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654,044, July 5, 1967, and a continuation-
in-part of 650,259, June 30, 1967, now
abandoned, and a continuation-in-part of
567,856, July 26, 1966, now Patent No.
3,520,949, dated July 21, 1970.

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 106/15 (AF); 424/81; 117/161, (P), (N); 117/148,
 130, 138.8 (A), 124 (C), 123 (D); 106/15;
 260/29.6

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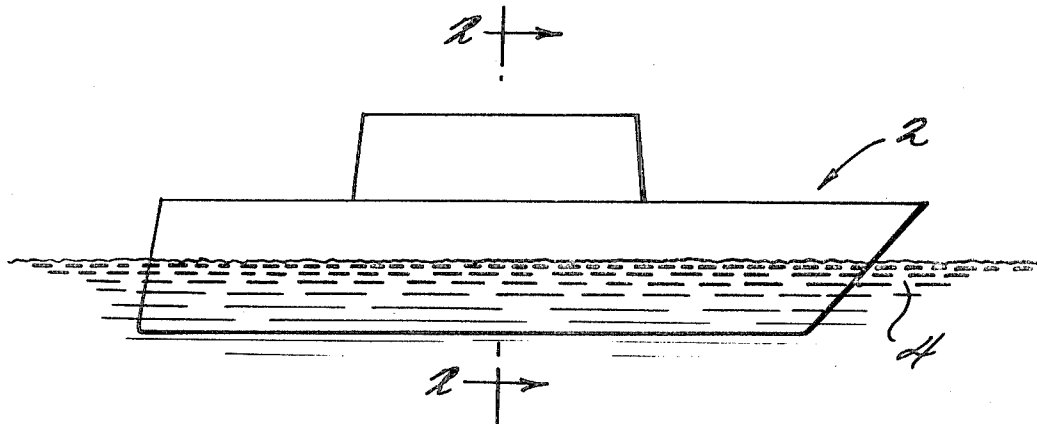
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[54] **MARINE STRUCTURE COATED WITH AN**
ACRYLIC INSOLUBLE WATER-SWELLABLE
POLYMER
 22 Claims, 2 Drawing Figs.

[52] U.S. Cl..... **114/67R,**
 106/15, 117/123, 117/124, 117/130, 117/138.8,
 117/148, 260/41R

[51] Int. Cl..... **C03c 17/00**

ABSTRACT: Hydrophilic acrylic resins are applied to the underwater portion of boats to reduce the drag on moving the boats through water. The resins are useful in antifouling compositions.



