

The Testing of Antifouling Paints

Tests are applied to antifouling paints for two different purposes. The paint chemist uses them as a guide in designing and improving his formulations. The ship owner needs them to determine whether specifications are met in an acceptable way. A different program of testing is required depending upon which of these objectives is desired. This chapter will attempt to define the purposes and virtues of the various test procedures used, and to point out the precautions and conditions which must be observed in order to obtain useful results. The Appendix presents directions for some tests which have been developed recently and are not adequately described in other publications. Other tests, well known to the paint industry and described elsewhere, are also necessary for the complete study of paints.

The problem most frequently confronting the paint chemist is the modification or improvement of a standard formulation. Chemical technology is constantly producing new materials which may be used to advantage. Changes of composition may be required because of cost or availability of certain ingredients. During periods of war this problem becomes acute because of shortages which develop in materials previously used. The modification of a formulation may affect its physical, chemical, or biological characteristics, and the testing program should be designed to survey these properties, and to eliminate the more unsatisfactory paints by relatively simple procedures. The more time consuming, expensive, and elaborate tests which require exposure in the sea should be applied only to formulations which preliminary tests indicate will give adequate performance.

The character of a paint depends upon the proportions of the several ingredients it contains. A large number of experimental formulations are required in order to define the characteristics of any given combination of ingredients accurately. The greater the number of ingredients, the larger the number of possible variations. The properties of the paint may be changed systematically either by varying the proportion of one ingredient to all the others, or by varying the proportions of two ingredients, leaving the others unchanged. To insure a complete test of the combination, and to determine the limits of effectiveness, each com-

ponent should be varied to the point where it gives unsatisfactory results. The less satisfactory formulations are successively eliminated as each test or group of tests is completed.

The preliminary tests should eliminate those formulations which may be expected to give poor physical performance and those which will not release the toxic embedded within the paint film. These include the accelerated laboratory tests and can be performed on large numbers of paints with little expenditure of time and effort. The paints which give the best results on the preliminary tests are submitted to selective survey tests. These determine, under natural marine conditions, the length of time the paint will maintain an adequate rate of toxic release and prevent the attachment of fouling. Its adhesion and other physical properties are also defined by these tests. The results may explain the reasons for the failure of the less satisfactory paints, and suggest the kind of modification required to obtain the best formulation. The conditions of application which will give optimum performance of the few best formulations may then be studied in order to determine the precautions which must be observed to avoid failures and unsatisfactory results. The performance of the paint should finally be compared to that of similar paints, or ones previously used, on the type of vessel and under the conditions for which it is designed.

If the object of the tests is merely to determine whether a given paint meets specifications, or is more satisfactory than the paints in use, many of these tests may be omitted. The panel test, to determine the ability of the paint to prevent fouling, and service tests, to compare the performance of the paint with that of its predecessor, are the most useful. If results are required quickly, or if several paints are under consideration, the accelerated chemical tests will be useful in eliminating the copper paints which release toxic too slowly.

PRELIMINARY ELIMINATION TESTS

These tests are applied to the entire group of formulations and eliminate those which will be unsatisfactory because of poor physical qualities or inability to release sufficient toxic to prevent

fouling. They do not eliminate the wasteful paints which release toxic too rapidly with a resultant short life. They include accelerated laboratory tests which can be performed quickly on a large number of samples.

Physical Tests

The physical tests include determinations of flexibility, hardness, and adhesion. All of the paints should be adjusted to a similar viscosity so that uniform ease and thickness of application may be obtained. These tests are adequately described in standard works and will not be reviewed here (14).

Chemical Tests

Accelerated chemical tests have been developed which eliminate many unsatisfactory formulations of copper paints. They are designed to determine whether a paint is capable of releasing the toxic embedded within the film. The tests are based on the assumption that the dissolution of paint ingredients is accelerated in artificial aging solutions in the laboratory in a way related to the rate of dissolution in the sea. Acid solutions, or ones containing a substance which will form a soluble copper complex, are used to accelerate the dissolution of copper or cuprous oxide; alkaline solutions are used to accelerate the dissolution of the matrix. The theory of toxic release upon which these tests are based is discussed in Chapter 16. Two such accelerated tests have been developed for paints containing copper as the toxic. They are not applicable to paints which depend upon other materials for their toxicity.

The Acid-Alkali Test

This test was designed by investigators of the Mare Island Naval Shipyard (6), and depends upon two successive extractions of a paint film applied to a panel. The first of these extractions is in sea water acidified to pH 4 with hydrochloric acid. Under these conditions the cuprous oxide exposed on the paint surface is dissolved rapidly, but the dissolution of the matrix is negligible. After the exhaustion of the surface-exposed toxic, the leaching rate in sea water is determined. The panel is then transferred to a bath containing tap water adjusted to pH 10.5 with sodium hydroxide. In this alkaline solution the soluble components of the matrix dissolve rapidly and thus uncover stores of cuprous oxide which were originally buried within the paint film. After the panel has

been rinsed, the copper leaching rate in sea water is measured again.

Comparison of the leaching rates after the successive treatments with the acid and alkaline solutions indicate whether the matrix has been dissolved by the alkaline solution.

1.) If the leaching rates in sea water are low after both the acid and alkaline treatments, the matrix of the paint was not soluble in the alkaline solution, and will not dissolve in sea water. This indicates that the paint will not maintain an adequate leaching rate in the sea. These formulations may be eliminated from the further tests, since experience shows that they are invariably unsatisfactory.

2.) If the leaching rate in sea water is low after the acid extraction and high after the alkaline treatment, the matrix of the paint was dissolved by the alkaline solution. This indicates that the paint will permit continuous extraction of the toxic by sea water and should be tested further.

3.) If the leaching rate in sea water is high after the acid treatment the release of the toxic does not depend on the solubility of the matrix. This indicates, however, that the toxic is available and suggests that the paint may be effective because of some other mechanism. A permeable paint, one with toxic particles in continuous contact, or one with a matrix whose solubility is unaffected by the pH of the solvent may behave in this way. These paints must be tested further to determine their effectiveness.

The details of the acid-alkali test are given in the Appendix of this chapter.

Glycine Test

Sodium glycinate at pH 10.5 rapidly dissolves both copper or cuprous oxide and a soluble matrix simultaneously (19, 23). The high pH accelerates the rate of solution of the matrix ingredients; the dissolved copper is kept in solution as copper glycinate complex. A paint capable of liberating copper at an adequate rate in the sea will liberate several thousand micrograms per square centimeter during three days in this solution, irrespective of whether the release of toxic depends on a soluble matrix or continuous contact of toxic particles. The acceleration factor is about one hundredfold, so that three days' extraction in sodium glycinate is equivalent to almost a year of extraction in the sea.

The results of the test can be evaluated by determining the amounts of copper and of matrix dissolved in the glycine solution. The copper can be

measured either by the carbamate method, after suitable dilution, or by direct colorimetry of the blue copper glycinate. The matrix is determined by acidifying and extracting with ether, the ether extract being dried and weighed.

The correlation between the copper released into the glycine solution during this test and the average copper leaching rate for many typical paints is given in Figure 1. The results of the test may be evaluated as follows:

1.) The paints which liberate less than 1.3 mg. of copper per square centimeter in 3 days in the glycine solution will not maintain adequate copper leaching rates for 6 months of sea immersion. These formulations may be eliminated from further tests.

2.) The paints which liberate more than 2.5 mg. of copper per square centimeter can maintain adequate average leaching rates for 6 months or more. These paints should be tested further.

3.) The paints which liberate intermediate amounts of copper may or may not be satisfactory, and require further testing.

The details of the glycine accelerated test are given in the Appendix of this chapter.

Both accelerated chemical tests will eliminate many unsatisfactory formulations, and will indicate those formulations which are most likely to give adequate leaching rates and resist fouling in the sea. They do not permit a prediction of the length of time a formulation will maintain an adequate leaching rate. The following example may be given: a paint which will leach in the sea at an average rate of 20 micrograms per square centimeter per day for 6 months might give the same results in either of the accelerated tests as a paint which would leach at a rate of 10 micrograms per square centimeter per day for a period of 12 months. The first paint has an unnecessarily high factor of safety and exhausts the stored copper in the film too rapidly. The second paint would, with the same amount of copper, prevent fouling for twice as long. To determine the duration of the effective period, the more time-consuming exposures in the sea are necessary.

The preliminary tests eliminate: a) all paints which have unsatisfactory physical characteristics, i.e., lack of adhesion, flexibility, toughness, etc.; and b) all paints which are certain to give poor antifouling performance.

SELECTIVE SURVEY TESTS

The purpose of the selective survey tests is to compare more exactly the paints which the pre-

liminary tests indicate to be promising. It is unnecessary to apply these tests, which are time-consuming and elaborate, to the paints eliminated by the preliminary tests. All of the tests included in this group require facilities for exposure to natural conditions in the sea. Several commercial test stations are now available, and a list of these has been prepared by the American Coordinating Committee on Corrosion (1).

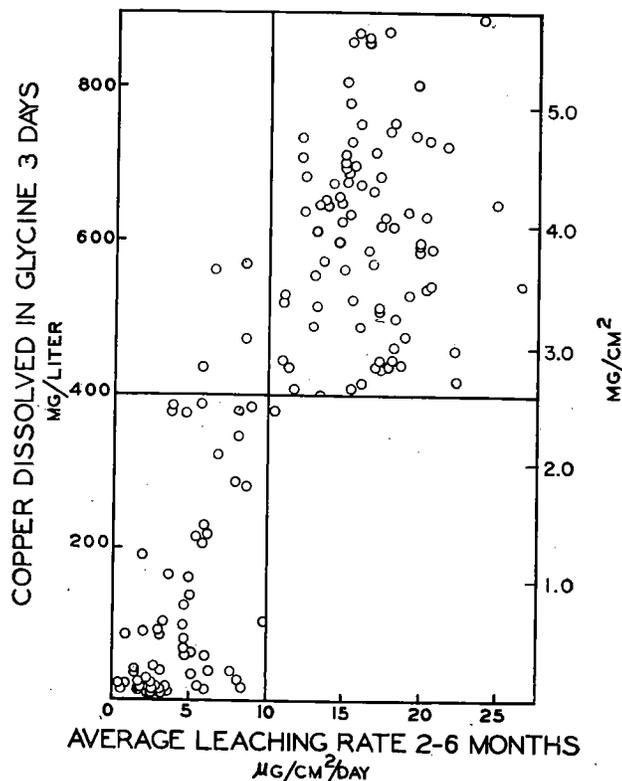


FIGURE 1. The amount of copper dissolved in the glycine test during 3 days compared to the copper leaching rates averaged between the second and sixth months of exposure for a variety of copper paints.

