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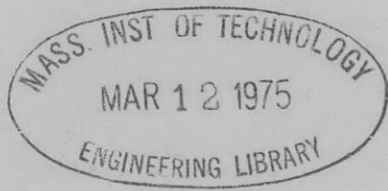
Report

ANTISLIME COATINGS PART III

ANTISLIME ORGANOMETALLIC POLYMERS OF OPTICAL QUALITY

by
J. A. Montemarano and E. J. Dyckman

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MATERIALS DEPARTMENT
Annapolis
RESEARCH AND DEVELOPMENT REPORT

Antislime Coatings, Part III,
Antislime Organometallic Polymers of Optical Quality

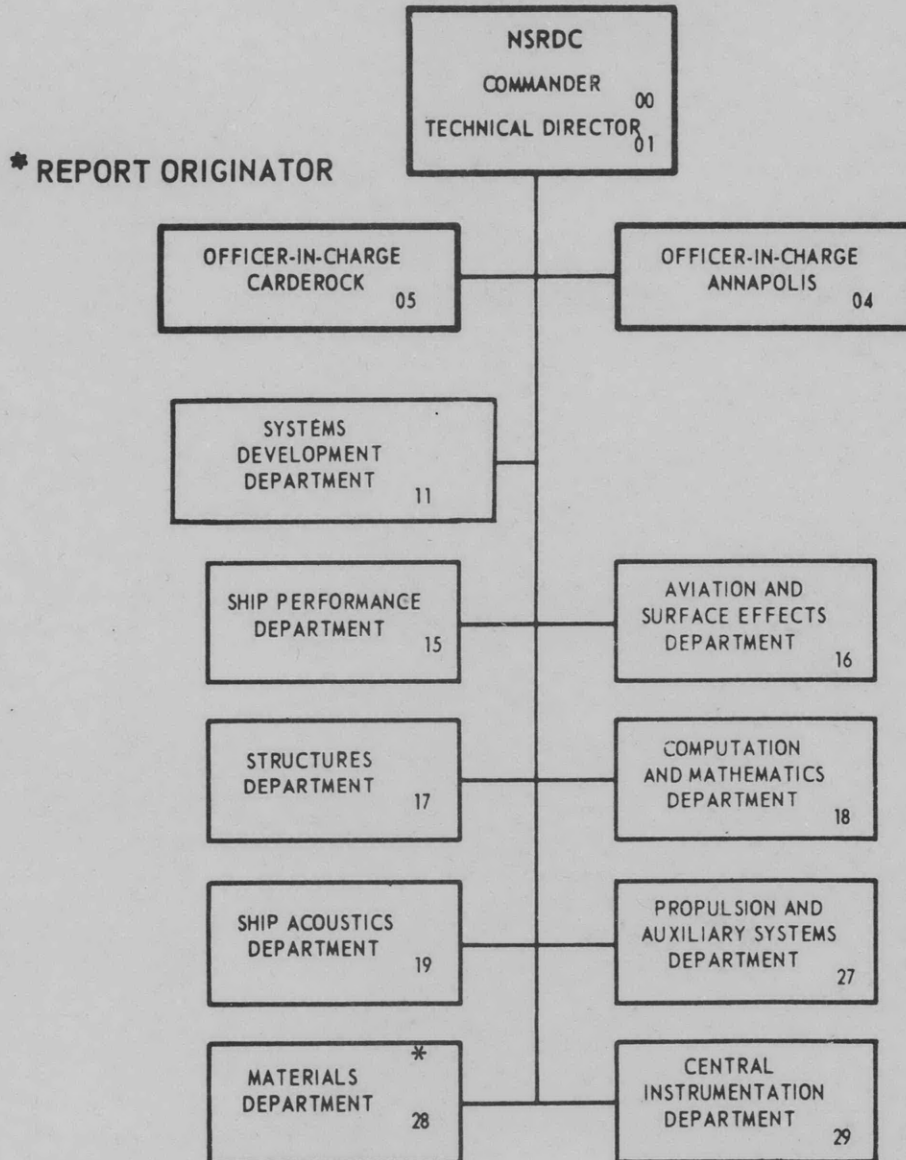
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PART III

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ABSTRACT

Organometallic polymers of optical quality have been prepared by various synthetic methods. The antisliming and antifouling performance of these polymers has been determined by clinical antibacterial assay and tropical field exposure trials. For the first time organometallic monomers have been copolymerized with fluoro-monomers in an attempt to couple the antisliming and nonwetting characteristics of each into an optical material for underwater use.

