Lead Industries Association, Inc.
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November 29, 1973

SUBJECT: ORGANOLEAD ANTI-FOULING PAINTS

TO THE MEMBERS OF THE LEAD INDUSTRIES ASSOCIATION, INC.:

This feature article from the October issue of "Paint and Varnish Production," describes successful exposure tests of organolead antifouling paint in salt and brackish waters in Connecticut and Maryland.

The paints, developed in an ILZRO research project, offer extended protection against marine fouling and are under trial by the U. S. Navy.

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Lewis E. Gage

Lewis E. Gage
Assistant Secretary and
Director of Communications

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Enclosure

OCTOBER 1973

ORGANOLEAD ANTIFOULANTS:

Promising new antifoulant

ORGANOLEAD-ELASTOMERIC *coatings have been found to offer extended protection against the growth of fouling organisms because of their gradual release of toxicants over the life span of the paint film. Here are the results of exposure tests carried out in fouling waters of Connecticut and Maryland.*

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A new form of antifouling paint, in which an organolead chemical is used as the toxicant in solvent dispersions of synthetic rubbers compounded from elastomeric polymeric materials, has shown considerable promise in various seawater immersion tests.

The new paints, developed in research sponsored by International Lead Zinc Research Organization, Inc. (ILZRO), differ basically from previously developed organolead-containing antifouling paints in that the earlier coatings were based on the principle that if cuprous oxide (Cu_2O) pigment were continuously exposed at the paint surface, marine plant and animal life would not be able to attach themselves. This type of resinous paint, with its high degree of pigmentation, has a limited surface stability under water, and this is manifested by "chalking." As the surface layer chalks away on a continuous basis new layers of paint are exposed, and with them new quantities of cuprous oxide as toxicant.

The new elastomeric antifouling paints do not develop surface chalking. Instead, they permit the organolead toxicant to be released gradually from the coating surface by diffusion. Such release continues to prevent the growth of plant and animal organisms on the coated surface during the life of the coating.

The amount of the lead-release, in terms of micrograms of lead per unit of area and time, is quite small. Exposure tests have shown, however, that it is effective in protecting coated panels, boats, outboard engines and other immersed surfaces to a high degree against fouling growth during exposure test periods ranging from 12 to 21 months. Laboratory tests have shown that the rate of lead-release remains, for a certain paint material, nearly constant during test periods of one year or more.

Previous research conducted by ILZRO established the effectiveness of organolead compounds in antifouling paints *(1)*. The paint systems studied then were of the vinyl-rosin systems, such as U.S. Navy Specification 121, of MIL-P-15931A, and the vinyl-high rosin paints of U.S. Navy Specification 121/63 of MIL-P-15931B.

In the first of these groups, the coating vehicle consists of PVC/AC copolymer Vinylite VYHH of Union Carbide Corp., and WW gum rosin of Hercules Incorporated in a ratio of 1:1. In the second group, the ratio is 1:4. In both test formulations, tricresyl phosphate was used as the plasticizer. As antifouling toxicant, both specifications use cuprous oxide in an amount about five times the total weight of vinyl resin and wood rosin in each paint.

In the earlier work, the amount of cuprous oxide in test paints was reduced by 50 per cent and replaced by equal parts of an organolead compound, such as triphenyl lead acetate (TPLA) or tributyl lead acetate (TBLA), and by pigments, such as red iron oxide and barytes. The antifouling effect of the organolead-containing formulation proved superior to that obtained with formulations containing cuprous oxide alone.

Elastomeric Vehicles

It must be noted that synthetic rubbers, or elastomers, represent polymer materials which possess mechanical properties similar to those of natural rubber: high deformability, rapid recovery of deformation and good mechanical strength. These materials may be described as "heterophase" substances *(2)*, meaning that they consist of more than one state, or "phase" of their essential base material.