Chemical Tests

The rate of release of the toxic from the paint film determines the effectiveness of the formulation in preventing fouling (cf. Chapters 14, 16). This test has proved useful in determining the direction which additional modifications should take in order to obtain the most satisfactory results. Paints which depend upon either copper or mercury may be evaluated in this way by the methods described in the Appendix. Similar methods have not been developed for other toxics. The leaching rate of the paint shows its ability to prevent fouling at the time the determination is made, but is in no sense an accelerated test; i.e., it does not predict the effectiveness of a paint after exposure for a longer time.

As stated in Chapter 14, a copper leaching rate of 10 micrograms per square centimeter per day has been found adequate to prevent fouling (3, 19, 21). Mercury leaching rates in excess of 2.0 micrograms per square centimeter per day are adequate, (28, 29, 30). Barnes (4) finds that when the mercury is released as a soap, which may be formed in some paints, leaching rates of 6 $\mu\text{g./cm.}^2/\text{day}$ may be inadequate to prevent attachment of fouling.

The change of leaching rate with time can be measured most easily by periodic determinations of the rate of release of the toxic in the laboratory under controlled conditions, using panels soaked in the sea between determinations (21, 29, 30). This procedure requires fairly convenient seaside facilities so that the panels can be brought into the laboratory without drying and without too long a period in a stagnant tank of sea water. Soaking the panels in a limited volume of sea water is not comparable to soaking in the sea because of the excessive concentration of toxic or matrix ingredients that will ultimately develop under these conditions. If convenient seaside facilities are not available, an average estimate of the leaching rate of the paint can be obtained by analyzing the toxic remaining on the panel after various periods of exposure (22, 28). Several painted panels can be immersed in the sea at any location, successive specimens being removed, dried, and returned to the laboratory at intervals for analysis. To give significant results, the paint must lose an appreciable proportion of its toxic during the exposure. With a paint containing a large reserve of toxic, this may require a long period of immersion, during which time the leaching rate may change greatly. The paint analysis technique is, therefore, not always satisfactory as a method for determining the leaching rate.

Most antifouling paints which fail to prevent fouling do so either because the toxic is bound within the film and no adequate mechanism for its release is provided, or because of exhaustion of the toxic in the film. The paints in the former group will have been eliminated by the preliminary tests. Even the best antifouling paints are effective only for a finite period of time, after which they release toxic more slowly and are liable to foul. The duration of the effective life of a paint is determined by the rate of release of toxic and by the available store of toxic within the film. The best paints have a nearly constant leaching rate which is high enough to prevent fouling with a reasonable factor of safety, but not so high as to cause the

premature exhaustion of the surface. These characteristics are indicated by the leaching rate test.

Barnes (3) has compared the results of leaching rate tests with the loss of cuprous oxide from raft-exposed panels and service applications. The rate of loss under service conditions was greatest. The leaching rate test indicated 60 per cent, and the panel test 50 per cent, of the actual loss of toxic observed in service. Such results must reflect the erosion of the paint surface as a result of the activity of the ships. Paints with different resistances to erosion would be expected to give different proportions among the three tests.

The leaching rate test should always be conducted simultaneously with tests of fouling resistance of the paints. The results of these two tests can then be accurately correlated.

Biological Tests

The panel test of the resistance of paints to fouling is perhaps the oldest of the tests applied. It continues to be one of the most important and valuable, provided it is performed under proper conditions. It evaluates the formulation in two important ways: the ability of the paint to prevent fouling, and the physical performance of the paint film or system when exposed to natural conditions in the sea.

In order to give useful results, panels must be exposed in a location where the larvae of fouling organisms are present in the water throughout the year. Nontoxic control surfaces must be submerged simultaneously in order to evaluate the intensity of fouling, which must be known to evaluate the results. If the intensity of fouling at the test location is low for several months of the year, an unsatisfactory paint might appear to be effective for a considerable time. If this same paint were immersed under conditions of high intensity fouling, it might foul immediately. All of the paints which are effective under severe conditions, on the other hand, are invariably effective under less severe conditions. These considerations require that the location of the testing service be in a tropical or subtropical area. The seasonal occurrence and intensity of fouling at various locations are described in Chapter 5.

In contrast to the panel tests, the leaching rate tests can be performed in a location or at a time at which the intensity of fouling is low. This is actually an advantage, since the unsatisfactory paints do not become fouled and their leaching rates can be measured more accurately.

Several methods of rating panels for resistance

to fouling and for physical performance have been devised. All of these methods probably give equivalent and satisfactory results, provided ratings are made by the same observers for each series. Intercomparison of the various systems is difficult since none of them depends entirely upon objective measurements. The biological fluctuations between places and from time to time are so great that the results may vary considerably even with the same paint. The only valid direct comparisons of paint performance are those for exposures in the same location at the same time.

Generally, the paints either completely prevent attachment or fail completely shortly after attachment starts. Under conditions of continuous high intensity fouling, the length of time a formulation gives complete or nearly complete protection from fouling attachment is probably the most useful criterion. The panels should, however, be rated periodically in order to determine the trend of changes in effectiveness.

Two types of rating systems are in use, the direct and the weighted rating. The direct ratings may assess the number of individuals attached or the percentage of surface area covered. The weighted ratings attempt to give different penalties depending upon the type of organism found. The weighting may be based upon the importance of the various organisms to ship resistance or other practical considerations, or on their tolerance for the toxic used. Since we do not have adequate data on either of these points, the weighted ratings are more subjective than the direct ratings. They always exaggerate the effect of differences in the composition of the fouling community present at the test site. Thus, if barnacles are rated most severely, a test location where barnacles are rare would inevitably give a better rating for a paint than a location where barnacles are present in large numbers.

The physical condition of the paint film is rated on the basis of blistering, cracking, checking, alligatoring, or adhesion failure. This is generally based upon the area of the panel affected by the type of failure observed. If the paint is applied to steel over a suitable anticorrosive system, ratings are also given for the prevention of corrosion and the performance of the anticorrosive coating.

The methods of exposure and a description and evaluation of several rating systems are given in the Appendix to this chapter.

As a result of the selective survey tests, a few of the formulations are chosen for additional study. For a given type of formulation these should not

exceed half a dozen paints. Sometimes only the most promising paint is selected for further test. The selected paints are studied to determine the optimum conditions of application and exposure.

CONDITIONS OF APPLICATION

The results of tests to determine the optimum conditions of application culminate in the directions for use which are provided the consumer to insure that he will obtain the best performance the paint is capable of giving. Investigations of the optimum drying time prior to immersion, the optimum thickness of application, and the effect of the conditions of the surface on the adhesion of the paint are made. If carried out extensively these tests can be extremely time-consuming. Certain generalizations can be made which may simplify the investigations.

1. *Thickness of application:* Increasing the thickness of coatings which operate because of a soluble matrix will prolong their effective life. When applied over steel, the prevention of corrosion invariably improves as the paint film thickness is increased. The primary disadvantage of increasing the film thickness is that longer drying is necessary to permit the evaporation of the solvent. This may prolong the time in dock, especially if multiple coats are to be applied. Furthermore, the thicker the film, the more difficult it is to prevent sagging and other physical failures of the paint.

2. *Drying time:* The importance of drying time as a factor influencing the fouling resistance of a paint has probably been unduly emphasized. The conditions under which the paint is dried may be more important than the actual time of drying. Direct sunlight, for example, may result in the formation of a skin on the paint surface which sometimes retards the leaching of copper for a short period. With modern paints it is not necessary to undock the vessel immediately after the application of the antifouling coating. Prompt undocking generally does no serious harm and has the advantage that it frees the dock quickly. The paint must, however, be given sufficient time to harden adequately before the ship gets under way. Otherwise, cold flow of the paint film will result (34). Hardening will continue either during drying in air or during stationary immersion in the sea. The hardening period must be lengthened as the thickness of the paint film is increased.

3. *Surface preparation:* The problem of surface preparation for the application of shipbottom paints is similar to those problems which arise with

any protective coating. Some paint systems give the best results if the ship is cleaned to the bare hull; others appear to benefit if applied over old, firmly adhering paint films.

The evaluation of the experiments performed in this category may utilize any of the tests mentioned above. Both the leaching rate and panel tests have been used. The ability of the paint to resist cold flow can be tested by accelerated methods. One of these, designed by the Norfolk Naval Shipyard (25), uses a cylinder which is rotated in the sea with a surface speed of about 29 knots. Discs rotated under water at a peripheral speed of 30 knots have been used at Miami (32, 34). Both of these tests are described in the Appendix.

SERVICE TESTS

The selection of the best formulation must always depend upon the performance of the paint on the type of vessel and under the conditions of service for which it is designed. Such service tests are the most expensive and time-consuming of all. Two methods are commonly used in designing and executing the service tests. One of these compares two paints on the same vessel by applying them to opposing sections of the hull of the ship. Thus, the port bow and starboard quarter are coated with one paint, and the starboard bow and port quarter with the comparison paint. This system provides large areas which are easily painted, eliminates positional effects which are dependent upon the normal docking or mooring position of the vessel, and gives four junctions where the paint performances may be directly compared. In order to get a statistically dependable result, several vessels must be used. This has the advantage of testing the paint under different conditions of service and exposure.

The application of several patches of two or more test paints or systems permits several different comparisons on the same vessel. All of the applications, however, are submitted to the same conditions of exposure, and several vessels must be used if exposure and service are also to be evaluated. To obtain the most useful results, the patches should be as large as possible while still giving an adequate number of comparisons. The application of a patch test uses less of the experimental paints, but requires careful supervision, and this frequently results in more careful preparation of the surface where these tests are applied. The bow and quarter test, on the other hand, is

generally no more difficult to apply and requires little more supervision than an over-all application of a single paint or system.

