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PIGMENT COLOR RESEARCH REPORT

Final Report

MARINE FOULING AND ITS PREVENTION

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NEWARK PLANT

CHEMICAL DIVISION - COLORS

Final Report

MARINE FOULING AND ITS PREVENTION

NOVEMBER, 1953.

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MARINE FOULING AND ITS PREVENTION

INTRODUCTION:

A treatise on "Marine Fouling and its Prevention" was prepared (1952) for the Navy Department (Bureau of Ships) by the Woods Hole Oceanographic Institution. It comprises a discussion in considerable detail of the following:

1. Problems of Fouling.
2. Biology of Fouling.
3. Prevention of Fouling.

A review of this work has been made in an attempt to decide if this general field was a promising one for diversification.

SUMMARY - RECOMMENDATIONS:

Work in the past on this problem has indicated that the only practical solution lies in the use of anti-fouling paints pigmented with copper or mercury compounds. For economic reasons, the former are more important.

The design of a satisfactory protective system involves both pigment and paint studies. Selection of the pigment requires consideration of its inherent toxic effect on marine organisms and its solubility. Prevention of marine growth has been shown to depend on the rate at which the toxic is released; this obviously will be controlled largely by the nature of the film matrix, that is, the paint vehicle and its behavior under the specific exposure conditions which are involved. From the viewpoint of practical use, the paint must be formulated, in addition, to give satisfactory performance in respect to the usual paint properties of adhesion, settling, reactivity, etc.

Generally satisfactory anti-fouling paints of various types have been developed by the Navy and others, based for the most part on cuprous oxide. From the currently available evidence, the probability of obtaining products of equal effectiveness from other metals is remote. Other copper compounds which have been investigated so far have not shown promise.

It therefore appears doubtful if any major research program at Newark on anti-fouling systems is justified. This conclusion is not based on the magnitude of the field, which is very large, but rather on the fact that the present method of pigmenting seems satisfactory for most purposes; future technological advances will probably fall more in the field of paint rather than pigment chemistry. However, for reasons indicated below, an evaluation of copper pyrophosphate as an anti-fouling pigment is suggested. Such a study would involve only a limited amount of work to reach a decision as to whether or not such a product would be worthy of commercial development.

DISCUSSION:

General

The problem of marine fouling is a very old one and obviously of great economic importance. It is particularly important in the case of ships, buoys and the like, but may also be a matter of concern in connection with under-water sound equipment, salt water piping, etc.

Various methods of attack have been used. They have included the use of copper (or other metal) sheathing, mechanical devices, electric devices and a wide variety of paints.

The only protective procedure which can be considered of practical interest is the latter, that is, the use of specially designed anti-fouling paints. These have been made from many materials, ranging from more or less orthodox pigments to tobacco juice, poison ivy and an arrow poison. The most worthwhile systematic work in this field has been done in the last 30-40 years by the Navy Department and others, notably the Bakelite Corp. Quoting from the Woods Hole report: "In the present state of the art, paints can be designed which do not foul as long as the physical integrity of the paint film is maintained. Further advances in the development of such paints will result from improvements in strength, toughness, and adhesion".

In general, the problems which are encountered are thus concerned more with paint properties than with pigment properties. In this respect, the fouling problem shows a parallelism with that of corrosion. In the case of finishes for steel ships, anti-fouling properties and corrosion resistance are closely related, as is pointed out below.

Formulation of Anti-fouling Paints

Apparently, the only pigments now used having the desired toxicity towards fouling organisms are metallic copper, copper compounds and mercury compounds. The use of the latter has decreased because of their high cost and the fact that as good or better results are obtained with the others. While metallic copper is still used, it presents no special advantage over cuprous oxide and is more expensive. It may also give rise to corrosion problems through electrolytic action, particularly on steel ships. Good protection against fouling can be obtained with cuprous oxide when properly formulated and applied with a suitable metal protective priming coat.

The toxic effect of cuprous oxide or other materials depends on the rate at which it is released from the paint film while in service. To be effective, this leaching rate must be approximately 10 $\mu g/cm^2/day$. "Some paints maintain an adequate leaching rate for a considerable period of time, whereas the leaching rates of others fall to inadequate values in a relatively short period. The leaching rate of certain successful paints <u>decrease steadily</u> from an initial high value. Such a paint may have an adequate leaching rate for many months .... Certain other effective paints have leaching rates which, after the first few weeks immersion, <u>remain nearly constant</u> for many months....."

There are two main types of successful anti-fouling paints: 1) Those in which the pigment is embedded in an <u>insoluble matrix</u>. In this case, it is necessary to load the paint with a large volume of toxic material; theoretically, enough to give continuous contact of the pigment particles. In practice, the amount is limited by the mechanical strength of the film. The vehicle may be a vinyl resin (straight or modified) or a phenolic/chinawood oil varnish. Bakelite's AF-14 (now MIL-P-15931) comprises Vinyl resin 8%, cuprous oxide 84%, rosin 8% The varnish type is easier to apply than "AF-14", and required a less carefully prepared surface.