The base material is contained in a high polymer, or three-dimensional, phase which, alone, is not molecularly dispersible and not volatile (even under vacuum or when exposed to elevated temperatures). In this state the polymer is capable of increasing its volume when it comes into contact with suitable fluids, fusible matter or "swellers" that penetrate the polymer matter.

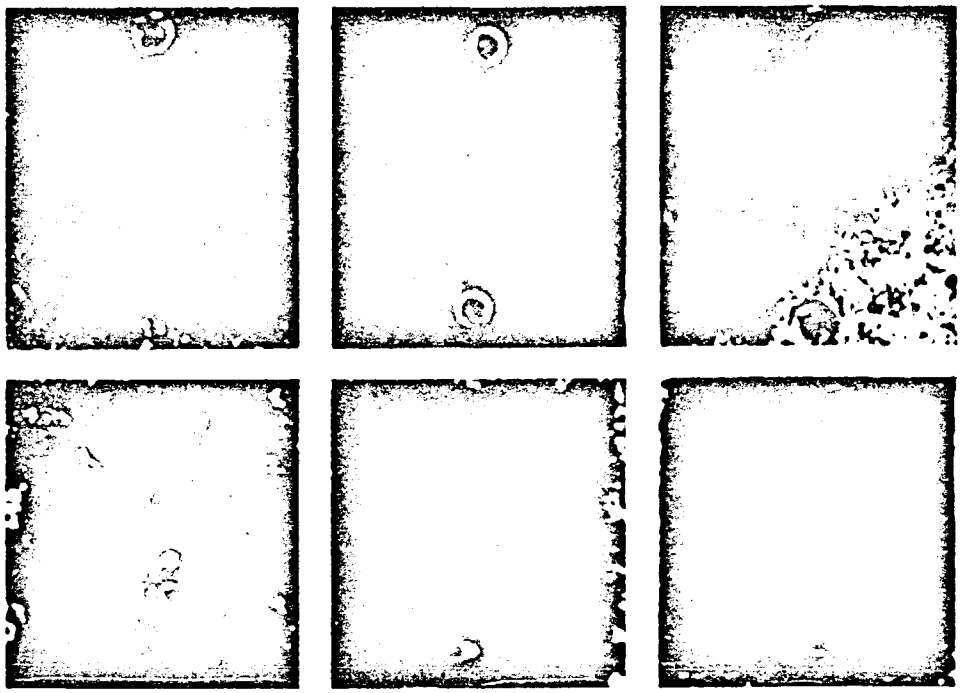


Figure 1 — Exposure series in creek flowing into Severn River, Md. Top row shows panels after four months of exposure, July to November, 1971. Bottom row shows same panels after 18 months. Panels (from left) are coated as follows: test paint Pb-1-39 without toxicant, same paint with ten g TPLA per 100 g, navy antifouling paint (MIL-P-15931, f. 121/63).

The "swollen" polymer has a uniform appearance. The soluble static, or "phase," of the base material represents a swelling substance that is, alone, volatile (at least under vacuum or at elevated temperature), and can, therefore, form a rubber-like substance with the tri-dimensional phase matter. The organolead matter penetrates the swelling or swollen polymer materials, or, in particular, their solvent dispersions, and influences the rubber-like materials, becoming a part of these rubbers.

These elastomeric solvent dispersions can be combined with ball-milled dispersions of pigments in solvents. When mixtures of the elastomeric dispersions and the pigment dispersion are further ball-milled together, a uniform dispersion is obtained. The organolead component can be added to the vehicle, during pigment milling, or to the final ball-milled paint.

In order to assure complete entry of the organolead component, the paint should be warmed during stirring to 50°C. (122°F.). Thus treated, the paint can be applied to metal, plastics, concrete or polymer-treated fiber glass surfaces. As the volatile swelling solvents evaporate, the pigmented rubber-based films dry into highly cohesive and dense coating films that are stable under fresh or sea water and under varying temperature conditions.

