxide	—	5 per cent (max.)
Tintels for light grey	carbon or veg. black and ultramarine or monastral blue	veg. black monastral blue
Extenders	remainder	remainder (barium carbonate 1 per cent max.)

analyses, 70 per cent linoleic and no linolenic acid. From this it seems probable that some modification of the linoleic acid structure on ageing of the film is responsible for the yellowing phenomena. Removal of linolenic acid or enrichment with linoleic acid appears to be the solution. Accordingly, in the production of alkyd media for exterior paints, a high linoleic acid content is specified, tobacco seed and soya bean being the only two oils allowed. The result has been a considerable improvement in colour stability. The approximate composition of the fatty acids is given in TABLE III.

There are, of course, at least two other factors which can contribute to yellowing. Incorporation of a phenolic resin with the alkyd can give rise to yellowing, which becomes most serious when a white finish is required. Phenolic resins are not, therefore, allowed in the new paint. The pigment composition has also to be considered. In the original Admiralty formulation antimony oxide was used with the rutile titanium oxide to reduce the chalking of the latter. Antimony oxide does not appear to be necessary with the modern chalk-resisting rutile titanium oxide and its omission has improved still further the colour stability of the paint. A comparison of the new paint to Admiralty Specification DNC/M/80 with the original is shown in TABLE IV.

Adhesion under Water-Soaked Conditions

The exterior paint system based on Specification DNC/M/73 over its undercoat of similar composition and red lead gave good results on the superstructure and upper parts of the hull, but on those areas near the waterline, stripping of the topcoat from its undercoat occurred when the paint became thoroughly soaked. An investigation into the problem had two interesting results. First of all, it showed the undercoat to be the weak link. Alterations were made to the formulation and eventually a new undercoat, a linseed stand oil/phenol formaldehyde resin varnish pigmented with titanium dioxide and extended with whiting, provided the answer. The second point of interest was the manner in which these water-soaked adhesion tests were carried out. Although the tape test proved generally satisfactory, it did not always give reproducible results and, more important, it did not show the weak interface in the paint system. A test developed at the Central Dockyard Laboratory, Portsmouth, did, however, meet all requirements and is now fairly well-known. It is known

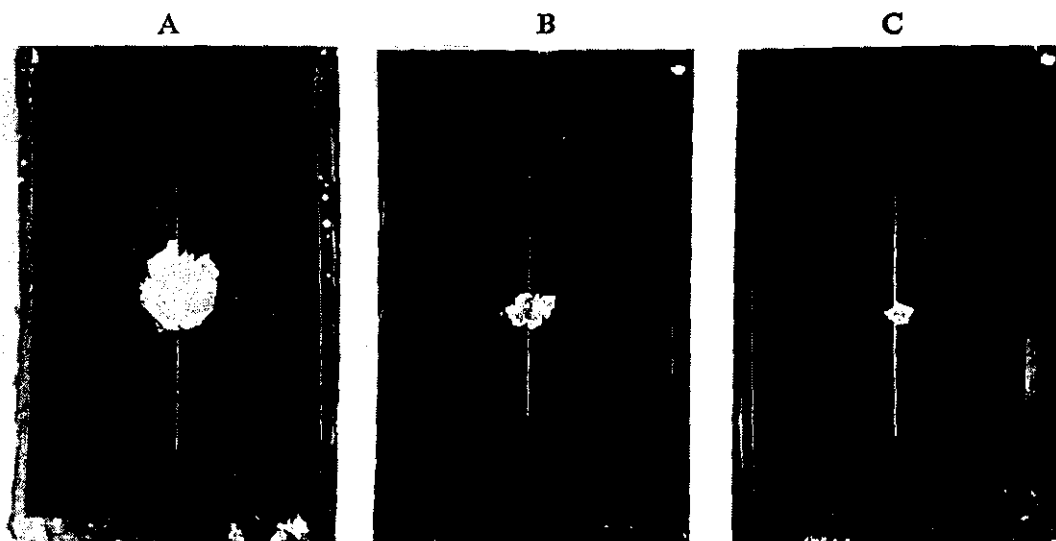


FIG. 5—EFFECT OF THE WATER JET TEST ON THE WATER-SOAKED PAINT FILM

as the Jet Adhesion Test. This apparatus has proved of great value in evaluating the intercoat adhesion of paint systems, especially when well soaked with water. FIG. 5 shows the results obtained with three paint systems, tested both in the dry and the water-soaked condition. Previous experience with these paints had shown that under water-soaked conditions, paint A was satisfactory, being superior to B, and much superior to C. This distinction is clearly made by the Jet Adhesion Test used with the water-soaked film.

Adhesion of paint, both to itself and to the metal substrate, is one of the fundamental problems which confront all paint chemists at one time or another and is the subject of a current inter-Service investigation.

Interior Paints

For the normal living spaces, such as messes and cabins, the requirements is for a decorative and pleasing finish applied over an anti-corrosive primer. In H.M. ships, however, there is the further requirement that the coating must be fire-retardant. At present this is achieved by keeping the total paint film thickness to a minimum and applying a three-coat system comprising one coat of zinc chromate and two coats of interior fire-retardant paint. The latter is based on a dammar resin with as high a pigment volume ratio as is consistent with the requirement of a semi-gloss finish. Antimony oxide is incorporated in the pigment mix, although the efficiency of antimony oxide in fire-retardant paints is open to question, unless there is chlorine present.

As possible alternatives, chlorinated rubber paints have been considered. They give better protection and are much superior against fire. They present some difficulties in application and the evolution of hydrochloric acid at high temperatures is a further objection.

Paints of the chlorinated alkyd type, actually based on hexachlorotetrahydrophthalic acid (H.E.T. acid) are another possibility, but the resins are not available in quantity in this country.

Aviation Fuel Tanks

Aircraft carriers must, of necessity, carry large quantities of aviation fuel and special care must be taken that these tanks remain clean. Any solid particle allowed to get into the fuel can block engine filters during flight and result in engine failure. This has happened—with fatal results. The coating scheme now employed is a primer followed by three coats of epoxy resin paint to a thickness of 6 mil. applied to a grit-blasted surface. So far, results have been

good—the only weakness is that epoxy coatings tend to blister when subjected to steaming-out, which is a common procedure for cleaning out aviation fuel tanks.

Mention is also made of paints based on zinc silicate for coating fuel tanks. These inorganic coatings, which normally require a curing agent, are very resistant to fuels and are in service on a number of commercial tankers.

In concluding this general account of ships' paints, attention has been concentrated on those of peculiar interest to H.M. ships, but even so, it has not been possible to cover many special types of paint, such as non-skid coatings for flight decks of aircraft carriers, heat-resistant paints for areas of the superstructure of guided missile ships, and so on. It is hoped, however, that some indication has been given of the nature and diversity of the problems encountered in the task of providing better paints for H.M. ships.