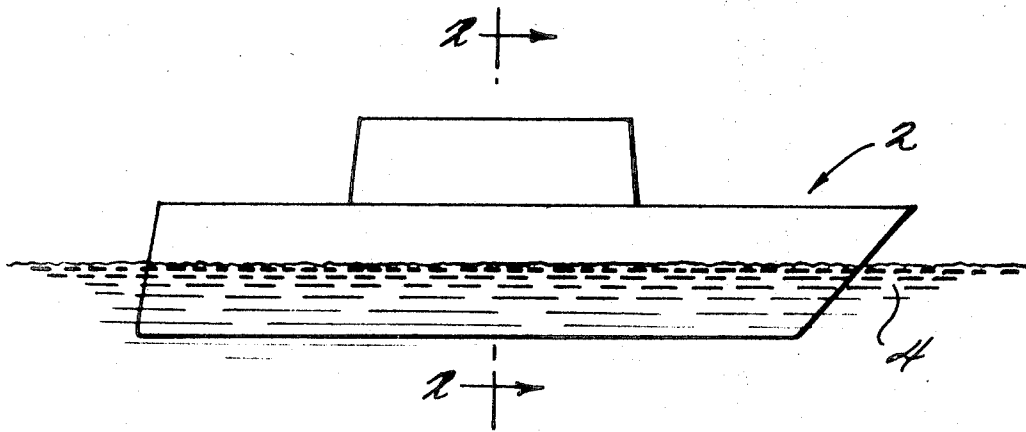


Fig. 1

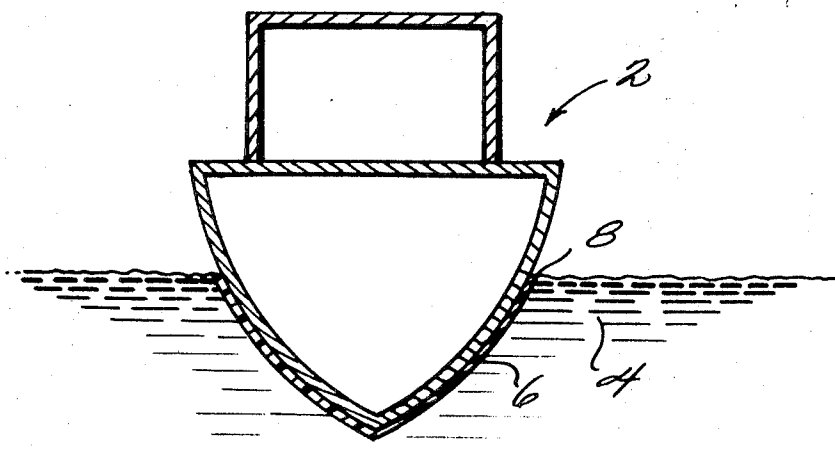


Fig. 2

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MARINE STRUCTURE COATED WITH AN ACRYLIC
INSOLUBLE WATER-SWELLABLE POLYMER

The present application is a continuation-in-part of application Ser. No. 654,044 filed Jul. 5, 1967 and application Ser. No. 650,259, filed Jun. 30, 1967 now abandoned and application Ser. No. 567,856 filed Jul. 26, 1966 now U.S. Pat. No. 3,520,949 issued Jul. 21, 1970.

The present invention relates to the use of water-insoluble hydrophilic acrylic resins.

It is an object of the present invention to reduce the resistance developed on moving watercraft through water.

Another object is to develop novel antifoulant compositions.

A further object is to provide watercraft and underwater static structures with an improved antifoulant coating.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiment of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by the use of water-insoluble hydrophilic acrylate and methacrylate polymers (hydrophilic acrylic resins) as coatings at least for the underwater portion of watercraft and underwater static structures.

The term marine coating is used in the present application and claims to cover both coatings for watercraft and underwater static structures. The term watercraft includes movable boats of all kinds, including but not limited to sailboats, yachts, inboard and outboard motor boats, rowboats, motor launches, canoes, kayaks, water skis, surfboards, ocean liners, tugboats, tankers and other cargo ships, submarines both of the atomic and conventional varieties, aircraft carriers, destroyers, etc. Underwater static structures include but are not limited to wharves, piers, permanently moored watercraft, pilings, bridge substructures, etc. The underwater surface can be made of wood, metal, plastic, fiberglass, concrete or other material.

The antifoulant compositions are useful as marine coatings to render the structure (moving or static) resistant to fouling by marine organisms such as barnacles, algae, slime, acorn-shells (Balanidae), goose mussels (Lepadoids), tube-worms, sea moss, oysters, brozoans, tunicates, etc.

It is critical that the hydrophilic acrylic resins be water insoluble since otherwise they cannot be permanently applied to the underwater surface. The hydrophilic acrylic resin should be capable of absorbing at least 20 percent of its weight of water and preferably does not absorb more than about 120 percent of its weight of water. It has been found that linear polymers which are usually alcohol soluble are preferable although cross-linked polymers can also be used providing they are applied while still in a workable condition. These coatings effectively reduce the "drag" or resistance developed on moving the coated surface through water.

If it is desired to employ the coating solely to effect friction reduction on racing or pleasure craft, for example, which do not remain static in water for extended periods, it is not necessary to incorporate an antifouling agent.

While not being bound by any theory it is believed that the mechanism of friction reduction is twofold. The coating absorbs a substantial percentage of water and the water-swollen coating exhibits a low contact angle with the water. In addition, the swollen coatings are soft, (particularly if a linear polymer is employed) and the softness can provide a hydrodynamic damping effect and reduce turbulence of the flow.

Preferably the hydrophilic monomer employed is a hydroxy lower alkyl acrylate or methacrylate or hydroxy lower alkoxy lower alkyl acrylate or methacrylate, e.g. 2-hydroxyethyl

acrylate, 2-hydroxyethyl methacrylate, diethylene glycol monoacrylate, diethylene glycol monomethacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, dipropylene glycol monomethacrylate and dipropylene glycol monoacrylate. The most preferred monomers are the hydroxyalkyl acrylates and methacrylates, particularly 2-hydroxyethyl methacrylate.