Since the service tests must be waterborne for considerable periods before the results can be observed, and since they are relatively expensive to apply, they are not useful in studying a large number of paints. All of the unsatisfactory formulations should have been eliminated on one count or another before service tests are attempted. This applies, whether the object is to aid in the development of a new formulation or the determination of the best formulation for a given service. Generally not more than two paints should be compared in any service test or group of tests, and it is obvious that reasonable assurance should be had that the new paint is as good as, or better than, its predecessor before these tests are undertaken.

The use of the selected paint in standard procedure and service may be considered the final test for an antifouling paint. Adequate means of comparing the results obtained with those of similar or previously used paints should be provided. This requires the inspection of the ship at each docking period, and the comparison of successive reports.

APPENDIX

Acid-Alkali Accelerated Leaching Test (6)

The paint is first extracted for 4 days in sea water acidified to pH 4.0 with hydrochloric acid in order to remove surface available copper. After washing, the copper leaching rate in sea water is determined. The panel is then stirred in a bath of tap water adjusted to pH 10.5 with sodium hydroxide, and another leaching rate in sea water measured after appropriate washing with tap water.

I. *Panels:* A ground glass panel (7.5×10 cm.) is painted on both sides and dried for 4 hours.

II. *Acidified sea water extraction:* The painted panel is immersed in a beaker containing 1,000 ml. of sea water acidified to pH 4.0 with hydrochloric acid. The pH is determined with a glass electrode pH meter. The acidified sea water is replaced daily, and the extraction is continued for 4 days, or until little additional solution of copper occurs (cf. Fig. 13, Chapter 16).

III. *Leaching rate determination:* The panels are rinsed in tap water, then in sea water. Each panel is then attached to a shaft of the rotating device illustrated in Figure 2, where it is held in a slot in a rubber stopper by rubber bands. A beaker containing 1,500 ml. of sea water is moved into position so that the panel is completely submerged. A water jacket, through which tap water at 25°C. is circulated, surrounds the beaker. The motor, geared to rotate the panels at 100 r.p.m., is then started. The amount of copper dissolved in the sea water during one hour is meas-

ured by the carbamate test (cf. Leaching rate test) and expressed as mg./l.

IV. *Alkaline extractions:* The beaker of sea water in the stirred leaching rate apparatus is replaced, after rinsing the panels, by a beaker containing 1,500 ml. of tap water adjusted with sodium hydroxide to pH 10.5. The painted panels are stirred in this solution for 2 hours. The beaker is then lowered and the panel rinsed thoroughly with tap water.

V. The leaching rate determination in sea water (III above) is then repeated.

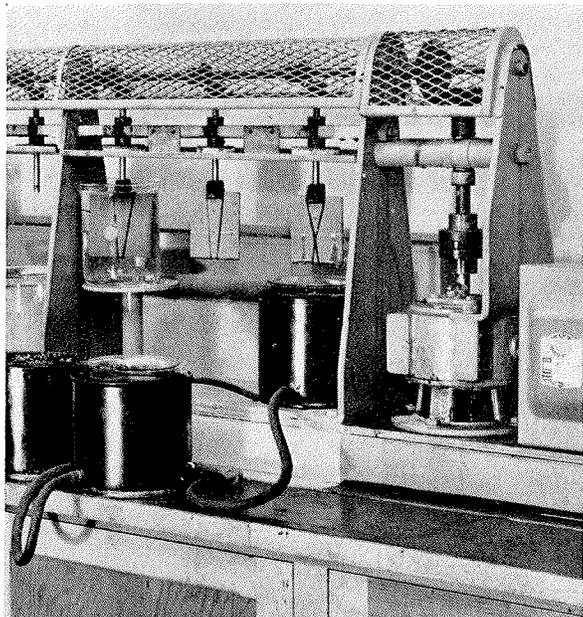


FIGURE 2. Apparatus for the mechanical stirring of leaching rate panels used in the acid-alkali test. The way the panel is held in a slot in a rubber stopper, and the water jackets to maintain constant temperature in the beaker of sea water are shown. (Mare Island Naval Shipyard official photograph.)

Glycine Accelerated Leaching Test (19, 23)

The liberation of copper from effective copper paints which operate either because of the solubility of the matrix or continuous contact of toxic particles can be accelerated about one hundredfold in an alkaline solution of glycine. This test is conducted as follows:

I. Glycine solution (0.025 M Sodium Glycinate; 0.48 M NaCl)

- 360 ml. of 1.25 N NaOH
- 33.75 grams glycine
- 504.0 grams NaCl
- Distilled water to 18 liters.

II. *Panels:* Ground glass panels (7.5×10 cm.) are painted on both sides and all edges. After drying 4 days, one panel is leached in 1,000 ml. of the glycine solution for 3 days. The solution is agitated by vigorous bubbling (cf. Leaching rate test).

III. The solution is analyzed for copper as follows:

A. If the copper concentration is below 100 mg./l. the determinations are made by the carbamate test, using 2 or 5 ml. samples diluted to 50 ml. with distilled water (cf. Leaching rate test).

B. If the copper concentration is greater than 100 mg./l.,

it is determined by direct colorimetry. With experience, the intensity of the blue color will indicate whether this limit has been reached or not. An excess of glycinate is required to develop the maximum color.

1. To 5 ml. of 1.5 N sodium glycinate solution in a test tube (112.605 gm. glycine, 250 ml. 6N NaOH, dilute to 1 liter with dist. H₂O), add 5 ml. of the unknown glycine leaching solution, and shake.
2. Read in a properly calibrated photometer, using a red filter with a spectral transmission range of 640–700 m μ .
3. Standardization of glycine colorimetry.
 - a. Place 10 ml. of a copper standard, containing about 5 mg. of copper per ml. in a 100 ml. volumetric flask.
 - b. Add about 2 ml. of a strong NaOH solution until precipitation appears.
 - c. Add about 2 ml. of 1.5 N Na glycinate, until precipitate clears.
 - d. Dilute to 100 ml. with the 0.025 M Na glycinate solution.
 - e. Place 1, 3 and 5 ml. of the standard solution thus obtained (0.5 mg./ml.) in test tubes containing 5 ml. of the 1.5 N glycinate. Make up to 10 ml. volume by adding the appropriate amount of the 0.025 M Na glycinate solution.
 - f. Read in the photometer as in 4 above. Calculate factors to give answers in mg./l., i.e.,

$$\frac{\text{ml. standard} \times \text{mg. Cu per ml.} \times 1,000}{\text{Photometer reading}} = \text{factor.}$$

The factors calculated for the various solutions should agree with a maximum error of 2 per cent.

IV. The matrix in solution is measured as follows:

1. To 100 ml. of the solution (filtered if it is not clear) in a 250 ml. separatory funnel, add 2–3 ml. concentrated HCl, and 50 ml. of ether, and shake vigorously.
2. After separation of the phases, draw off and discard the bottom aqueous phase. Wash the ether solution twice with 10 ml. of distilled water.
3. Drain the ether solution into a weighed 50 ml. Erlenmeyer flask, and evaporate on a steam bath with a filtered stream of air playing on the ether surface.

Caution: Do not place the ether solution on the steam bath without this air stream to aid in the evaporation. Unless some means is employed to remove the heat from the solution, an excessive vapor pressure will develop at the bottom of the flask and will be released explosively, causing the solution to be thrown out of the flask.
4. Wipe the flask and remove the last traces of water in a vacuum dessicator.
5. Weigh, and repeat the drying in vacuo until 2 successive weights agree within 0.2 mg.
6. Multiply the weight of residue by the factor 10.5 to convert to milligrams of matrix per liter of the glycinate solution. (The factor is 10.5 and not 10.0, because one ether extraction of the aqueous solution removes only about 95 per cent of the matrix.)



FIGURE 3. Leaching rate setup in which agitation is obtained by bubbling air through the sea water, as used at Woods Hole. One panel (150 sq. cm.) is leached in 750 cc. of sea water. The arrangement of beakers, panels, compressed air lines and sampling flasks is shown.

Copper Leaching Rates (5, 18, 20, 21)

The copper leaching rate should be measured after various times of soaking in the sea or in running sea water to determine how this characteristic of the paint changes with time. Aging of the panel in stagnant sea water, in artificial sea water, or in salt solutions is not comparable to aging in the sea, because materials dissolved from the paint accumulate in the solution and interfere with the leaching process. The set-up used for the determination of leaching rates is shown in Figure 3. The method described here is the one developed at the Woods Hole Oceanographic Institution. The method used by British investigators differs from this mainly in the size of panels used and in the holder they have developed for the leaching rate panels (cf. Fig. 4).

I. *Panels*: Sandblasted glass panels, 7.5×10 cm., are painted on both sides. Similar results are obtained if primed steel panels are used, but the presence of iron in solution interferes with the colorimetric determination of copper. After painting, the panels are allowed to dry for 1 to 4 days. Prolonged drying times change the results obtained with some paints.

II. *Leaching solution*: Clean aerated sea water is used as the leaching solution. The pH of the solution should be between 8.0 and 8.2, and the chlorinity of the sea water should be 17 parts per thousand. The temperature is adjusted to 19 to 23°C. In this range a change of 1°C. results in a 3 per cent change in the rate of solution of cuprous oxide (cf. Chapter 15). The ratio of the area of paint exposed (in square centimeters) to the volume of leaching solution (in cubic centimeters) is 1:5. Thus, one panel (150 sq. cm.) is leached in 750 ml. of sea water, two panels in 1,500 ml., etc. If panels of a different size are to be used, the volume of solution should be selected to maintain this

ratio. The British investigators use an area:volume ratio of 1:8, and leach the paint at 25°C. (18).

III. *Agitation*: The leaching bath is stirred by a vigorous stream of air bubbles (20 bubbles per second or more) liberated at the bottom of the beaker. Each air line must have a water trap followed by a cotton trap to remove oil and dirt. The agitation must be more vigorous the faster the leaching rate. Above a leaching rate of about 100 $\mu\text{g./cm}^2/\text{day}$, bubbling is inadequate, and mechanical stirring must be used for accurate results.