Conventional rubber dispersions require for their "curing," or drying into dense coatings, the presence of sulfur or organosulfur compounds or accelerators. The application of heat is also usually required to transform the dispersions into stable rubber or "vulcanized" rubber layers. The new elastomeric dispersions, however, as well as their pigmented forms, which contain organolead compounds throughout, do not require the presence of sulfur or organosulfur compounds, or the application of heat. They form highly coherent, dense coatings at room temperature.

Since the properties of heterophase polymer substances vary with the increasing ratio of their tri-dimensional phase matter, and since the organolead mixtures examined in this study have a tendency to increase the volume of the available rubbery polymers, the resulting coatings have stronger mechanical properties than had been the case for the earlier mixtures of elastomers. Furthermore, it is possible, during evaporation of the volatile swelling solvents from the coating film, to apply two or more additional coats of the elastomeric paint, which swell together into uniform, heavier coatings.

Since the organolead compound has been incorporated into the coating material itself, it is to be found in each layer of a multi-coat dry film. The lead-release takes place uniformly and continuously throughout all layers of the film. It is possible, therefore, to remove by abrasives (such as brush boats) any part of the film while retaining the lead release property in the portion of the film that remains.

It is evident that such properties offer important possibilities for the

Figure 3 — Outboard engines after exposure in Connecticut coastal waters from May to late fall, 1972. Only lower portion of engine at left was coated with elastomeric antifouling paint containing TPLA. Entire immersed portion of engine at right was coated with the new antifoulant paint.

It was one of the purposes of the laboratory tests to observe the characteristics of the test panels under extended exposure in fresh water or in synthetic seawater. In changing the test waters at various time intervals, it becomes possible to test the water of the preceding period for its content of lead matter.

By comparing such results with waters of several exposure periods, one may establish the stability of the rate of lead-release over a given exposure time or study eventual changes which might occur during extended exposures. It is also possible to compare corresponding tests paints containing one kind of organolead matter, such as tributyl lead acetate, with other paints containing another organolead compound, such as triphenyl lead acetate.

The determination of the lead matter in the immersion water was made in accordance with the dithizone test method (6) as a modification of ASTM Standard C-555-64-T (a method developed originally for the determination of lead-release from glazed ceramic surfaces). Table I offers data on this type of extended investigation on two corresponding test paints, one of which contained triphenyl lead acetate. Here the lead-release in micrograms of lead per square centimeter per day was nearly the same in the first 273 days of immersion as during the next 100 days (0.012 microgram Pb/cm²/day and 0.011 microgram Pb/cm²/day).

In the case of the paint containing tributyl lead acetate, the lead-release was considerably higher in the first 302 days, showing a decrease in the subsequent 100 days. This phenomenon results from the fact that tributyl lead acetate has a greater leaching rate than the triphenyl lead acetate, which has a considerable degree of stability that is desirable for long-term exposures.

It is to be noted that lead-release does not take place in the form of an inorganic lead salt. The released matter can be extracted from the immersion water by shaking it with ethyl ether. When the ether extract is applied to a microscope slide, and the ether is allowed to evaporate, the residue, when viewed under the microscope (450 X), has the appearance of typical polymeric materials. (The chemical constitution of such water-released matter has not as yet been investigated.)

Table I — Lead-Release Differences Between Organolead Components in Elastomeric Paints During Laboratory Immersion Tests in 500 ml Water