There can also be employed polymers of acrylamide, methacrylamide, N-alkyl substituted acrylamide and methacrylamide such as N-propylacrylamide, N-isopropyl acrylamide, N-isopropyl methacrylamide, N-propyl methacrylamide, N-butyl acrylamide, N-methyl acrylamide and N-methyl methacrylamide, diacetone acrylamide, N-(2-hydroxyethyl) acrylamide and N-(2-hydroxyethyl) methacrylamide.

Likewise, there can be employed copolymers of these monomers with each other or with other copolymerizable monomers. In fact, if the hydrophilic monomer gives a product which is water soluble, e.g. polyacrylamide, it is necessary to employ a copolymerizable monomer to render it only water swellable rather than water soluble. The copolymerizable monomer can be used in an amount of 0.05 to 50 percent. Preferably, comonomers include methyl acrylate, ethyl acrylate, isopropyl acrylate, propyl acrylate, butyl acrylate, sec. butyl acrylate, pentyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, sec. butyl methacrylate, pentyl methacrylate, lower alkoxyethyl acrylates and methacrylates, e.g. methoxyethyl acrylate, methoxyethyl methacrylate, ethoxyethyl acrylate and ethoxyethyl methacrylate, triethylene glycol acrylate, triethylene glycol methacrylate, glycerol monoacrylate and glycerol monomethacrylate.

There can also be used unsaturated amines, *p*-aminostyrene, *o*-aminostyrene, 2-amino-4-vinyltoluene, alkylamino alkyl acrylates and methacrylates, e.g. diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, *t*-butylaminoethyl acrylate, *t*-butylaminoethyl methacrylate, piperidinoethyl acrylate, piperidinoethyl methacrylate, morpholinoethyl acrylate, morpholinoethyl methacrylate, 2-vinylpyridine, 3-vinyl pyridine, 4-vinyl pyridine, 2-ethyl-5-vinylpyridine, dimethylamino propyl acrylate, dimethylamino propyl methacrylate, dipropylaminoethyl acrylate, dipropylaminoethyl methacrylate, di-*n*-butylaminoethyl acrylate, di-*n*-butyl aminoethyl methacrylate, di-sec. butylaminoethyl acrylate, di-sec. methacrylate, dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl ether, diethyl-aminoethyl vinyl sulfide, aminoethyl vinyl ether, aminoethyl vinyl sulfide, monomethylaminoethyl vinyl sulfide, monomethylaminoethyl vinyl ether, N-(gamma-monomethylamino) propyl acrylamide, N-(beta-monomethylamino) ethyl acrylamide, N-(beta-monomethylamino) ethyl methacrylamide, 10-aminodecyl vinyl ether, 8-aminooctyl vinyl ether, 5-aminopentyl vinyl ether, 3-aminopropyl vinyl ether, 4-aminobutyl vinyl ether, 2-aminobutyl vinyl ether, monoethylaminoethyl methacrylate, N-(3,5,5-trimethylhexyl) aminoethyl vinyl ether, N-cyclohexylaminoethyl vinyl ether, 2-(1,1,3,3-tetramethylbutylamino) ethyl methacrylate, N-*t*-butylaminoethyl vinyl ether, N-methylamino-ethyl vinyl ether, N2-ethylhexylaminoethyl vinyl ether, N-*t*-butylaminoethyl vinyl ether, N-*t*-octylaminoethyl vinyl ether, 2-pyrrolidinoethyl acrylate, 2-pyrrolidinoethyl methacrylate, 3-(dimethylaminoethyl)-2-hydroxypropyl acrylate, 3-(dimethylaminoethyl)-2-hydroxypropyl methacrylate, 2-aminoethyl acrylate, 2-aminoethyl methacrylate. The presently preferred amino compounds are alkylaminoethyl acrylates and methacrylates, most preferably *t*-butyl aminoethyl methacrylate.

While linear polymers (including both homo- and copolymers) are preferred when the hydrophilic resins are

used only to reduce the resistance on moving a coated watercraft surface through water there can also be employed cross-linked hydrophilic copolymers. Such cross-linked copolymers are frequently advantageously employed when antifouling agents are included in the composition to insure more permanent adherence to the underwater structure.

Preferably, the cross-linking agent is present in an amount of 0.1 to 2.5 percent, most preferably not over 2.0 percent, although from 0.05 to 15 percent, or even 20 percent, of cross-linking agents can be used. Of course, care should be taken that cross-linking agents are not used in an amount which renders the product incapable of absorbing at least 20 percent of water.

