Biological evaluation of anti-fouling paints

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THE problem of marine fouling and its prevention is a subject of very great economical interest to all the maritime nations of the world. Fouling of ship's bottoms in particular, causes appreciable reduction in speed due to the increased frictional resistance. Innumerable methods to prevent fouling are there but the only method that is being mostly followed is the application of anti-fouling paints at required intervals.

Orton (1930), Edmondson (1937, 1939), Zobell (1939), Pyefinch (1945, 1948), Harris (1946), Barnes (1948), Komarovsky (1953, 1957), Wisley (1964) and Greenblatt (1964) after having experimented with various anti-fouling paints of both commercial and laboratory origin have observed that such compositions exhibited as short a life as 10 to 12 weeks and also as long as 2 years depending upon their physical and chemical characteristics. The primary object of an anti-fouling paint film is to prevent the settlement of plant and animal forms for a prolonged period and all other properties are of secondary nature. The present study is largely concerned with an attempt to elucidate the behaviour and the biological efficiency of a number of commercial antifouling paint compositions.

A number of commercial anti-fouling paint compositions manufactured in India are available in the market and it appears that no adequate and authentic data on their biological efficiency have been assessed by any standard tests. According to the Indian standard specification, IS: 1419-1959, an anti-fouling paint composition formulated as per this specification should not break down in less than 35 weeks at the time of the exposure test and a later ammendment to this has indicated that the composition should have a copper leaching rate of not less than 10 micrograms per square centimeter per day (10 ug./cm^2/24 hrs.), for a period of 25 weeks. It is possible to evaluate the efficiency of anti-fouling paints under laboratory and field conditions.

Materials and method

Samples of five different commercial anti-fouling paints were procured from the local market and were designated with pseudo names as AF-1/62, AF-2/62, AF-3/62, AF-4/62 and AF-5/62. A new experimental paint composition (AF-6/62) designed and formulated in the departmental laboratory was also included for the present tests for comparative studies. The commercial compositions all had cuprous oxide as the toxic pigment in varying grades whilst the departmental sample had copper-aceto-arsenite.

Mild steel panels were used as test blocks as per the prescribed standard. Each panel measured 12″×8″×18 SWG and were thoroughly degreased and cleaned before use in the conventional manner. The freshly cut edges were carefully sealed with water-proof adhesive tapes so as to avoid the possible effects of early corrosion of the metal. Suitable metal primer and undercoats were given on the panels to build up an adequate film thickness to give an effective barrier to protect the bare metal from sea-water corrosion. The panels thus treated in this manner were finally painted with one coat of the different anti-fouling paint samples to be tested. The painted panels were all marked suitably and arranged four inches apart in special grooves in a wooden immersion rack. Each sample of paint was tested in duplicate panels and were exposed to the free settlement of the marine fouling organisms along with the non-toxic control panels which were without the final coat of anti-fouling paint.

Test site and method of exposure

The test site located inside the Port of Cochin had previously been specially surveyed and selected as the best in view of the quality and quantity of the marine fouling organisms present throughout the year with continuous settling populations. For further details on the test site, reference is drawn to an earlier publication of the author (1963). The immersion rack with the treated test panels and the controls were suspended at the test site from an experimental raft. The panels were exposed below the low water mark but well above the mud-line. The exposure was done in such a way as to carefully avoid as much as possible all external factors that are likely to have some influence on the fouling organisms like surface illumination, water current, tidal range, pollution and angle of exposure.

Inspection and rating

The test panels that were initially immersed in the month of September were inspected at the end of every 30 days till the following May covering a period of 9 full months of worst fouling days in the Port of Cochin.

At each inspection, every panel was carefully examined and all the minutest details as regards to the presence and absence, the quantity and quality of fouling and the condition of the paint film were recorded. After each inspection the rack was re-immersed in the same position as it was before at the test site. The behaviour of the controls were closely compared with each of the treated test panels at every inspection and the trend of fouling was watched with a view to record the first sign of breakdown of the compositions under test. The method of rating followed was one of direct reading obtained on visual examination and by allotting simple percentage on the surface area covered by the fouling forms on each test panel. The presence of the free living marine organisms encountered along with the sedentary foulants were ignored as less important. The monthly assessment on the fouling based on the above rating for each panel is presented in Table No. I. Regular hydrographical data comprising water temperature, salinity, dissolved oxygen and hydrogen-ion concentration from the test site were collected and are presented here in Table No. II.