IV. *Time of sampling*: The sample should be taken before the concentration of copper in solution exceeds 0.5 microgram per ml. Above this concentration the rate of solution from the paint decreases, and insoluble compounds of copper are precipitated. Specific times may be selected for routine work. Sampling at one hour gives accurate values for leaching rates up to 60; two hours up to 30; four hours up to 15 $\mu\text{g./cm}^2/\text{day}$, etc.

V. *Soaking*: The panels are soaked in the sea, and leaching rates determined at monthly intervals to discover how they change with aging of the paint. The paint must not be allowed to dry during the transfer between the sea and the leaching bath. Figures 5 and 6 show the float and racks used for the immersion of these panels at Woods Hole.

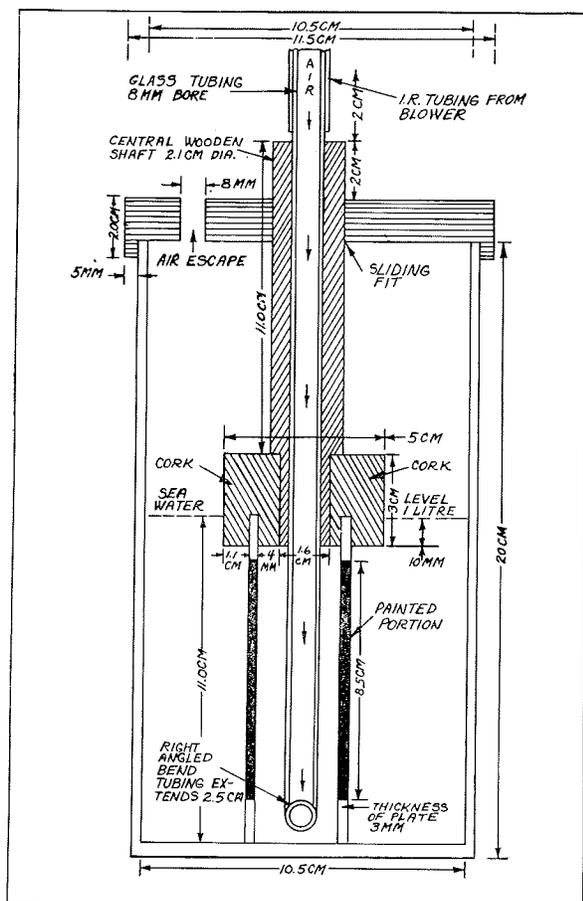
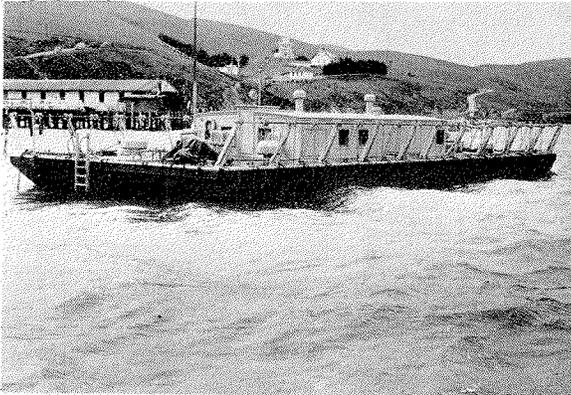
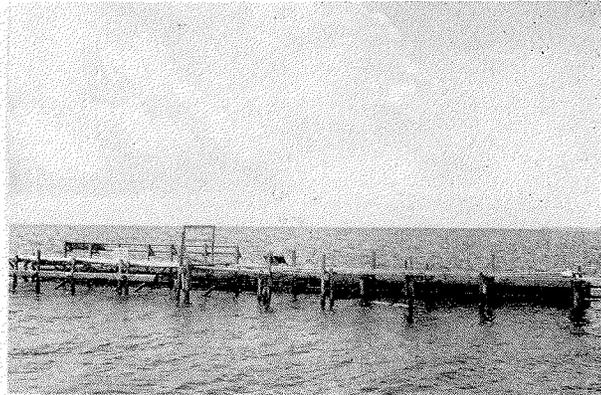


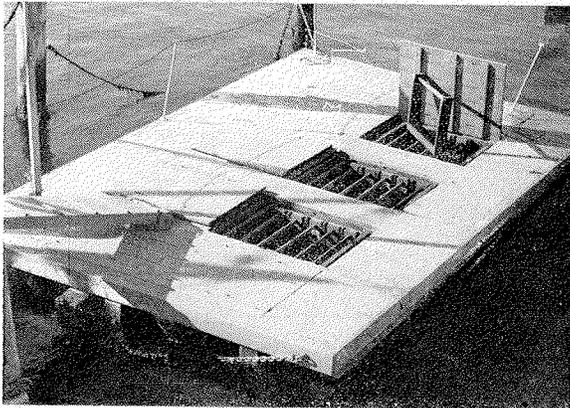
FIGURE 4. Diagram of arrangement used by British investigators in which two panels ($11 \times 7 \times 0.3$ cm.) with a total painted area of 250 sq. cm. are leached in one liter of sea water. The panels are held in slots in a shellac-impregnated cork which is, in turn, supported by a hollow wooden shaft through which the compressed air tube of glass passes. (After Kenworthy, 18).



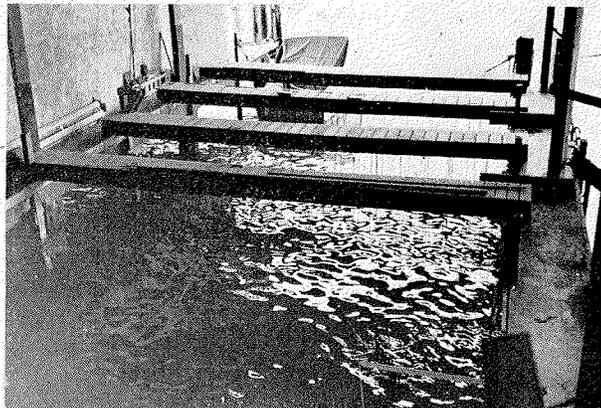
A



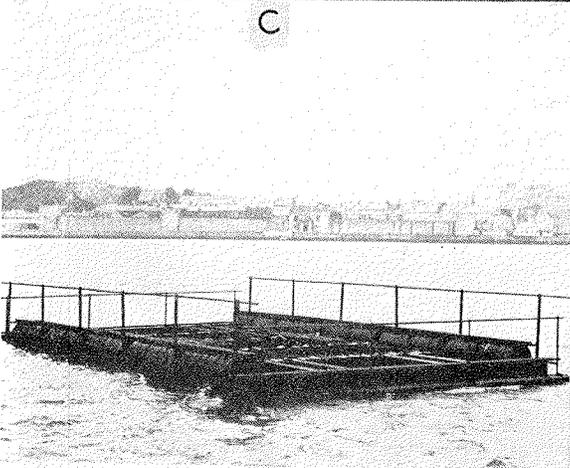
B



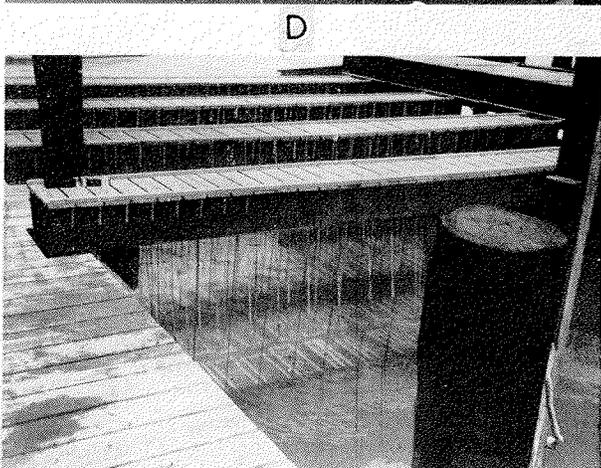
C



D



E



F

FIGURE 5. Various locations for the exposure of antifouling paints in the sea.
 A. Barge used by Mare Island Naval Shipyard at Point Reyes, California. Mare Island Naval Shipyard official photograph.
 B. Racks of Subtropical Test Service at Tahiti Beach, Florida.
 C. Raft used by Woods Hole Oceanographic Institution for the exposure of leaching rate panels.

D. Exposure station at Miami Beach Boat Slips used by Woods Hole Oceanographic Institution for the exposure of fouling test panels.
 E. The raft at Caernarvon, England, used by the Marine Corrosion Subcommittee. (From Hudson, 16).
 F. Bureau of Ships, U. S. Navy Department Test Station at Miami Beach, Florida.