ADMINISTRATIVE INFORMATION

This work is authorized under Program Element 62756N, Task Area ZF61412001, Task 09400, Work Unit 1-2853-105 as described in the 1 July 1972 Program Summary.

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INTRODUCTION

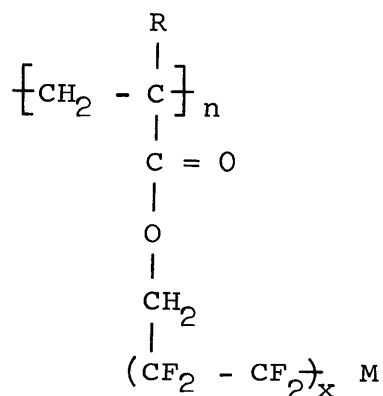
Detailed studies of the settlement of macrofoulants and the preconditioning of submerged surfaces by slimes¹ have indicated that the effectiveness of an antifouling system depends partly on its ability to prevent slime formation. Sliming of submerged optical surfaces, in addition to being a precursor for macrofouling, also distorts viewed and/or photographed images. The mitigation of slime from periscope headwindows and other underwater optical devices is a problem under extensive Navy investigation. To date, slime is removed from periscope headwindows manually, although experimental devices such as mechanical scrubbers, ultra-violet illuminators, chlorine gas generators, piezoelectric vibrators, and water repellent coatings are being evaluated for their antisliming performance. None of these devices, however, have proved to be effective against slime formation for extensive periods of time.

The first report² of this series indicated that organometallics such as tributyltin oxide and tripropyltin oxide are effective biocidal agents against isolated sliming bacteria. The chemical incorporation of these agents onto an acrylic backbone was proposed as a novel, long-lived antislime coating. The selection of an acrylic resin for the backbone, such as a polymethacrylate, is desirable because of the transparency and rigidity of this acrylic.³ The preparation of monomers of organotin methacrylates and their polymerization has been described by Montermoso.⁴ The chemically bound organometallic moieties on such polymer backbones are expected to show a low rate of release due to the slow hydrolysis of the carbon-oxygen bond. Thus, the adaptation of organometallic polymers as slimicidal coatings would effectively provide submerged optical devices with long-lived sliming protection due to the chemical conservation of antislime agents.

¹Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

Surface wetting by water and oils adds to the distortion of images viewed through periscope headwindows. A solution to this problem currently under study suggests coating the headwindow with a silane or a fluorocompound. The nonwettability of various fluorochemicals was first investigated by Zisman who explained this unique characteristic in terms of surface chemistry.⁵ The nonwetting of fluorochemicals by other liquids is related to their very low surface energy. In order for a liquid to wet a surface it must possess a lower surface energy than that of the surface with which it is in contact. Generally, fluorochemicals have a low surface energy and, thus, very few liquids will spread on their surfaces.

Quartz periscope headwindows possess a high surface energy and are readily wetted by water and hydrocarbons. Reducing this surface energy may be accomplished by coating the headwindow with a fluoropolymer. Candidate nonwetting coatings include such resins as polyfluoroalkyl acrylates. The structure of these fluoropolymers can be written as follows:



where R is either a hydrogen (H) or an alkyl group (CH₃), M is either a CF₃ or a CF₂H group, x represents the number of CF₂-CF₂ groups in the side chain, and n indicates the number of repeating monomeric units. The composition, length, and orientation of the side chain will affect the wetting properties of the polyfluoroalkyl acrylates.⁶ For example, a polyfluoroalkyl acrylate containing very short chain lengths, where x is 1 or 2, will exhibit a higher surface energy than a similar polyfluoroalkyl acrylate on which the side chains are composed of 7 or 8, CF₂ groups. Certain long-chained polyacrylates are transparent, water-white polymers which can be effectively coated or deposited on a quartz surface, thus producing a surface having the degree of nonwetting necessary for periscope headwindow use.