TABLE I

GENERAL ESTIMATION OF THE MAJOR FOULING FORMS SETTLED ON THE TOXIC AND NON-TOXIC TEST PLATES

Time of inspection	Commercial AF1	Commercial AF2	Commercial AF3	Commercial AF4	Commercial AF5	Laboratory preparation AF6 experimental	Non-Toxic control	Remarks
1st month September	20% Barnacles Hydroids	15% Barnacles Hydroids	Nil	Nil	Nil	Nil	25% Barnacles Hydroids Bryozoans	No damage to paint film. Slime formation on all panels
2nd month October	35% Barnacles Bryozoans	20% Barnacles Bryozoans	Nil	Nil	5% Barnacles	Nil	40% Barnacles Tube-worms Bryozoans	Paint film intact
3rd month November	50% Barnacles Tube-worms	35% Barnacles Tube-worms	Nil	Nil	10% Barnacles	Nil	6% Barnacles Tube-worms Bryozoans	Paint film intact
4th month December	65% Barnacles Tube-worms Oysters	60% Barnacles Tube-worms Oysters	Nil	Nil	35% Barnacles Tube-worms Oysters	Nil	70% Barnacles Oysters Tube-worms	Superimposed growth of oysters on control; AF1 and AF2 blistering.
5th month January	75% Barnacles Oysters Tube-worms	75% Barnacles Oysters Tube-worms	3% Barnacles Tube-worms	2% Barnacles	50% Barnacles Oysters	Nil	75% Barnacles Tube-worms Oysters	AF1, AF2 and AF3 show sign of rusting and blistering
6th month February	85% Barnacles Oysters Tube-worms	80% Barnacles Oysters Tube-worms	5% Barnacles Oysters	5% Barnacles Oysters	70% Barnacles Oysters	2% Barnacles Oysters	90% Oysters Tube-worms	AF5 blistering and panel rusting
7th month March	Withdrawn	Withdrawn	15% Barnacles Oysters Tube-worms	10% Barnacles Oysters Tube-worms	Withdrawn	5% Barnacles Oysters	Withdrawn	Observations on AF3, AF4 and AF6 were continued.
8th month April	—	—	35% Oysters Tube-worms Barnacles	30% Oysters Tube-worms	—	10% Tube-worms Oysters	—	AF6 blistering.
9th month May	—	—	55% Oysters Tube-worms	35% Oysters Tube-worms	—	20% Tube-worms Oysters	—	Panels withdrawn. AF4 in tact.

TABLE II
THE MONTHLY AVERAGE HYDROGRAPHICAL DATA COLLECTED FROM THE CENTRAL INSTITUTE OF FISHERIES TECHNOLOGY TEST SITE DURING THE PRESENT STUDIES

	Hydrographical Particulars			
	Water Temp. °C.	Salinity % °	Dissolved oxygen Ml/L	pH
September	29.0	5.0	5.0	7.2
October	29.0	9.9	4.8	7.6
November	30.0	17.8	6.0	7.6
December	29.0	25.3	5.2	6.9
January	29.0	32.3	4.2	7.4
February	30.0	34.0	5.2	7.6
March	31.0	32.5	6.1	7.4
April	33.0	32.7	4.8	7.2
May	31.0	32.2	3.6	7.6
June	29.0	29.3	4.1	7.4
July	28.0	1.6	5.8	7.4
August	28.0	4.4	6.8	7.2

Service test

Since raft exposure tests do not produce all the conditions that are normally met with on a ship's bottom, the present samples of commercial paints were tested also under actual service conditions before a final assessment on their efficiency is made. Normally only paints that give promising results under raft tests are selected for further evaluation study on a boat, since service tests are time consuming and elaborate. During the present studies, it was however possible to employ only two commercial paints, AF4/62 and AF5/62 for service tests. Four sections opposing each other were selected on the under water hull of a departmental fishing boat and the two paints were tried on those areas following the same schedule of surface preparation, priming and top coat antifouling as was done on the test panels for the raft exposure studies. Similar test coupons were also located on the rudder both on the starboard and port sides.