(a) Triphenyl Lead Acetate (TPLA)		
Base Pb 1.39 with 5 g TPLA per 100 g paint — immersed in distilled water		
First 273 days	Average lead release	— 0.012 microgram Pb/cm²/day
	Total lead release	— 3.276 micrograms Pb/cm²/273 days
Next 100 days	Average lead release	— 0.011 microgram Pb/cm²/day
	Total lead release	— 1.100 micrograms Pb/cm²/100 days
	Total	— 4.376 micrograms Pb/cm²/373 days
Calculated, per year (365 days): 4.782 micrograms Pb/cm²		
Calculated for 1 sq ft of surface per year (1 sq ft = 929 sq cm)		
Lead release: 3,978 micrograms (1 microgram = 1 x 10⁻⁶ g)		
Total lead release: 0.003978 g lead/sq ft surface/year		
(b) Tributyl lead acetate (TBLA)		
Base Pb 1.39 with 3.3 g TBLA/100 g paint — immersed in distilled water		
First 302 days	Average lead release	— 0.056 microgram Pb/cm²/day
	Total lead release	— 16.912 micrograms Pb/cm²/302 days
Next 100 days:	Average lead release	— 0.015 microgram Pb/cm²/ day
	Total lead release	— 1.5 micrograms Pb/cm²/100 days
	Total	— 18.412 micrograms Pb/cm²/402 days
Calculated, per year (365 days): 16.717 micrograms Pb/cm²		
Calculated for 1 sq ft surface per year:		
Lead release: 15.530 micrograms		
Total lead release: 0.015530 g lead/sq ft surface/year		

Lead Release Data

Table I also shows the total lead-release per square centimeter of coated surface per year of immersion in varied 500-milliliter quantities of water, and it calculates the annual lead-release from a square foot of surface. For the triphenyl lead acetate paint, the lead-release amounts to 4,000 micrograms, or 0.004 gram of Pb per year. If the paint were applied to a ship, this total of lead would be released per square foot of surface throughout all the waters through which the ship might travel during the year.

It is of interest, therefore, to compare these data with the known lead content of the water before the immersion of the coated surface. A recent

maintenance of "clean" surfaces in tropical waters where marine fouling is prevalent. This cleaning action can occur even after removal of the top coating layers, and while the surface is under water, without requiring a dry dock.

Elastomers Used

The following elastomeric polymers have been used in the development of this study:

(1) Solvent dispersions of a commercial polyisoprene, Goodyear's Natsyn 400, a styrene-butadiene-styrene block polymer, Shell Chemical's Kraton 1101; a chlorosulfonated polyethylene, Du Pont's Hypalon 30, and a modification of the coating by the addition of an unsaturated polyamide resin, General Mills' Versalon 1140. The organolead chemical was, in most cases, used as the only accelerator in the drying of the coatings.

(2) In another system, a fluid butadiene-acrylonitrile polymer, B. F. Goodrich Chemical's Hycar 1312, was used jointly with a fluid polyurethane, Du Pont's Adiprene L 167, again using the organolead compound as the only accelerator component in the system.

(3) Other elastomers have been introduced in similar compositions, such as a poly-epichlorohydrin, B. F. Goodrich Chemical's Hydrin 100.

Organoleads Used

Generally, organolead chemistry deals with compounds in which a carbon atom of at least one organic group is attached directly to a lead atom *(3)*. The materials that have primarily been used in the coatings of this study belong to the group of organolead salts of the general type of R_3 Pb X, in which R represents a group attached to lead by carbon, and X an anionic group.

The materials used for the most part can be further classified as triaryl or trialkyl lead acylates, such as triphenyl lead acetate, tributyl lead acetate and others. These materials were developed initially by the Institute for Organic Chemistry, TNO, in Utrecht, The Netherlands, and have since been produced industrially in the United States as well as in Europe.

In one interesting form, the organolead material is delivered after being wetted with a high-boiling aromatic fluid to avoid dust formation during handling and dispersion. This product is supplied by Ciba-Geigy Marienberg GmbH in Germany under the name Irgarol BI 547.

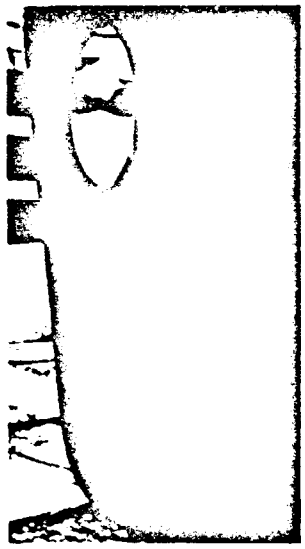


Figure 2 — Ship's rudder painted with experimental elastomeric antifouling coating after exposure in Connecticut coastal waters from June to December, 1971.