Ideally, a foul-free, nonwetttable surface would be free of visual distortions caused by sliming and poor drainage of water and oils. The copolymerization of an organotin monomer and a fluoroalkyl monomer would produce this antisliming, nonwetting headwindow coating. The biocidal activity displayed by the organometallic units would prevent growth of slime on the headwindow while the fluoromonomeric units of low surface energy would eliminate the spreading of water and oil on its surface. In addition to protection for periscope headwindows, the organometallic fluoropolymer promises antislime protection for deep submersible vehicle viewports, transparent observatories, and working craft with transparent hulls.

MATERIALS AND METHODS

Clear organometallic polymers were prepared by two general methods. The first method of preparation involved a condensation reaction between an organometallic oxide or hydroxide and an acrylic polymer. During this reaction, the organometallic moiety chemically attached to the carboxylic group of the polymer, producing water as a by-product. The water formed by this reaction was removed by azeotropic distillation. The organometallic polymers prepared in this manner along with pertinent experimental data are listed in table 1. The second method of preparation entailed homopolymerization and copolymerization of monomeric organometallic acrylates and fluoromonomers. (The commercial source or synthetic preparation of each monomer is listed in tables 2 and 3.) All monomers prior to polymerization were uninhibited either by vacuum distillation or by neutralization with a weak base. Solution and bulk polymerization techniques were used to synthesize the organometallic polymers as outlined in tables 2 and 3. In solution polymerization, the monomers were reacted with an initiator in a solvent under reflux until the polymerization was complete. In bulk polymerization³ the monomers, and an initiator (0.5% by weight) were reacted in a loosely capped jar for 8 minutes at 90° C.* The vessel was then cooled rapidly to room temperature and the prepolymer syrup which resulted was degassed by placing the container under vacuum.

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

TABLE 1
PREPARATION OF ORGANOMETALLIC POLYMERS
BY AZEOTROPIC DISTILLATION

Organometallic Polymer Synthesized		Reactants			
Polymer Letter	Polymer Name	Organometallic	Backbone Polymer	Molar Ratio of Organometallic to Backbone Polymer	Solvent
A	Poly (tributyltin methacrylate)	Tributyltin Oxide	Cross Linked Poly-methacrylic Acid (Rohm and Haas Aberlite IRC 50)	1:2	Toulene
B	Poly (trimethyltin methacrylate)	Trimethyltin Hydroxide	Cross Linked Poly-methacrylic Acid (Rohm and Haas Aberlite IRC 50)	1:1	Toulene
C	Poly (tributyltin methacrylate)	Tributyltin Oxide	Polymethacrylic Acid (Polysciences, Inc.)	1:2	Benzene
D	Poly (tripropyltin methacrylate)	Tripropyltin Oxide	Cross Linked Poly-methacrylic Acid (Rohm and Haas Aberlite IRC 50)	1:2	Toulene
E	Poly (tripropyltin methacrylate)	Tripropyltin Oxide	Polymethacrylic Acid (Polysciences, Inc.)	1:2	Benzene

The container was then flushed with nitrogen, tightly capped, and placed in an oven at 40° C for 18 hours. After this curing period, the temperature of the oven was raised slowly to 97° C and held at this temperature for 30 minutes. The curing cycle was then completed and the oven was allowed to reach room temperature before the curing vessel was removed.

Organometallic polymers were evaluated for their antifouling capability in field and laboratory tests. In preparation for field tests, polymers prepared by solution polymerization and azeotropic distillation were cast from solution on 12- x 10- x 1/4-inch plexiglass panels. Evacuation of the solvent from the coated surface was accomplished by keeping the panels in a vacuum chamber at 0.5 mm Hg at 180° C for 1 week. Those polymers (A, B, D, G) which were powders and could not be coated directly on test panels were incorporated into an acrylic and/or vinyl resin system which could be coated on the panels.