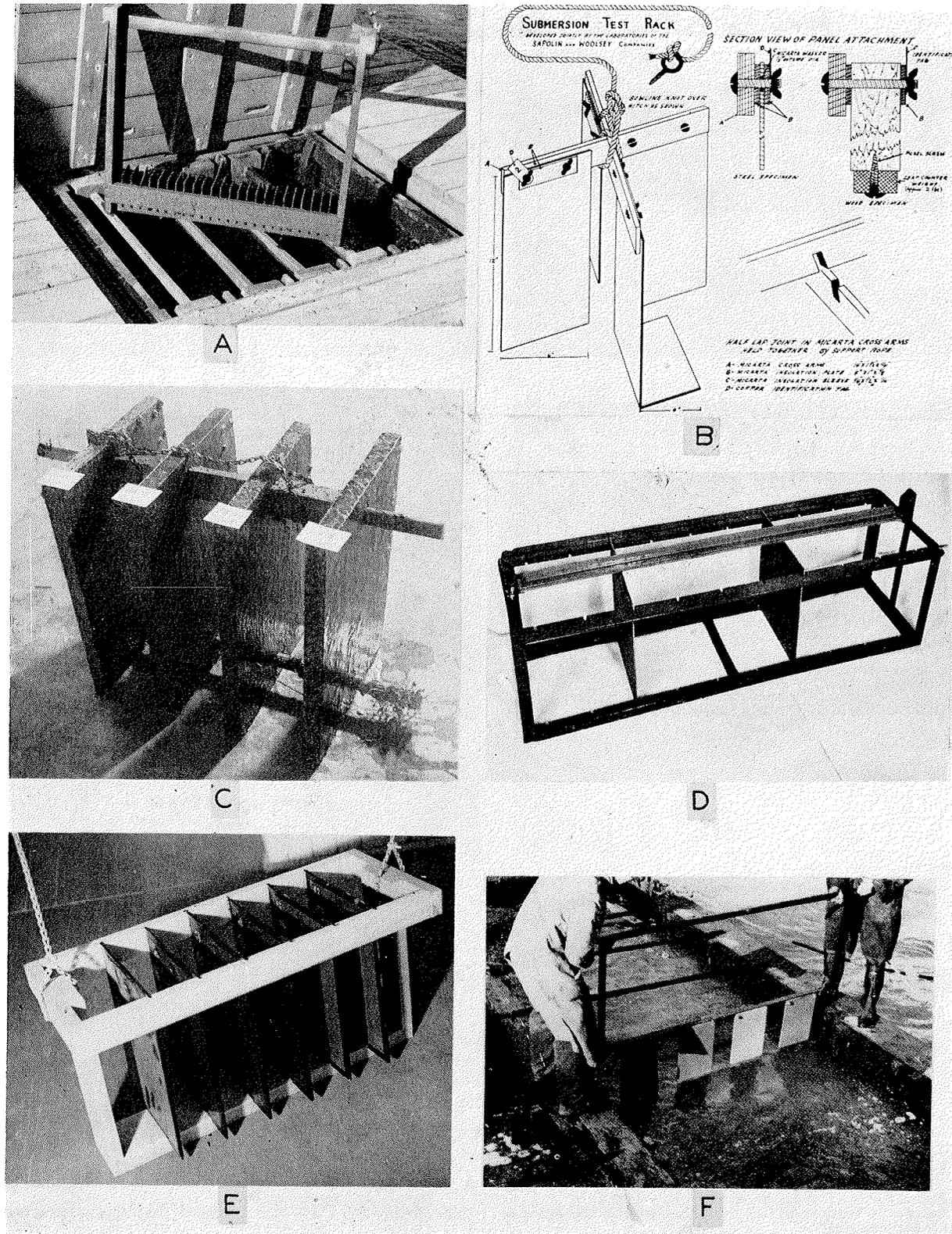


FIGURE 6. Racks used for suspension of painted test panels.
 A. Racks used to hold leaching rate panels at the Woods Hole Oceanographic Institution.
 B. Rack used by Sapolin and Woolsey Paint Laboratories at North Florida Test Station. The racks are of Micarta, and the panels are bolted in place with brass bolts.
 C. Rack used to hold wooden panels at the testing station at Miami Beach Boat Slips.

D. Metal rack designed to hold 10 steel panels 10"×12" in size. Used by Mare Island Naval Shipyard Test Station at Point Reyes, California.
 E. Wooden rack designed to hold 6 steel panels 10"×12" in size. Similar racks hold 8 steel or wood panels 8"×10" in size. Used at Buships Test Station, Miami Beach, Florida.
 F. Racks used at Plymouth, England, by Marine Corrosion Sub-Committee (16).
 See also Techniques for sea water corrosion tests (24).

VI. *Calculation of leaching rates:* The leaching rate is calculated from the copper concentration by the following equation:

$$\text{L.R.} = \text{mg./l.} \times \frac{\text{Volume (ml.)}}{\text{Area (cm.}^2\text{)} \times \text{Time (hrs.)}} \times 24.$$

For the standard panels and volume this becomes:

$$\text{L.R.} = \text{mg./l.} \times \frac{120}{\text{Time (hrs.)}} = \mu\text{g./cm.}^2\text{/day}$$

VII. *Copper determination—carbamate method:* The diethyl dithiocarbamate colorimetric method described by Callan and Henderson (7) and Coulson (8) is used with only slight modifications.

1. A 50 ml. aliquot of the leaching solution is placed in a 100 ml. volumetric flask. The solution should contain between 0.3 and 2.0 mg. of copper per liter.
2. Add small piece of red litmus paper, 0.5 ml. of a 50% citric acid solution, and 10 to 12 drops of NH_4OH until the solution is neutralized, then add 3 more drops of NH_4OH .
3. Add 2 ml. of the carbamate reagent, (0.1% aqueous solution), and 10 ml. of amyl acetate (amyl alcohol or carbon tetrachloride can also be used to extract the copper carbamate complex).
4. Stopper and shake for 5 minutes or longer until all the color is in the acetate layer.
5. Add distilled water to raise the acetate into neck of flask and draw off the acetate layer down to about $\frac{1}{4}$ inch from water. Filter (to remove water) into a test tube.
6. Measure copper content in a colorimeter or properly standardized photometer as soon as possible, because the color changes in light, and the evaporation of the acetate will increase the concentration of the colored material. We have used a Klett-Summerson photoelectric colorimeter. For solutions containing between 0.3 and 2.0 mg./l., a green filter (No. 54, approximate spectral range 520–580 millimicrons) was used. For solutions containing less than 0.4 mg./l., a blue filter (No. 42, approximate spectral range 400–465 millimicrons) gives more accurate results.
7. Standardization, calculation of factors:
 - a. A strong copper sulfate solution ($\text{Cu} = 5 \text{ mg./ml.}$) is made by dissolving a weighed amount of pure copper metal in nitric acid, and boiling with two additions of sulfuric acid (to remove nitrates) until white fumes appear. Dilute with about 10 volumes of water and boil again until white fumes appear. Dilute the solution to a known volume, and compare the concentration with any previous standard both by titration with thiosulfate and by the colorimetric method. Record the concentration on the flask in mg./ml. This standard is made in large batches (2 liters) and stored in sealed glass containers each one of which contains about 200 ml.
 - b. Dilute the standard copper solution (5 mg. Cu per ml.) to obtain a solution containing 0.01 mg. Cu per ml. Place 5 and 10 ml. samples of this diluted solution in 100 ml. volumetric flasks, dilute to about 50 ml., and continue steps 1 to 6 above.

The dilute solution should be prepared fresh each time a standardization is performed.

c. Calculate the factor as follows:

$$\frac{\text{ml. of standard} \times \text{mg. Cu per ml.}}{\text{Photometer reading}} = \text{factor (f).}$$

The factor should be calculated separately for each solution, and should agree with all others with an error not greater than 2%. The average factor is used. When calculating copper in terms of mg./l. the above factor should be multiplied by the dilution factor. Thus, if a 50 ml. sample is used, $20 \times f \times \text{photometer reading}$ gives the result in mg. Cu per liter.

d. The calibration must be checked weekly, and also whenever any change in the photometer (bulb, filters, tubes, etc.) is made.

VIII. *Mercury determination—dithizone method.*¹ The analysis depends on the reaction of mercury with dithizone (diphenylthiocarbazon) which changes from its normal green to a bright orange color. Titration volumes for the unknown may be compared with those of standards run simultaneously, or the change in color may be measured photometrically (Winkler, 35). The method described below is the one developed by Barnes (2).

1. An aliquot of 92 ml. of the leaching solution is placed in a 250 ml. separatory funnel, 2 ml. 25% by volume HNO_3 added. After shaking, add 1 ml. hydroxylamine hydrochloride, and shake.
2. Add 5 ml. of 10% cobaltcyanide solution, shake, and allow to stand 10 minutes. This forms a copper complex, stable in acid solutions, and prevents interference with the analysis.
3. Add 10 ml. of dithizone solution and shake for 1 minute at approximately four shakes per second. The dithizone is purified by repeated extraction with ammonia (Sandell, 31). A stock solution containing 1 g./l. in chloroform may be stored in a refrigerator. This is diluted fiftyfold just before use, giving a final strength of approximately 20 mg./l.
4. Insert a roll of filter paper in the stem of the funnel, and draw off the chloroform layer into the photometer cell.
5. Determine transmission in a properly calibrated photometer, using a blue-green filter. Barnes (2) used an Ilford 603 filter in a Spekker Photoelectric Absorptiometer. The reading must be taken rapidly since the color changes when exposed to intense light. The volumes for solution and dithizone must be strictly observed, both for unknowns and for standards, in order to obtain the same equilibrium conditions for the dithizone-mercury reaction and for the extraction of the products.

The copper leaching rate measured in this way is characteristic of the paint and is an indication of the amount of toxic exposed on the paint surface at the time the determination is made. Variations in the conditions of the test will influence the determined leaching rate value. The most important variables include the size of the panels relative to the volume of the leaching solution, the rate of agitation of the bath, and the pH, temperature, and chloride content

¹ Barnes (2) describes a method by which both copper and mercury are estimated with dithizone.

of the sea water used. The effect of these variables on the solution rate of cuprous oxide has been discussed in Chapter 15. A brief review of these results, indicating where possible the effect which departures from the standard method have upon the leaching rate of the paint, is included here.

In addition to these variables which influence the rate of solution of the exposed toxic, the temperature of the sea during the soaking period which precedes the determination also influences the value observed. This is probably because it determines the amount of cuprous oxide exposed on the surface of the paint.

I. *Area of paint and volume of solution:* The amount of copper dissolved in the leaching bath at any given time is directly related to the area of the panel, and inversely related to the volume of the solution. The standard method uses a paint area of 150 square centimeters in a volume of 750 ml. of sea water (21). Any change in area or volume requires the selection of an appropriate time so that the value $\text{area} \times \text{time} / \text{volume}$ remains equal to that defined in the standard procedure. The relation between the concentration of copper and the value of this quantity has been presented in Figure 11, Chapter 15.

II. *Rate of agitation:* Experience has shown that agitation by means of a stream of air bubbles is adequate for most leaching rate measurements. If the leaching rate of the paint is greater than about $100 \mu\text{g./cm}^2/\text{day}$, bubbling is inadequate, since the rate of solution of the cuprous oxide is limited by diffusion. Figure 4, Chapter 15, presents the relation between the rate of mechanical agitation and the leaching rate of two paints with high leaching rates. Since agitation by bubbling gives an adequate measurement of the leaching rate up to values about ten times the minimum essential leaching rate, it is satisfactory for all routine procedures.