2) In the second type of paint, a <u>relatively soluble binder</u> is used, commonly rosin, with sufficient plasticizer added to obtain flexibility. Other resins may be added to control the rate of solution. The paint may be of the "hot melt" type (rosin/paraffin vehicle) and applied in the molten state, or of the ordinary solvent type. Hot melt paints have been effective in preventing fouling for periods of two to five years on Naval vessels. The solvent type paints are low in cost, but when properly formulated may have a service life of "well over a year". Some have shown poor resistance to erosion. The essential characteristic of all soluble binder paints is the fact that both pigment and binder dissolve during use. Their degree of pigmentation is much lower than that of the insoluble binder type.

Working out the details of an anti-fouling paint formulation involves the consideration of numerous paint properties which may be fully as important as toxicity to marine organizms. The technology is rather specialized and manufacture of these products is limited to a relatively small number of producers.

A finishing system worked out by the Bakelite Corporation, having the advantages of rapid-dry, good durability and effective anti-fouling characteristics is the following:

Coat #	Paint	Film Thickness	Drying Time
1	"Wash Primer" (MIL-P-15328A)	0.3-0.5 mil.	20 min.
2,3,4,	Anti-corrosive primer*	3x (1.3-1.6 mils)	3 x 60 min.
5,6,7	Anti-fouling paint (AF-14)**	3x (2.6-3.3 mils)	3 x 60 min.

*The Bureau of Ships #120 primer (MIL-P-15930) which is pigmented with basic zinc chromate is recommended.

**"Insoluble matrix" type. The composition of AF-14 (MIL-P-15931) is given earlier in this report.

Evaluation of Anti-fouling Agents

The usefulness of any product as the toxic component of an anti-fouling paint depends on various factors.

1. Toxicity to marine organisms. A great many species have been recorded as causing fouling difficulties. Some are more easily controlled than others. As indicated above, of the various metallic salts which have been investigated, those of copper and mercury are the most effective. Zinc, iron and manganese are less effective; arsenic, tin, lead, cadmium, aluminum, chromium (VI) even less so. Many organic materials have been examined, but since they are usually quite specific in their action, none are considered as specially promising. "DDT", for example, prevents the attachment of barnacles but is not effective against any of the other common fouling organisms.

2. The product must possess the necessary solubility in sea water. The rate of solution (which is the important factor) can, of course, be controlled to a certain degree by the paint formulation, but some compounds may be too soluble or too insoluble to be practical. Cuprous oxide has a solubility of 8.6×10^{-5} mols/liter and is satisfactory. Cupric oxide is much less soluble (1.4×10^{-8} moles/liter, and is said to be unsatisfactory. Products of much higher solubility than cuprous oxide might give paints of short life unless their rate of solution could be controlled by proper choice of vehicle.

3. The cost of the pigment is of course important, particularly in highly pigmented paints. In view of the good performance of cuprous oxide, it would be difficult to promote more expensive products unless they showed an outstanding quality advantage.

4. There have been objections to cuprous oxide because of its color; for example in yacht paints. Availability of a relatively colorless product would give greater flexibility in this respect.

5. Paint properties such as ease of dispersion, settling characteristics, reactivity, etc., should be acceptable.

Special Anti-fouling Problems

Application of anti-fouling paints to metals (e.g. steel ships) presents special problems since the results may be complimated by corrosion effects unless the anti-fouling coat is insulated by a barrier coat of some sort. The possibility of (metallic) copper paints causing electrolytic corrosion has been mentioned above. Apparently the leaching rate of cuprous oxide paints is depressed after corrosion has set in; the mechanism is not entirely clear.

Fouling may be a problem not only with ships, buoys, etc., but also with salt water pipes on ships or in power stations and oil refineries. The use of chlorine, Dowicide, etc., is usually effective as a remedy. Various toxic organic compounds have also been used.

Conclusions and Recommendations

In view of the present state of the art it is doubtful if any major research program at Newark on anti-fouling systems is justified. The evidence indicates that cuprous oxide as a pigment is perfectly satisfactory except that its color may be objectionable for some used. Some work has been done on other copper compounds, viz. cupric citrate, cuprous chloride, basic cupric carbonate, cuprous thiocyanate, cuprous iodide, cuprous sulfide and cupric derivatives of acetyl acetone and n-caproic acid. As nearly as can be judged from the Woods Hole report, none of these showed obvious promise.

A-6-D, which has been reported to decrease mildew growth, has been suggested as a possible pigment for anti-fouling paints; however, qualitative tests indicate that its copper solubility may be too low. Copper pyrophosphate (AA-26-D), which we prepared some time ago in the semi-works, might be satisfactory, and it has the advantage of being practically colorless. The ingredient cost of AA-26-D is approximately $20/100# and it should be very simple to make. The current selling price of cuprous oxide is $42.50-$49.50/100# (Chem. Eng. News, Oct. 1952). There is considerable difference in specific gravity between the two products: - Cu_2O - ca 6.0, AA-26-D - ca 3.0. The greater bulk of AA-26-D might be an advantage since, in some cases at least, leaching rates are proportional to pigment volume in the film.

Evaluation of a sample of AA-26-D by sub-tropical exposure in sea water is recommended.

MPH