TABLE 2 - PREPARATION OF ORGANOMETALLIC POLYMERS
BY SOLUTION POLYMERIZATION
(SOLVENT-BENZENE)

Organometallic Polymer Synthesized		Reactants			
Polymer Letter	Polymer Name	Organometallic Monomer*	Comonomer*	Molar Ratio of Organometallic Monomer to Comonomer	Initiator
F	Poly (tributyltin methacrylate/methyl methacrylate)	Tributyltin Methacrylate ⁴	Methyl Methacrylate	1:4	Benzoyl Peroxide ⁽¹⁾
G	Poly (triphenyllead methacrylate/methyl methacrylate)	Triphenyllead Methacrylate ⁷	Methyl Methacrylate	1:6	Methyl Ethyl Ketone Peroxide ⁽²⁾
H	Poly (tributyltin methacrylate)	Tributyltin Methacrylate ⁴	-	-	Methyl Ethyl Ketone Peroxide ⁽³⁾
I	Poly (tributyltin methacrylate/methyl methacrylate)	Tributyltin Methacrylate ⁴	Methyl Methacrylate	2:1	Benzoyl Peroxide ⁽³⁾
J	Poly (tributyltin methacrylate/methyl methacrylate)	Tributyltin Methacrylate ⁴	Methyl Methacrylate	1:1	Benzoyl Peroxide ⁽³⁾
K	Poly (tributyltin methacrylate/methyl methacrylate)	Tributyltin Methacrylate ⁴	Methyl Methacrylate	1:1.5	Benzoyl Peroxide ⁽³⁾
L	Poly (tributyltin methacrylate/1H, 1H, 7H-dodecafluoroheptyl acrylate)	Tributyltin Methacrylate ⁴	1H, 1H, 7H-dodecafluoroheptyl acrylate	1:1	Benzoyl Peroxide ⁽³⁾

*Preparation of each monomer found in reference following that monomer

- (1) Benzoyl Peroxide was used 0.5% by weight in this reaction
- (2) Methyl ethyl ketone peroxide was used 3% by weight in this reaction
- (3) The catalyst was used 1% by weight in this reaction

These panels were then positioned vertically in racks and submerged at a depth of 4 feet upon arrival at NAVSHIPYD PEARL. The panels were photographed monthly at this exposure site and the antifouling performance of the organometallic polymers was recorded.

TABLE 3 - ORGANOMETALLIC POLYMERS PREPARED
BY BULK POLYMERIZATION

Organometallic Polymers Synthesized		Reactants	
Polymer Letter	Polymer Name	Monomers	Ratio of Monomers (A:B)
M	Poly (tributyltin methacrylate/methyl methacrylate)	(A) Tributyltin Methacrylate, ⁴ (B) Methyl Methacrylate	1:1
N	Poly (1H, 1H, 7H-dodecafluoroheptyl acrylate)	(A) 1H, 1H, 7H-dodecafluoroheptyl Acrylate (PCR)	-
O	Poly (1H, 1H, 7H,-dodecafluoroheptyl methacrylate)	(A) 1H, 1H, 7H-dodecafluoroheptyl Methacrylate ^{8,9}	-
P	Poly (1H, 1H, 7H,-dodecafluoroheptyl methacrylate/methyl methacrylate)	(A) 1H, 1H, 7H-dodecafluoroheptyl Methacrylate; ^{8,9} (B) Methyl Methacrylate	1:1
Q	Poly (tributyltin methacrylate/methyl methacrylate)	(A) Tributyltin Methacrylate; ⁴ (B) Methyl Methacrylate	1:2
R	Poly (tributyltin methacrylate)	(A) Tributyltin Methacrylate ⁴	-

In laboratory studies, organometallic polymers were tested for their toxicity against sliming bacteria. The isolation and culturing of these bacteria has been previously described. Poly (tributyltin methacrylate) (H) and poly (tributyltin methacrylate/methyl methacrylate)(J) were selected as trial polymers. A dilution series of 100, 10, and 1 ppm was prepared by dissolving each polymer in dichloromethane. A similar dilution series was prepared for tributyltin oxide as a control since its relative toxicity to these organisms was known.²

A set of 90 mm diameter, marine agar, culture plates were then streaked with a heavy inoculum of sliming bacteria, X2 and X19. After a 3-hour incubation period, two sterile, 8 mm diameter, stainless steel penicylinders were placed in each half of the inoculated plate equidistant from the edge and center of the plate. The prepared solutions of the polymers, the control, and the undiluted solvent were pipetted into individual sets of penicylinders. Each dilution was tested at least twice to establish its relative toxicity. After 48 hours of incubation at 19° C, the plates were examined and the diameter of the "ring of inhibition" (area of no bacterial growth) surrounding each penicylinder was measured.