III. *Temperature of leaching bath:* The rate of solution of cuprous oxide increases with an increase in the temperature of the leaching bath. The relation between the solution rate of cuprous oxide and temperature is shown in Figures 5 and 6 of Chapter 15. In the vicinity of 20°C . the change in leaching rate is 3% per degree (10). It is recommended that the leaching rate be measured at 20° ; if, however, it is necessary to measure it at a different temperature, the following table of correction factors may be found useful.

TABLE 1. Factors for Correcting Leaching Rates to Standard Temperature (20°C .)

Temperature of Measurement	Factor to Correct L.R. to 20°C .
0	2.57
5	2.06
10	1.55
15	1.22
18	1.07
20	1.00
22	0.94
24	0.88
26	0.82
28	0.77
30	0.73

IV. *pH of the leaching bath:* The rate of solution of cuprous oxide, and consequently the value obtained for the leaching rate of the paint, is directly proportional to the hydrogen ion concentration (10, 12). This relationship is shown in Figure 7, Chapter 15. The solubility of rosin, a common constituent of the matrix of a paint, on the other hand, is directly proportional to the hydroxyl ion concentration (Figures 1 and 2, Chapter 17). Variations in the

pH of the sea water will, therefore, have a direct effect on the measured leaching rate, including both the effect on the amount of cuprous oxide exposed on the surface after the period of sea soaking, and on the rate of solution of the cuprous oxide in the leaching bath. If clean aerated sea water is used both for the soaking and for the leaching rate bath, the pH will be found to be generally between 8.0 and 8.2. This variation will have little effect on the determined leaching rate. If, however, the pH of the leaching bath is very different from this range, it should be adjusted.

V. *Chloride ion content of the leaching bath:* The solution rate of cuprous oxide is a linear function of the square of the chloride ion concentration when measured at a constant ionic strength (Figure 8, Chapter 15). In sea water diluted with distilled water, however, the leaching rate is proportional to the chloride ion concentration (10, 11, 13). This condition is commonly encountered with sea water diluted with rain or drainage. The sea water used in the leaching bath should have a chloride ion concentration of 17 parts per thousand as determined by the standard method of titration (26). At this chlorinity the specific gravity is 1.0235 at 17.5°C ., referred to distilled water at the same temperature. If the chlorinity is greater than this, the solution may be diluted the appropriate amount with distilled water. If suitable sea water cannot be obtained, the following artificial solution has been found to give approximately similar results with a cold plastic paint: sodium chloride, 0.48 moles per liter (28.0 g. per liter); sodium bicarbonate, 17 mg. per liter; sodium carbonate, 3 mg. per liter, aerated to reach equilibrium with atmospheric carbon dioxide (20).

VI. *Temperature of sea during soaking period:* The temperature of the sea water in which the panels are soaked will influence the rate of solution of both the matrix and the toxic. The net result will be to determine the amount of the toxic exposed on the surface, which, in turn, determines the value of the leaching rate measured in the laboratory under standard conditions. The sea temperature during the soaking period may also influence the formation of surface deposits which have been shown to affect the leaching rate, (Figure 15, Chapter 16). It is impossible to predict, *a priori*, what the net effect of these changes will be upon the leaching rate of the paint. It has been found that the soaking temperature has little or no effect on the leaching rate of 143, a Navy cold plastic paint. Both 16X and BK-1, however, give higher leaching rates following a period of soaking in cold water (0° – 9.9°C .) than following a period of soaking in warmer water (10° – 22°C .). The amount of variation among individual determinations is, however, greater than the difference observed at the two extremes of temperature. It seems probable, therefore, that these differences may be neglected for practical routine purposes (36).

Barnes (5) has studied the accuracy of leaching rate determinations and found a coefficient of variance of 13.6% for a group of paints studied over an exposure period of 215 days. The variation was less than this for paints which consistently prevented the attachment of fouling. The variability arising from laboratory work was found to be comparatively small, and it was concluded that further refinements of the leaching rate technique are unnecessary unless the errors arising from composition, painting and exposure conditions are brought under more adequate control.

Leaching Rates by Paint Analysis (22)

Analysis of the paint film after various times of soaking permits the calculation of average leaching rates, and may also give valuable information concerning the rate of disintegration of the entire paint. The process is more laborious and less accurate than the standard method of measuring leaching rates after various times of soaking, but may be useful for laboratories located too far from the sea to permit the convenient testing of paints for the leaching rate, which must be done before they have dried. The panels for paint analysis may be submerged at any of the marine testing stations, washed, air-dried, and returned to the laboratory for analysis. If only the copper content of the film is desired, the paint is digested from the panel (C. below); if matrix studies are also contemplated, the paint is dissolved from the panel by paint solvents (E. below).

- A. Several weighed ground-glass panels of any convenient size are painted with each formulation. These are dried to constant weight to determine weight of paint. The amount of copper on each panel is computed from the analysis of the coating on one of the panels.
- B. The remaining panels are immersed in the sea in appropriate racks, and at various times one is sacrificed for analysis. Before digestion the paint is soaked in distilled water overnight, to remove sea salts, and is dried to constant weight. The difference between this and the initial weight is the total loss of paint.
- C. The paint is digested from the panel as follows:
 1. The panel is broken and placed in a 500 ml. Kjeldahl flask with 25 ml. of concentrated H_2SO_4 and a boiling chip.
 2. Warm carefully and then heat to boiling. The paint will char and come off the glass. When the flask is full of sulfuric acid fumes, remove it from the flame and cool in a hood.
 3. Add 25 ml. of concentrated HNO_3 (cp) and heat until all brown fumes are gone and white sulfuric acid fumes fill the flask. Cool in hood. If the solution is clear or clear green, the digestion is complete. If the solution is yellowish, muddy, reddish, black, or yellow-green, add another 25 ml. of HNO_3 and boil until the flask is full of white fumes. Continue adding nitric acid in 25 ml. portions and boiling until the solution is clear or green.
 4. When the flask is cool, add 50 ml. of distilled water. Heat very gently at first to prevent bumping, and boil until white sulfuric acid fumes fill the flask. Cool to room temperature. Add 100 ml. of distilled water; heat gently at first; then boil vigorously for 10 to 15 minutes. This is necessary to get rid of all remaining nitric acid, which interferes with the titration.
 5. Cool, dilute to about 200 ml., and filter the solution into a 500 ml. volumetric flask, using No. 40 Whatman filter paper. Wash, dilute to volume, and shake.
 6. Remove all glass from the Kjeldahl flask (being sure to recover all chips), dry, and weigh. This weight will agree with the original if none of the panel was lost.

- D. The copper is determined by titration as follows:
 1. To 50 ml. of the solution (about 1 gram/l.) in a 250 ml. Erlenmeyer flask, add 10 ml. of KI solution (200 g./l.). This will produce a cloudy, yellow-orange solution, owing to liberation of free iodine.
 2. Titrate with sodium thiosulfate (5 g./l.) until the yellow-orange color turns to a creamy color, then add 5 ml. of a 1% starch solution, which will result in a blue-black color. Complete the titration by adding sodium thiosulfate until one drop changes the color from a pinkish-violet to white.
 3. Standardize the thiosulfate against a standard copper solution (about 1 gram/l.), adding 5 ml. of 6 N H_2SO_4 before adding the KI solution.
 4. Compute final Cu_2O by multiplying the weight of paint after exposure by the per cent Cu_2O in the digested sample.
 5. Interferences with the titration method: Samples containing large amounts of iron, mercury, oxides of nitrogen, ammonia, and acetates, can not be titrated since the end points are not sharp or are too high. The oxides of nitrogen will be removed by the procedure described. Samples containing the other impurities may be diluted and analyzed by the carbamate method.
- E. Analysis of paint for both copper and matrix.
 1. Dissolve the paint from the panel in a volatile solvent, (the solvent to be used will depend on the nature and composition of the paint). Evaporate the solvent on a steam bath with a stream of filtered air playing on the surface. Dry in vacuum desiccator to constant weight.
 2. Cover dried paint with about 40 ml. 50% HCl and 30 ml. ether, stopper and shake vigorously. This will dissolve all the Cu_2O and matrix of most paints. If matrix ingredients insoluble in ether are used, suitable solvents must be selected. Inert pigments will not dissolve and are filtered off.
 3. Transfer to separatory funnel and draw off the aqueous phase. Wash the ether twice with distilled water, and add washings to the aqueous portion. Wash the aqueous portion twice with ether, and add to the ether portion.
 4. Warm the aqueous solution to remove ether, and dilute to volume. Determine copper as in D above, adding 5 ml. of 6 N H_2SO_4 before the KI, as is done with the standard copper solutions.
 5. Dry the ether residue to constant weight to determine the total matrix.

Panel Testing

The exposure of painted panels to natural conditions is both the oldest and one of the most useful techniques available for the study of antifouling paints. Metallic panels were immersed in the sea by Sir Humphry Davy in 1824 in his study of copper for metallic sheathing of wooden vessels (9). Since that time panel tests have been conducted increasingly, until today many commercial marine exposure stations are available to the paint chemist (1). In spite of this long experience the advantages of panel tests are still not fully exploited in many cases. This is because adequate controls of the exposures are not always used and the biological factors which determine the usefulness of a testing location are not appreciated.

SELECTION OF A TEST SITE

The testing station is preferably located in a region where the larvae of fouling organisms are present in the water and attaching to surfaces at all seasons of the year. Under these conditions the duration of the effective life of the coating can be accurately determined regardless of the time of immersion of the panel. If, on the other hand, there are long periods when the larval forms are not present, a paint may appear to give satisfactory performance merely because of this paucity of life. The only locations where continuous settling populations are found are in tropical or subtropical waters.

The mere selection of a location in tropical or subtropical waters does not insure, however, that continuous attachment of fouling organisms will be found. The general characteristics of the ecological habitat are equally important. The adults of fouling organisms must be common nearby. The quickest and best way to find out whether a given location has the desired population is to expose nontoxic test panels periodically and observe the growth. The chapters on the geographical and seasonal distribution of fouling organisms summarize much information which will be helpful in selecting sites for exposures.