It has been pointed out that the organolead matter is introduced in the preparation of the new antifouling paints either to the elastomeric vehicle, during pigment dispersion or into the ball-milled paint. The elastomeric polymers are commercially widely available. In the years between 1962 and 1972, the production of synthetic rubbers increased in the United States from 1,574,000 long tons to 2,424,000 long tons, an increase of 54 per cent *(4)*.

Exposure Studies

In order to follow the development of the elastomeric antifouling coatings in selected exposure tests, studies were made in laboratory water immersion tests as well as in ocean underwater exposures. For the laboratory tests, cold-rolled steel panels coated with two coats of wash primer (MIL-P-15328B, formula 117) and two coats of the organolead elastomeric antifouling paints were used. In the outdoor seawater exposures, hot-rolled, sand-blasted steel panels coated with 0.7 to 0.8 mil of wash primer and 4.5 to 4.75 mils of red lead vinyl primer (MIL-P-15929B, formula 119) were utilized.

On the early exposure test panels, these primers were followed by about 13 mils of elastomeric paint with no organolead component but containing sulfur and a sulfur accelerator. These coatings were topped with 3.0 to 3.5 mils of organolead elastomeric antifouling paint (without sulfur components).

The sulfur-containing coatings were developed in the course of the work of this research group *(5)* under the sponsorship of the U.S. Naval Applied Science Laboratory, Brooklyn, N.Y., which was later transferred to Annapolis, Md. The organolead elastomeric antifouling coatings without sulfur components were developed by the same research group under the sponsorship of ILZRO. These panels comprised Exposure Group I, and were exposed in fouling waters of the estuary of the Severn River in Maryland.

In later tests, the organolead elastomeric antifouling paints were applied directly over the primer coats in a thickness of nine to ten mils. These panels comprised Exposure Group II.

The test paints of Group I were dark in color, since their pigmentation consisted of zinc oxide and channel-type carbon black; the panels of Group II were light gray in color, and were coated with experimental test paint referred to as G-4 paint. The same G-4 paint formulation was used in other exposure tests, such as on a fiber glass motor boat where, over the wash primer, it was applied as the only additional coating material.

After exposure for a season in barnacle-rich coastal waters of Connecticut, no trace of marine growth was observed, and the exposure test was repeated during the following season. In another test group, the G-4 paint was used as a protective coating on outboard ship engines and exposed in Connecticut coastal waters. The results of these exposures are discussed later in this article.

Most recently, the paints have been applied to aluminum and to formed acrylic polymer objects. The paint was also applied to hot-rolled steel test panels over a commercial inorganic zinc primer of the type of U.S. Specification MIL-P-38336. Here, the paints of Group I, as well as those of Group II, were applied successfully.

It is also worth mentioning that the viscosity of the elastomeric paints can be modified for spray application instead of brushing.

book (7) reports that the global mean for lake or river water is one to ten micrograms of lead per liter. Higher values may exist in areas adjacent to lead ore deposits, heavily traveled highways, etc. What these data reveal is that the amount of lead released from one square foot of painted surface would not have significant influence on the existing lead concentration in seawater.

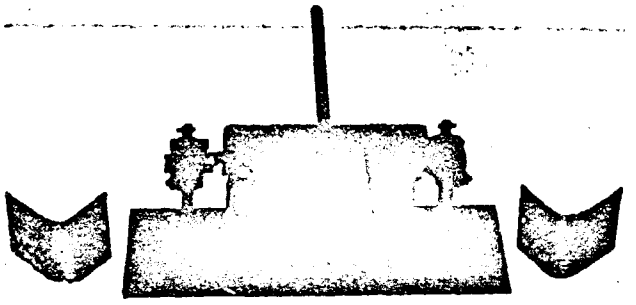
Control tests were made on two water samples, one taken from the estuary of the Severn River at Annapolis, Md., the other from the Harlem River adjacent to the NYU Aerospace facility in the Bronx, N.Y. The first test showed an average lead content of 12.6 micrograms per liter in dithizone tests; the other showed 6.4 micrograms of Pb per liter.