RESULTS AND DISCUSSION

Azeotropic distillation and solution polymerization techniques produced film forming and granulated organometallic polymers. These polymers could either be coated directly on test surfaces or incorporated into a supporting resin which could then be utilized as a coating. Bulk polymerization of organometallic, acrylic, and fluorinated monomers yielded transparent castings 1/8- to 1/2-inch thick indicating that this polymerization method could produce thick cross sectional organometallic polymers for structural applications. Of the organometallic polymers prepared by the above three methods, 14 were transparent (figure 1), and thus, suitable for optical uses (table 4). In most cases, organometallic polyacrylates containing tributyltin or tripropyltin pendant groups produced coatings of optimum transparency. Slight yellow coloration in some of these products was attributed to impurities in the starting materials. Incorporation of trimethyltin and triphenyllead moieties onto the acrylic backbone notably decreased the transparency of those organometallic polymers. The hardness of the organometallic polyacrylates was improved by utilizing methyl methacrylate as a comonomer in the polymerizations.

The antifouling performance of the organometallic polymers was evaluated during tropical field exposure to marine organisms at NAVSHIPYD PEARL. Exposed panels were rated for their antifouling performance on the percentage of surface covered by foulants, such as slime, tubeworms, barnacles, and marine borers.

TABLE 4 - PHYSICAL CHARACTERISTICS OF
SYNTHESIZED ORGANOMETALLIC POLYMERS

Polymer Letter	Organometallic Polymers	Physical Appearance	% Metal Content* in Polymer		Antifouling Performance	
			% Metal	Metal	Months Exposed	% Antifouling Performance
A	Poly (tributyltin methacrylate)	White Powder	27.77	Sn	4	100
B	Poly (trimethyltin methacrylate)	Cream Granules	8.74	Sn	4	0
C	Poly (tributyltin methacrylate)	Transparent, Colorless Film	28.22	Sn	5	100
D	Poly (tripropyltin methacrylate)	White Powder	31.71	Sn	4	60
E	Poly (tripropyltin methacrylate)	Transparent, Colorless Film	34.19	Sn	4	100
F	Poly (tributyltin methacrylate/methyl methacrylate)	Transparent, Colorless Film	16.28	Sn	4	100
G	Poly (triphenyllead methacrylate/methyl methacrylate)	Tan Powder	24.89	Pb	1	20
H	Poly (tributyltin methacrylate)	Transparent, Colorless Film	29.05	Sn	1	100
I	Poly (tributyltin methacrylate/methyl methacrylate)	Transparent Colorless Film	25.39	Sn	2	100
J	Poly (tributyltin-methacrylate/methyl methacrylate)	Transparent, Colorless Film	21.03	Sn	1	100
K	Poly (tributyltin methacrylate/methyl methacrylate)	Transparent Colorless Film	-	-	2	100
L	Poly (tributyltin methacrylate/1H, 1H, 7H-dodecafluoroheptyl acrylate)	Transparent, Colorless Film	15.50 29.77	Sn F	2	100

*Samples Analyzed at Galbraith Laboratories by Atomic Absorbtion Spectrophotometry

After several months of exposure, certain of the organometallic polymers showed 100% antifouling performance as illustrated in table 4. The antifouling performance exhibited by a polymer depended on its organometallic moiety. Those organometallic polymers containing organometallic groups of 9 or 12 carbon atoms (the tripropyltin and the tributyltin groups) proved to be the most effective antifoulants.¹⁰

The organometallic polymers (H, J) tested proved to be effective antislime agents against isolated sliming bacteria X2 and X19 (figures 2 and 3). The sliming bacteria were shown to be as susceptible to 1 ppm solutions of these organometallic polymers as they were to 1 ppm solutions of tributyltin oxide, the control.