CONTROL EXPOSURES

Regardless of the location of the testing service, it is essential to expose control, nontoxic surfaces in order to take a census of the attaching organisms throughout the year. Two types of immersion of control panels should be used. A nontoxic panel should be submerged with each set of test paints and allowed to remain in the water for the duration of the test. A control panel should also be immersed at monthly or bi-weekly intervals throughout the year. Panels which are exposed in parallel with the test surfaces give a picture of the accumulation of fouling during the course of the test, but such panels may foul heavily during the first months of exposure and give little information on subsequent conditions. The panels exposed monthly give a picture of the number of fouling organisms in the water each month. If such panels do not accumulate any fouling during a given period, it is clear that the test panels can not be expected to foul even though their toxicity has failed. If, however, a large population of fouling organism attaches to a monthly control panel, it is clear that the unfouled test panels are still effectively preventing fouling at that time.

There has been considerable controversy in the past as to the ideal surface to use for the control panel. No surface has been found which gives a complete sample of the available population. The populations found on various materials have been described in Chapter 13. Cement blocks have been used at the Mare Island Naval Shipyard, and the fouling is removed and weighed at monthly intervals. Wood and glass panels have been used by the Norfolk Naval Shipyard and the Woods Hole Oceanographic Institution, where the population has been assessed by weighing of the organisms after removal and by counting individual specimens. While it is probably true that none of these surfaces gives a complete census of the population, they all give a significant indication of the severity of the conditions. The seasonal distribution of fouling organisms is discussed in Chapter 5.

The use of a standard paint or paint series as toxic controls is also to be recommended. Comparison of the test

results with the fouling on the standard paints gives a clearer appreciation of the value of the new paint; and if a standard series with known leaching rates is used a biological estimate of the leaching rate may be obtained. This is of especial value if the paint contains a toxic substance not measured in the leaching test.

METHODS OF EXPOSING PANELS

The physical requirements for a testing station may be met in a variety of ways, each of which has its advantages. The panels may be hung individually or in racks from a permanent dock or pier. Rafts and floats of various sorts have also been used and are especially desirable where the rise and fall of tide is great. Algae are the forms which are most seriously affected by the structure from which the panels are suspended. In locations where dense shade prevails, or where the panels are suspended more than a meter or so below the surface, the growth of algae is seriously limited. For these sea forms the use of floats or rafts where the panels may be hung near the surface, and may remain at the same depth of all stages of the tide, is advantageous. These same conditions, however, may decrease the intensity of barnacle sets.

The barnacles and various other sedentary organisms attach more rapidly to dark surfaces, and the best way to collect them is on the under-side of a dark, horizontally suspended panel. If, however, the fouling intensity is sufficient, an adequate number of barnacles and other fouling forms will always be found on panels hung vertically in the sea. Since this method of suspension is easier and more conservative of space, it is the method most frequently used. Figure 5 shows various testing stations which are in use for the submersion of antifouling paints.

The painted panels are frequently grouped in racks which may hold eight to a dozen different panels. Investigations at Miami have shown that there is no significant difference in the populations found in different positions in racks with 3-inch spacing, though the barnacles on the outer panels were most frequently consumed by fish. In some cases this may result in premature physical failure of the paint. It was also found that adjacent panels do not influence one another when spaced 3 inches apart. The insertion of highly toxic paints 3 inches from glass panels in these racks had no effect on the population accumulating on the glass. At this same location orienting the panels so that their surfaces were parallel to the tidal current resulted in a 34 per cent increase in the population, compared to panels oriented at an angle of approximately 30 degrees to the current.

Various types of racks have been used to hold the test panels, and several are illustrated in Figure 6. Wooden racks are convenient to make and use, and may be protected from fouling and from teredo and other wood destroying organisms by painting with an antifouling paint. The effect of the paint on the test panels is negligible, being restricted to a narrow band at the points of contact. Steel racks are more permanent, but are heavy and unwieldy to handle, and appropriate gear must be provided. They should also be protected from fouling and corrosion by suitable paint systems. Racks of brass have been used, and need no painting for protection, but the danger of galvanically accelerated corrosion of steel panels in these racks is always present. The panels may also be suspended separately from ropes, chains, or wires. The panels must be hung far enough apart to avoid banging together, and this

requires much more space than an equal number of panels in racks.

Panels of diverse sizes have been used. The large panels are unwieldy and difficult to handle; small panels may give erroneous results because of the relatively large influence of the edges, where failure frequently begins. The panels used generally lie within the limits of area between 150 to 700 square inches, including both sides of the panel. The common sizes are, in inches: 6×12, 8×10, 10×12, 10×15, 12×18, and 18×18. In comparing a large number of formulations the British investigators sometimes use panels 2 feet square, each side of which is subdivided into 6 patches (8×12) for the application of the test and control paints (16). Where comparisons have been made, no differences in the performance of paints on panels within this range of sizes have been found. The conditions of exposure may be used to determine the most convenient panel size.

the surface area covered. The results are frequently expressed as fouling resistance which is 100 per cent minus the assigned penalty. The paints exposed for the Navy are penalized 5 per cent for slime, scum, and incipient fouling, and all subsequent penalties are deducted from 95 per cent. The Miami testing station deducts one per cent for each individual specimen attached; encrusting or spreading forms are assessed by the surface area covered. The Mare Island and Norfolk Naval Shipyards base their ratings on percentage of the area which has permitted attachment. It is not necessary for the surface to be completely covered, however, since a sprinkling of forms evenly distributed on the surface indicates that the entire area is permitting attachment. Both of these systems rate fouling performance severely, and are most useful in determining how long a surface prevents fouling completely.

The paints generally rate either better than 80 per cent or less than 20 per cent with these systems. Very few paints

TABLE 2. Weighted Ratings for Fouling Attached to Test Panels. The Numbers in the Table are Penalties to be Subtracted from 100% to give Final Rating. (Modified after Jackson, 17)

Per Cent Area Covered	Grading	Algae	Filamentous Bryozoa	Hydroids	Sponges	Tunicates	Annelids	Barnacles	Borers, Tereidos, etc.	Encrusting Bryozoa	Mollusks
0	—	0	0	0	0	0	0	0	0	0	0
5	X	2	1	1	1	2	3	3	12	2	2
10	X	3	3	4	4	5	6	6	14	4	4
20	XX	5	5	6	6	7	9	10	17	7	6
40	XXX	7	7	9	8	9	12	15	20	10	10
60	XXXX	9	9	12	10	11	15	20	30	13	15
80	XXXXX	10	12	16	12	14	15	30	40	18	18
100	XXXXX	10	15	20	15	15	15	40	50	20	30

RATING EXPOSURE TESTS

The panels submerged for fouling tests should be rated for the resistance of the paint to the attachment and growth of fouling, the physical performance of the paint, and, if steel panels are being used, the ability of the paint system to prevent corrosion. Supplementary observations, such as color changes and chalking of the paint film, may be desirable for special purposes. It should be remembered, however, that effective copper antifouling paints generally accumulate a noticeable deposit of greenish copper compound on the surface within a short time after exposure. Such a deposit should not, under any circumstances, decrease the rating of the paint film.

"The criterion of failure of a test area by fouling should be a clearly defined all-or-none matter. As soon as any kind of fouling appears on a test plate or ship, the antifouling mechanism has failed; the rest is merely a matter of allowing the fouling time to grow to a size large enough to be a serious impediment to the vessel." This statement, which summarizes the viewpoint of British investigators (15), should be generally accepted. Ratings may be assigned in different ways, but a paint must completely prevent fouling to be considered a success, and the length of time a paint is successful is considered its most important characteristic. The simplest rating system is to consider that the paint has reached the end of its effective life when a panel has either fouled or rusted, or both, to such an extent that repainting should be carried out in practice. The panels should be inspected at monthly intervals, and an evaluation of the surface given. Two types of ratings are used for this purpose, the direct and the weighted rating.

The *direct rating* of the fouling on the paint film depends either upon counts of individuals or upon an estimate of

are rated between these values, apparently because once fouling starts to attach to more than a small area of the surface it quickly covers the entire panel. The paint is considered satisfactory only so long as it rates 95 to 100 per cent. Ratings below 80 per cent are unsatisfactory. Intermediate ratings are considered to indicate good or fair performance.

The *weighted rating* system assigns graded penalties for different types of organisms. One such system is shown in Table 2, which gives the penalties assigned for various organisms present to different extents (17). Intermediate values are given for different sizes of the organisms. When inspected in the field, the amounts of each type of organism present are rated in percentages. By reference to Table 2 the appropriate penalties for these amounts of fouling are found. These are added together and subtracted from 100 per cent to give the final rating. This rating system is more lenient than the direct system described above. For example, a panel whose surface was covered as follows: 5% algae, 40% hydroids, 20% barnacles, and 30% annelids would rate zero on the direct system [95% - (5+40+20+30)]. The same panel would rate 67%, [100 - (2+9+10+12)], on the weighted rating. Complete coverage of the panel with any single fouling form would never give a rating of zero on the weighted system. A worthless paint exposed in waters where only filamentous bryozoa were settling would still be rated 85 per cent, even though completely covered. If exposed under more severe conditions, the rating for the same paint would decrease accordingly, not because the paint is any worse, but because the biological conditions to which it is exposed are worse.

If the relative tolerance of the various forms to toxics were known accurately, a weighted system might be de-

TABLE 3. Sensitivity Factors of Common Fouling Organisms at Millport, England (27)

Sensitivity of Organism	Sensitivity Factor	Type of Organism	
		Plant	Animal
Low	0.5	Amphiprora (D)	
	1.0	Ulothrix (G)	
		Acanthes (D)	
	2.0	Enteromorpha (G)	Tubularia (H)
	3.0	Hecatonema (B)	
	5.0	Ectocarpus (B)	
	5.5		Balanus (Ba)
	6.0	Fragilaria (D)	Obelia (H)
	8.0	Red Algae	
	9.0	Cladophora (G)	
High	10.0	Ulva (B)	Pomatoceros (T)
		Laminaria (B)	Mytilus (M)
		Desmarestia (B)	Anomia (M)
			Jassia (C)
			Membranipora (P)
			Didemnum (A)

D—Diatom
G—Green Algae
H—Hydroid
B—Brown Algae

Ba—Barnacle
T—Tubeworm
M—Mollusc
C—Crustacea
P—Polyzoa (Bryozoa)
A—Ascidian (Tunicate)

vised which would give results directly related to the toxicity of the paint. This information is not available, and, until it is, weighted ratings will give an unwarranted illusion of precision.