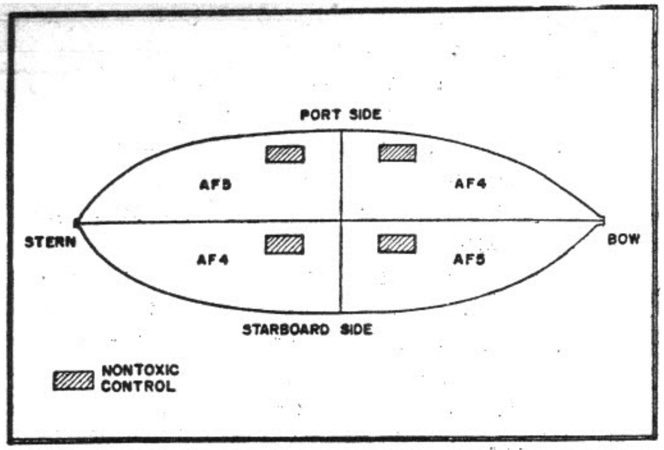
One sample of paint covered locations on the port side bow (AF4) and starboard stern quarter (AF4) of the boat while the other sample covered the selected areas on the Port side stern quarter (AF5), and starboard bow (AF5) of the same vessel as shown in Fig. 1, and thus avoided the possible positional effects of the painting system. A small area in each quarter on the hull left without any coating of antifouling paint served as controls. The vessel was waterborne for a period of six months in the Cochin waters before she was dry-docked for inspection.

On the dry dock the quality and quantity of fouling organisms settled on the hull both on the painted (A.F. paint) and un-painted (control) areas were carefully examined and recorded. The performance of the different antifouling paint systems on the hull were evaluated on the basis of their fouling resistance and the data collected is presented in Table No. III and the conditions photographed as in Fig. 2 and 3. The fouling complex gathered on both the sides of the rudder of the vessel under turbulent conditions at the stern area was also recorded.

TABLE III
DATA ON THE ASSESSMENT OF FOULING AT DIFFERENT TREATED LOCATIONS ON THE HULL FOR A SERVICE PERIOD OF SIX MONTHS (OCTOBER—MARCH)

Position	Eye estimation	Barnacles	Oysters	Tube-worms	Hydroids	Bryozoans	Algae	
Port side bow AF4	Very light 3%	2% on the water-line zone	—	—	—	—	1%*	Fig. 2
Port side quarter AF5	Very heavy 85%	10%	65%	2%	2%	4%	2%*	Fig. 2
Starboard bow AF5	Very heavy 80%	8%	60%	3%	2%	5%	1%*	Fig. 3
Starboard quarter AF4	Very light 4%	1% scattered	—	—	2%	—	1%*	Fig. 3
Controls	Very heavy 80%	10%	60%	4%	2%	3%	1%*	
Portside rudder upper half AF4	Very light 3%	2%	1%	—	—	—	—	Fig 4
Lower half AF5	Very heavy 80%	78%	1%	—	—	—	—	Fig 4
Starboard rudder upper half AF5	Very heavy 75%	72%	1%	—	—	2%	—	Fig. 5
Lower half AF4	Very light 4%	4%	—	—	—	—	—	Fig. 5

*on the water-line zone



Discussion

The efficiency of an antifouling paint depends on its resistance to settlement of the various marine organisms for a maximum period under severe and free fouling conditions through continuous release of toxic ingredients over the entire period of immersion. Leaching rate experiments and raft exposure tests are the two reliable methods by which the final performance of any marine anti-fouling paint composition can be predicted to a very reasonable extent. The later test conducted at pre-determined locations aims directly at the biological efficiency of the paint system and it is the standard method recommended and is being widely followed by all marine paint testing stations of the world.

Assessing the performance of anti-fouling compositions in a raft exposure test is a complicated problem requiring adequate knowledge on the biology of the fouling organisms and correct interpretation of their settlement. The marine fouling organisms encountered at the test site in the Port of Cochin were abundant both in quality and quantity at the time of the present observation. Under the hydrographical conditions reported, the acron barnacle, *Balanus amphitrite;* the bivalve mollusc, *Ostrea* sp., the tubiculous polychaete, *Hydroides norvegica* and the encrusting bryozoan, *Membranipora* sp. were the most dominant fouling forms likely to merit more detailed attention. Next in abundance were the colonial coelenterates represented by hydroides like *Tubularia* and *Oblia;* the sabellids and the erect bryozoans all of which were freely settling on the untreated control test panels as well as on other non-toxic objects under immersion in and around the test site indicating that the bulk of fouling recorded is well drawn from members of the natural fouling population present in the Port of Cochin. Many of

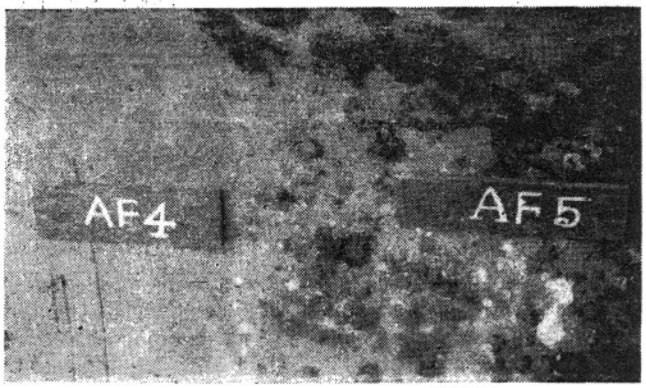


Fig. 2

Condition of fouling on the starboard side of the boat.