CONCLUSIONS

Organometallic polymers are effective as combatants against microorganisms involved in the sliming of underwater surfaces.

The facile synthesis and antifouling performance of organometallic polymers indicate the usefulness of these transparent materials as slimicidal underwater optics and optical coatings.

FUTURE WORK

Additional organometallic polymers will be synthesized with structural underwater applications in mind, such as the fabrication of high buoyancy foams, glass reinforced plastics, buoys and cable sheathing. Future work on the development of organotin fluoropolymers will be sponsored under the cognizance of NAVSHIPS as a part of Project S3643, Task 12372.

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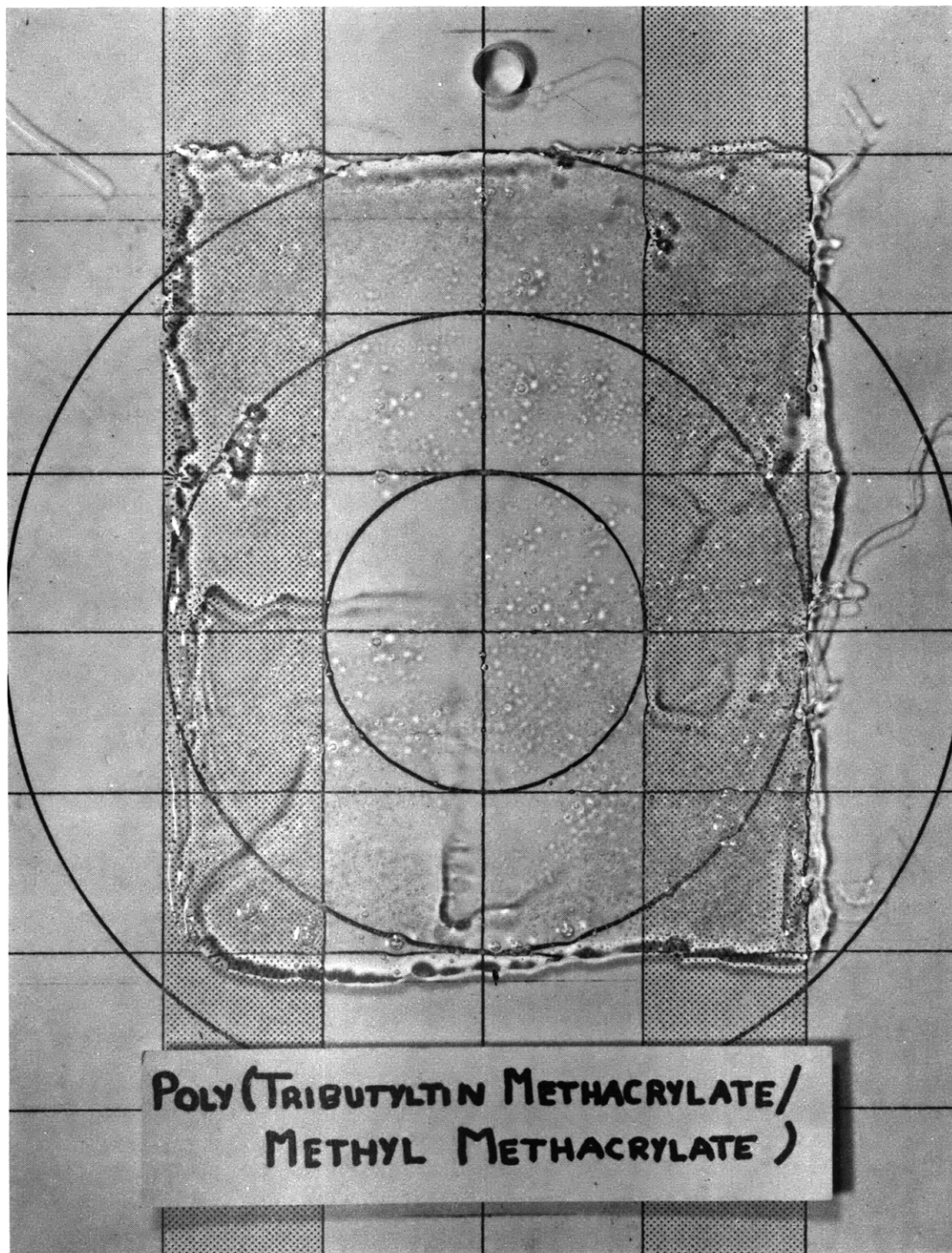