The British investigators have assessed the sensitivity of various organisms insofar as it is known, and have assigned them sensitivity factors which are given in Table 3 (27). In inspecting the panels, each fouling form is assessed on a geometrical scale from 0 to 7 on the basis of numbers of organisms settled. Each rating with a value of 1 or more is then multiplied by the sensitivity factor for the organism. These products are added together, and the sum is divided by the number of kinds of organisms to obtain the adjusted rating. Fouling on nontoxic surfaces is treated in a similar way, and the ratio between the adjusted ratings of the toxic and nontoxic surfaces gives an estimate of the antifouling properties of the paint (27).

The authors' own assessment of this method of rating is that it "has been successful to a limited extent, but should be capable of wider application with a fuller knowledge of the amounts of fouling occurring on paints of known toxicity." It is also pointed out that the sensitivity factors used apply to plates immersed at a depth of roughly 18 inches, and that algal sensitivity will vary with the depth of immersion and the resulting change in light intensity. Adjustments of the correcting factor may be necessary at various times during the fouling season, based upon the population of the form in the water.

The sensitivity of various organisms, and their geographical and seasonal distributions are not sufficiently well known to make this system applicable to all testing stations. Its use would require the determination of sensitivity factors for the forms present at each location. For example, it has been found at Miami that *Balanus amphitrite niveus* is more resistant to copper paints than either *B. improvisus* or *B. eburneus*. It is apparent that a sensitivity factor of 5.5 for all barnacles of the genus *Balanus* would not be applicable at Miami. The encrusting bryozoan, *Watersipora cucullata*, is more resistant to copper than any of these barnacles. It is, however, less resistant to mercury than is *B. amphitrite niveus* (33). A single factor

could not be applied to either of these two forms unless the tests are restricted to paints containing only one of these toxics.

This system seems too complicated for general application since it requires accurate identification and enumeration of each *species* of organisms present, as well as determination of their sensitivity factors. It requires an inspector of great experience and wide biological knowledge, and is, to say the least, time consuming. If the position is taken that the attachment of *any* macroscopic fouling on the paint indicates its failure, the elaborate rating systems are unnecessary. A list of the type of fouling present, and a direct rating of the paint on the basis of either numbers or per cent of surface covered, gives as useful information as any of the weighted or adjusted methods. The direct method also gives results which are more nearly comparable between different places and times, provided the fouling intensities are high, since the rating is independent of the kind of organisms present, and depends merely upon the numbers which can attach to the test surfaces.

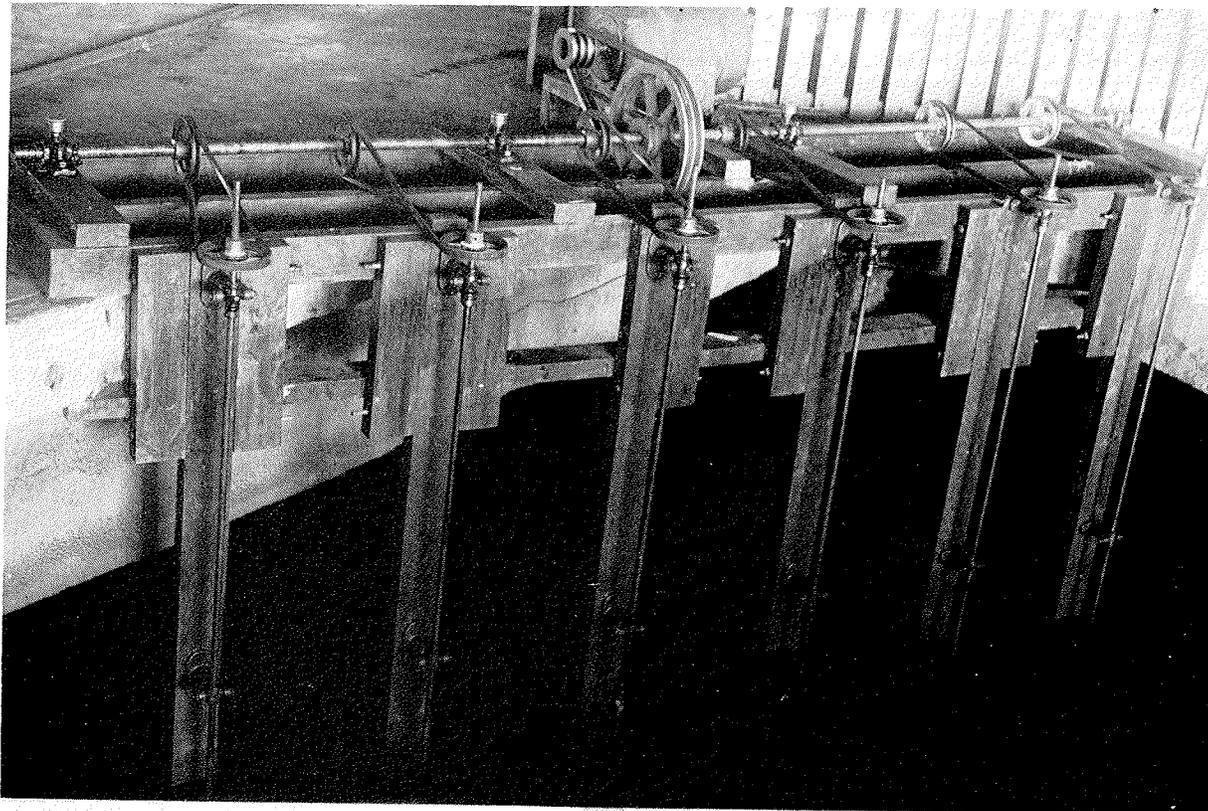
Resistance to Erosion

Many paints which may be otherwise satisfactory are eroded rapidly as a result of motion through the water. Two devices have been developed to give an accelerated test of the resistance of the paint film to water erosion. They depend upon the rotation of a cylinder or of a disc underwater to simulate the motion of a ship. In these tests centrifugal forces which have no counterpart under service conditions are applied to the paint film. Pronounced thinning of the paint film, or cold flow with resultant stripping of the film, are evidences of failure.

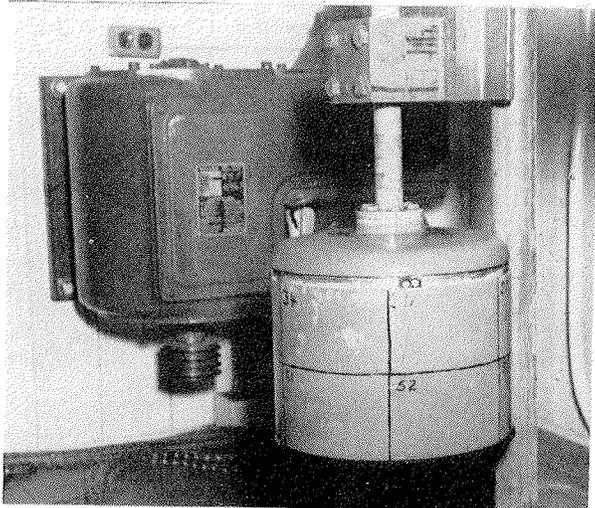
The apparatus designed by the Norfolk Naval Shipyard (25) consists of 1/8-inch mild steel cylindrical sleeves 12 inches in diameter and 8 inches long. One of these is mounted on and insulated from a vertical steel shaft which is belt-driven by a 3-horsepower motor through a Reeves variable speed drive. The shaft, with its painted cylinder, can be raised for inspection or for changing the sleeve. In use, the cylinder is submerged to a depth of about 3 feet and rotated to give a surface speed of approximately 29 knots. One of the painted steel cylinders attached to the shaft is shown in Figure 7B.

The apparatus used at Miami (32) is also shown in Figure 7(A & C). This consists of 14-inch diameter steel or plywood discs, which are rotated under water at 820 r.p.m., giving a peripheral speed of about 30 knots. The discs are bolted to a 1/2-inch cold rolled steel shaft, which is belt-driven, with appropriate reduction, by a 3-horsepower motor. Six shafts are individually mounted on wooden 2x4's by means of three adjustable babbitt bearings of the shaft hanger type. The vertical posts are bolted to guides which are part of the main motor and shaft assembly framework. Each shaft may be removed separately for inspection or for replacement of the disc.

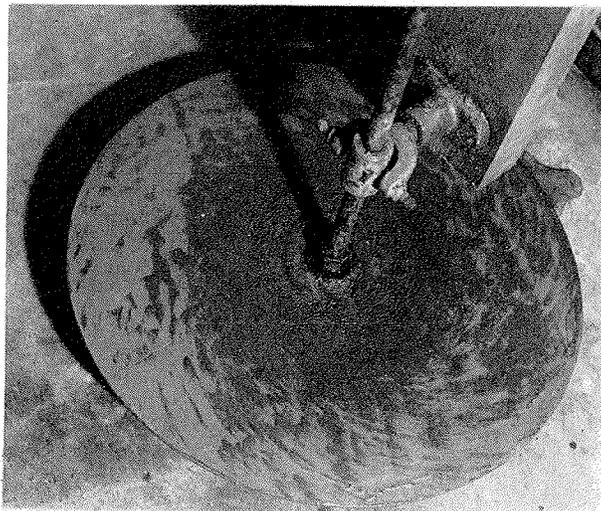
Both of these tests submit a paint film or system to a severe test, but direct correlations with service conditions have not been made. Failures may be observed in the first few hours of rotation, and the tests are seldom run for more than a few days. The apparatus has been found particularly useful in comparing the effects of adding various large molecular weight resins to simple paint formulae (25, 32), and in determining the effect of thickness of the paint film on the time necessary to permit its hardening (34).



A



B



C

FIGURE 7. Apparatus for testing erosion of antifouling paints. A and C show the rotating disc device used at Miami, Florida. B shows the rotating cylinder used by Norfolk Naval Shipyard. For explanation see text.

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