Fresh Water Exposure

The panels of Exposure Group I were described earlier in this paper. Their antifouling coatings comprised elastomeric paints containing five to ten grams of triphenyl lead acetate or tributyl lead acetate per 100 grams of test paint. These were exposed side by side with a similar elastomeric paint based on a sulfur accelerator, but not containing organolead toxicant. They were exposed together with panels coated with the same primer and elastomeric paints, but topcoated with a common type of antifouling paint based on cuprous oxide pigmentation with a vinyl-high rosin vehicle (Navy Specification MIL-P-15931B, Type 121/63). This same paint was also used containing cuprous oxide as well as some organolead component.

The exposure tests in the fouling waters of a creek flowing into the Severn River in Maryland showed that after four months, from July to November, 1971, the elastomeric paint without toxicant was covered with a beginning plant growth which, after 18 months of exposure, became the site of barnacle attachment. The same paint with organolead toxicant showed the attachment of barnacles to the supporting exposure board, but none on the painted panel. The antifouling paint, MIL-P-15931B, showed the beginning of plant growth after four months of exposure, with progressive fouling after 19 months.

Another organolead elastomeric paint was also exposed. This paint was based on a butadiene-acrylonitrile polymer and a fluid polyurethane, but was heat-reacted with a smaller amount of triphenyl lead acetate and pigmented either with carbon black and zinc oxide or carbon black and one-half zinc oxide and one-half cuprous oxide. Neither type of this paint showed fouling growth after 18 months of exposure. (They have been further inspected after 22 months of exposure and are still without any marine attachment or fouling growth). Some of the exposed panels are shown in the photos of Figure 1.



In exposure tests of Group II, using organolead elastomeric antifouling paints directly over the primer system, the coatings were pigmented either in the same manner as Group I, or with the major portion of the carbon black replaced by a fine-particle-sized amorphous silica that is produced by hydrolysis of silicon tetrachloride. This material is commercially available from Degussa, Inc., under the Aerosil-380 trade name, at a particle size of about five millimicrons. The pigment dispersion in the test paint consists, then, of zinc oxide, amorphous silica in some cases, and a slight tinting — either a small amount of carbon black, red lead oxide or other pigments.

The paints were exposed in Maryland, on the same type of test panels as were the coatings of Group I, as well as in the barnacle-rich coastal waters of Connecticut; the tests are continuing. Especially interesting was the application of the experimental G-4 paint on a fiber glass motor boat directly over a wash primer undercoat. While the Connecticut coastal waters in which the boat was operated are heavily infested by barnacles, the painted rudder (Figure 2) showed high resistance to fouling after exposure from June to December, 1971.

The results were the same when similar applications were carried out on the boat during the following season. This time, however, a new form of triphenyl lead acetate was used, containing ten per cent of an aromatic anti-dusting agent (Ciba-Geigy Mannenberg GmbH's Irgarol BI 547).

Coastal Water Exposure

The organolead antifouling elastomeric paint G-4 was applied to outboard engines which were exposed in the Connecticut coastal waters. One of the engines was painted only on the lower part; while the other engine was painted over the entire immersed area. The engines were exposed from May to late fall, 1972, when they were photographed, as shown in Figure 3. There is an abundance of marine growth on the unprotected part of one engine, while the test paint shows high resistance to fouling wherever it was applied.

Concerning the use of such coatings on engines, it is of interest that the elastomeric antifouling paints are not affected by contact with mineral oils, despite their being air-dried. The paint was not dissolved after a 15-day immersion in warm vacuum pump mineral oil at 100°F. (38°C.). The release of lead matter into the oil was tested in a manner similar to that previously described for lead content in immersion water.