Figure 1
Typical, Transparent, Film Forming,
Organometallic Polymer

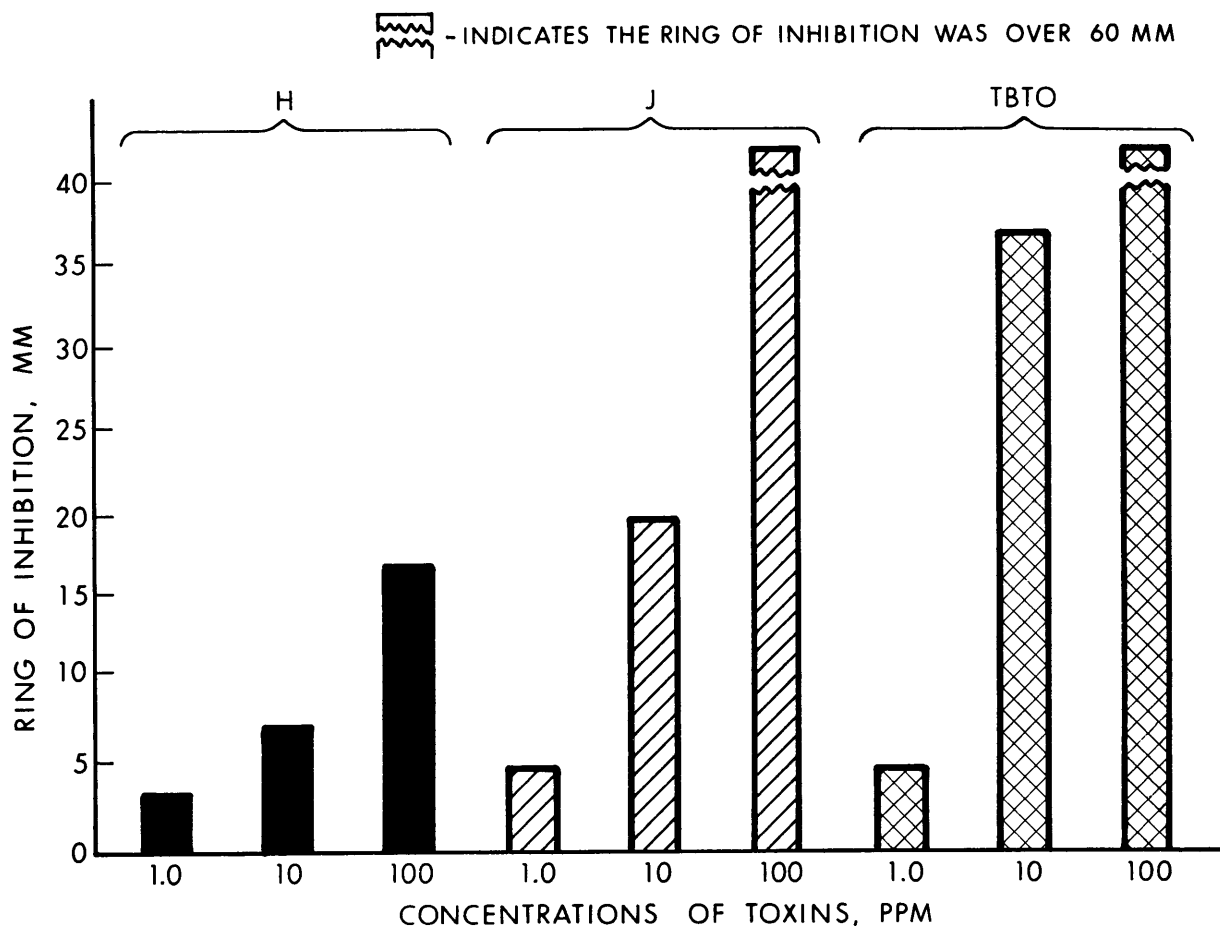


Figure 2 - Toxicity of H,
 Poly (tributyltin methacrylate), J, Poly
 (tributyltin methacrylate/methyl methacrylate) and
 Tributyltin Oxide to Slime Bacteria, X2