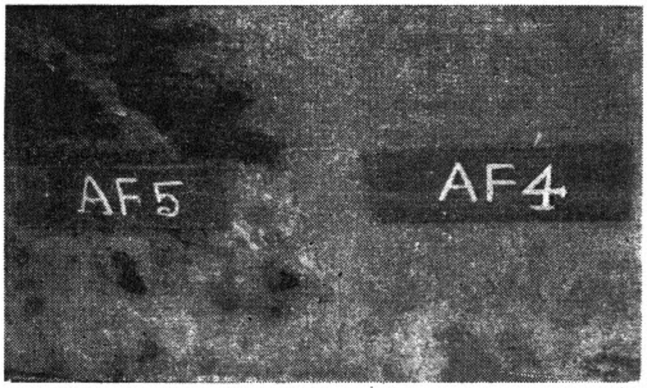


Fig. 3

Condition of fouling on the port side of the boat.

Condition of fouling on the rudder

port side.

Fig. 4

star board side.

Fig. 5

Note: AF4 has been free from fouling consistently.

these forms because of their structure and growth are by far the most serious of all the fouling organisms settling on a ship creating a permanent resistance to its normal motion. The green algae, *Enteromorpha* was the only plant fouling form present in trace quantities on the test panels. Apart from these, few minor sedentary and free living forms were also present but were not considered in detail being less important foulants.

On the untreated non-toxic controls all the fouling forms were recorded from time to time. The initial fouling on AF1 and AF2 was due to *Balanus amphitrite* and *Tubularia* sp. besides the usual bacterial slime within 30 days of immersion. Barnacles which are supposed to be highly resistant to toxic substances were observed on AF3 and AF4 only after 120 days of immersion. The highly sensitive oysters and tubeworms that were settling on all the treated panels at the end of about 200 days of immersion clearly indicated the non-toxic nature of the surface. AF5 on the hull and rudder of the boat was also heavily fouled by barnacles, and oysters whilst AF4 was practically free even after six months of service life.

The comparative toxicity of the different compositions has been assessed by noting the reaction of the settling marine organisms on the painted test panels. The quality and quantity of marine growths settling on the toxic test panels fluctuated to a greater or lesser extent according to their sensitivity factors. Panels treated with compositions AF1 and AF2 were the first to be fouled within four weeks of immersion and throughout the experiment upto the sixth month they continued to be as bad as the non-toxic controls. AF5 which was not at all fouled during the first 30 days of exposure gathered fouling in slow degrees and 50% of the surface was covered by the fifth month. AF3 and AF4 were completely free from fouling for the first four months but were attacked to the extent of 55% and 35% respectively during the next five months indicating a reduction in their resistivity. AF6 was not fouled for the first five months and even at the end of the ninth month had only 20% of its surface fouled, incidentally proving that copper and arsenic combination has a prolonged toxic effect when compared to cuprous oxide present in the commercial products tested, Balasubramanyan, *et. al.* (1964).

As a result of anti-fouling research conducted during 1942-44 by British investigators (Haris, 1946) it was recommended that the criterion of failure of a test area by fouling should be clearly defined "all-or-none" basis. As soon as any kind of sensitive fouling organism appears in appreciable amount on a test plate or ship's bottom, the anti-fouling mechanism has failed, it is then merely a matter of allowing sufficient time for the foulants to grow to a size large enough to be a serious impediment to a vessel. If the complete absence of any fouling form on the toxic panel is taken as the criterion for judging its biological efficiency AF1, AF2 and AF5 get eliminated by the first inspection itself after 30 days of exposure and thereby cannot be considered to satisfy the prescribed standards for an anti-fouling paint.