The lead-release after the 15-day test amounted to 2.84 micrograms per square inch, indicating that organolead elastomeric antifouling paint can also be employed under immersion conditions where contact between fouling water and oil is to be expected, such as with offshore drilling rigs.

Other exposure tests are under way in Australian waters, and in an area of Rhodesia where the antifouling paint has been applied to irrigation ditches

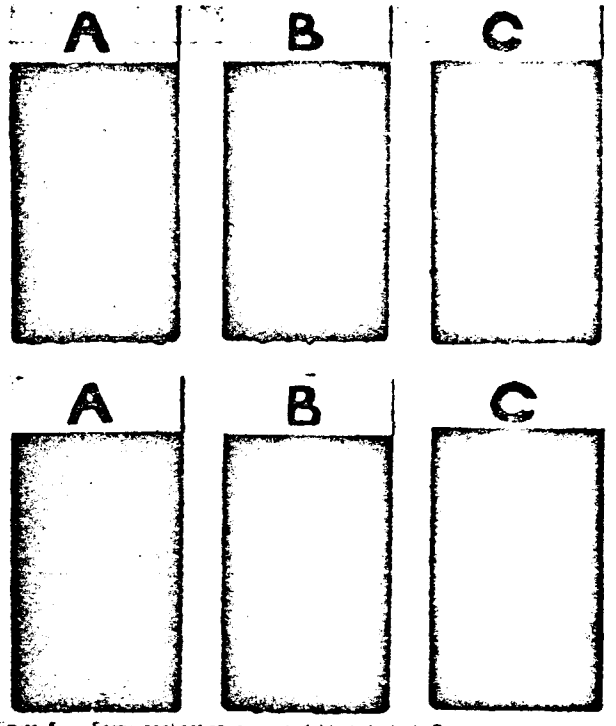


Figure 5 — Spray application over sand blasted steel. Panels in top row were coated with four-component rubber systems, while those in bottom row were coated with fluid butadiene-acrylonitrile-polyurethane system. All systems contain organolead compounds. Panels A are bare steel, B were pre-coated with wash primer, C were pre-coated with inorganic zinc primer.

harboring snails which transmit the tropical disease, schistosomiasis (also known as snail fever). The preliminary results are encouraging.

Recent Developments

In view of the fact that the new elastomeric paints are based on dispersions of polymeric swelling materials, the influence on drying and adhesion of wet substrates and low temperatures was studied. In these tests, the elastomeric paints were applied to moistened wash-primed steel panels and, in some cases, at temperatures below normal for conventional coatings application.

Controlled conical mandrel tests, as shown in Figure 4, were carried out on the panels. It was found that such applications do not interfere with the drying or adhesion of the elastomeric antifouling paints.

These application characteristics of the new antifouling paints are of considerable practical importance. In the case of surface cleaning or partial paint-surface removal by mechanical cleaning equipment at sea, it might be desirable to apply additional coats of paint over moist surfaces or when the moisture content of the air is high.

In a current development, modifications of the viscosities of the elastomeric G-4 paints were made. These modifications facilitate the formulation of paint vehicles that can be applied by spray or brush over extended areas. This developmental work is still in progress, but Figure 5 shows spray applications over bare sand-blasted steel (A), over wash-primed sand-blasted steel (B), and over sand-blasted steel with inorganic zinc primer (C).

Acknowledgments

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Since New York University discontinued its School of Engineering and Science, in mid-1973, the Coatings Research Laboratory has been transferred to the Chemistry Department, Manhattan College, Hayden Hall, Bronx, N.Y. 10471, where these studies are continuing.

The use of the exposure site in the estuarial waters of the Severn River at Annapolis, Md., was made possible through the cooperation of Dr. Eugene C. Fischer and Mr. Edward Dyckman of the Oceanographic Laboratory, U.S. Naval Ship Research and Development Laboratory. The author expresses his appreciation for this assistance.

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