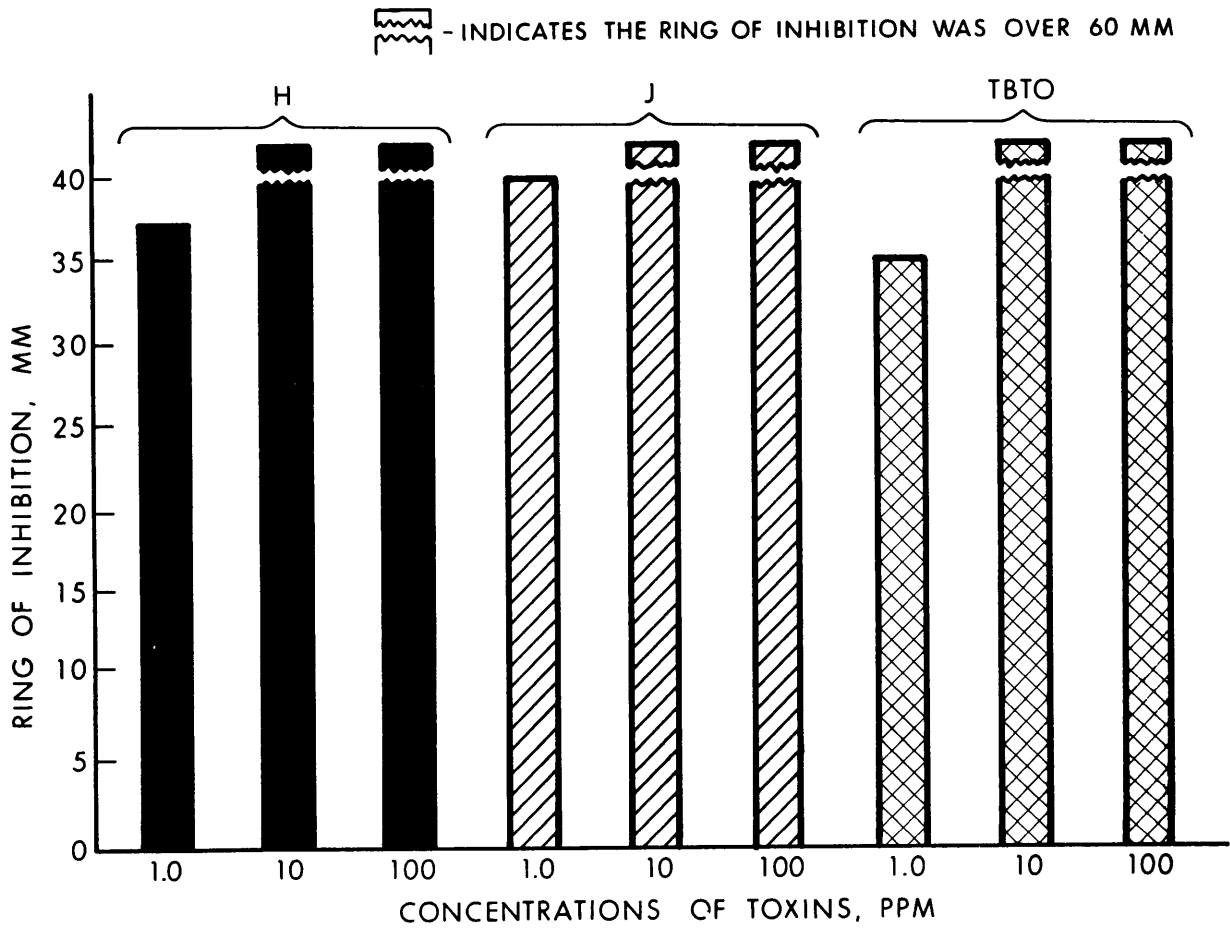


Figure 3 - Toxicity of H,
 Poly (tributyltin methacrylate), J, Poly
 (tributyltin methacrylate/methyl methacrylate and
 Tributyltin Oxide to Sliming Bacteria, X19

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