By the same principle; the fouling-free life of AF3 and AF4 can be placed at four months whilst AF6 can with stand upto five months. If 5%, 10% and 15% of fouling are considered to be only negligible the performance of the above paints can be credited with further three months of effective service. The months of June, July and August were found unfavourable to continue the tests further due to a severe drop in the salinity on account of monsoon rains. The test panels had to be withdrawn after May. This sudden reduction in salinity appears to keep the fouling population under check for a period of three months and ships do not gather much fouling during that time in the Port of Cochin.

Apart from raft exposure the commercial preparations of AF4 and AF5 were under service test from October to March when severe fouling conditions persisted. It is seen from Table II and the enclosed photographs — Figures 2 to 5 — that areas painted on the hull with AF5 have been severely fouled by all the organisms that were found on the test panels treated with the same composition and AF4 was comparatively free from any of the major fouling forms throughout except in few spots where the paint film was damaged due to mechanical causes. Wherever AF4 and AF5 were used on the rudder the amount of fouling was also similar to that noted on the hull but instead of oysters more of barnacles were noted. Thus it is seen that the performance of AF4 and AF5 was mostly of the same magnitude both under raft exposure and service tests. The fouling forms that were able to settle freely on AF5 could not do so on AF4 under identical conditions. The present observations only confirm the fact that AF4 has been adequately toxic and preventing all the fouling forms normally settling on the non-toxic controls as well as on the other treated panels for a prolonged period. It is quite evident now that from the present lot of commercial antifouling paints tested only AF4 would have given adequate protection on boats when others would not have served any purpose at all and hulls treated with such inferior paints would have been heavily fouled by the time their dry-docking is due. Since ship bottom paints are specific in their function, their performances should not be left to mere chance.

Some of the commercial antifouling paints resist fouling for a prolonged period whilst others fail in a relatively short period under identical conditions. The efficiency of numerous anti-fouling paints that were put to test in the Kaneohe bay by Edmondson (1937) failed within 10 to 12 weeks. Orton (1930) had evaluated the life of some antifouling compositions to be of more than 3 years whilst some were effective only for a few weeks. Variations in the performance of the different paint compositions may be due to the use of toxic materials very much differing in their properties or difference in the toxic loadings or dissimilarity in their leaching rates.

The most widely used toxic pigment in all antifouling paints is the cuprous oxide in different loadings depending upon the types of paints formulated. According to Miller (1946) the factor responsible for the resistance of fouling is the leaching rate of the paint, rather than the copper content. Barne's (1948) investigations on antifouling paints revealed that a leaching rate of 10 micro-grammes of copper per square centimeter per day is adequate to prevent fouling, which is widely accepted and with a leaching rate less than this fouling cannot be prevented. Ketchem *et al*. (1945). The presence and absence of a fouling complex or a single fouling form on the toxic panel very much depends upon the sensitivity factor of the organisms and to quote Pyefinch (1948) "even though immersions are carefully planned, the fullest possible check must still be made on the biological characteristics of the whole immersion period. to ensure that estimates of length of antifouling life are not vitiated by unusual variations in the general biology of the fouling organisms themselves". Observations have also been quite similar in the Port of Cochin to those of Edmondson and others (1939) made in Hawaiian waters that during periods of high productivity of organisms. even the coatings usually most effective were often readily fouled. Thus it appears that the final performance of an antifouling paint is governed by very many factors each of which is as important as the other. However. the existance of a well defined correlation between fouling resistance and the leaching rate of the toxic pigment cannot be ignored. In fact, accelerated leaching technique will give a suitable indication of the probable fouling free life of an antifouling paint much earlier than raft tests and as such before finalising a standard paint for the prevention of fouling, evaluation tests have to be taken up in a series of sequences like leaching rate exnriments. raft exposure tests and service tests for each batch of paint formulated.

The time required for ships bottoms to foul depends on the efficient and reliable performance of the protective coating which sooner or later breaks down during service due to the exhaustion of the toxic ingredients. Once the paint coating is damaged or inactivated, fouling develops soon, necessitating dry-docking for the renewal of the paint. If periods between dry dockings are lengthened by such a toxic paint coating, the problem of preventing marine fouling is considerably solved.

Summary

A number of commercial antifouling paints and a laboratory experimental paint composition were all put to raft exposure tests for a period of 9 months in the Port of Cochin with a view to studying their relative biological efficiency.

The efficiency of the different compositions were assessed by the quality and quantity of the many marine sedentary fouling organisms settling on them as compared with non-toxic controls.

Two of the paints were further subjected to tests under actual service conditions. The probable life of the different antifouling paints have been evaluated based on the results of the raft exposure and service tests. The performances of the different antifouling paints are discussed in detail.

Acknowledgement

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