Typical examples of cross-linking agents include ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,2-butylene dimethacrylate, 1,3-butylene dimethacrylate, 1,4-butylene dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, diethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, divinyl benzene, divinyl toluene, diallyl tartrate, allyl pyruvate, allyl maleate, divinyl tartrate, triallyl malamine, N,N'-methylene bis-acrylamide, glycerine trimethacrylate, diallyl maleate, divinyl ether, diallyl monoethylene glycol citrate, ethylene glycol vinyl allyl citrate, allyl vinyl maleate, diallyl itaconate, ethylene glycol diester of itaconic acid, divinyl sulfone, hexahydro-1,3,5-triacryltriazine, triallyl phosphite, diallyl ester of benzene phosphonic acid, polyester of maleic anhydride with triethylene glycol, polyallyl glucose, e.g. triallyl glucose, polyallyl sucrose, e.g. pentaallyl sucrose, sucrose diacrylate, glucose dimethacrylate, pentaerythritol tetraacrylate, sorbitol dimethacrylate, diallyl aconitate, divinyl citraconate, diallyl fumarate.

There can be included ethylenically unsaturated acids or salts thereof such as acrylic acid, cinnamic acid, crotonic acid, methacrylic acid, itaconic acid, aconitic acid, maleic acid, fumaric acid, mesaconic acid and citraconic acid. Also, as previously indicated there can be used partial esters such as mono 2-hydroxypropyl itaconate, mono 2-hydroxyethyl itaconate, mono 2-hydroxyethyl citraconate, mono 2-hydroxypropyl aconitate, mono 2-hydroxyethyl maleate, mono-2-hydroxypropyl fumarate, monomethyl itaconate, monoethyl itaconate, mono Methyl Cellosolve ester of itaconic acid (Methyl Cellosolve is the monomethyl ether of diethylene glycol), Mono Methyl Cellosolve ester of maleic acid.

The polymers can be prepared as casting syrups, e.g. as prepared in applicants' parent application, as aqueous dispersions, by aqueous suspension polymerization or as solutions in organic solvents such as ethyl alcohol, methyl alcohol, propyl alcohol, isopropyl alcohol, formamide, dimethyl sulfoxide or other appropriate solvent.

Polymerization can be carried out at 20° to 150° C., frequently 35° or 40° C. to 90° C. and can be completed after applying as a marine coating. The polymerization can be carried out employing a free radical catalyst in the range of 0.05 to 1 percent of the polymerizable monomers. Typical catalysts include *t*-butyl peroxoate, benzoyl peroxide, isopropyl percarbonate, 2, 4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide and dicumyl peroxide. Irradiation, e.g. by ultraviolet light or gamma rays, also can be employed to catalyze the polymerization.

In addition to the examples of polymerization set forth in the parent applications there can be employed polymers prepared, for example, as in examples A—G below. Unless otherwise indicated in the specification and claims all parts and percentages are by weight.

EXAMPLE A

One thousand grams of silicone oil (polydimethyl siloxane, 100 grams of 2-hydroxyethyl methacrylate and 0.33 grams of

isopropyl percarbonate were charged to a flask equipped with an agitator and heating mantle. The flask was rapidly agitated at 100° C. under a nitrogen atmosphere. After 15 minutes the slurry was filtered not to isolate the polymer. The polymer powder was reslurried in b 300 ml. of xylene, filtered and dried. A 98 percent yield of 2 to 5-micron particle size alcohol soluble powder was obtained.

EXAMPLE B

Example A was repeated using xylene in place of the silicone oil and employing 300 grams of 2-hydroxyethyl methacrylate and the quantity of isopropyl percarbonate increased to 0.99 gram. An 85 percent yield of polymer beads was obtained.

EXAMPLE C

The procedure of example A was repeated replacing the 2-hydroxyethyl methacrylate by 100 grams of 2-hydroxypropyl methacrylate to produce a thermoplastic solvent soluble hydrophilic finely divided bead polymer.

EXAMPLE D

Eight hundred grams of ethylene glycol monomethyl ether, 180 grams of 2-hydroxyethyl methacrylate, 20 grams of acrylic acid and 2 grams of *t*-butyl peroxoate were charged into a flask. The solution was heated and stirred under a carbon dioxide atmosphere for 6 hours. The product of this example while thermoplastic and solvent soluble has the capability of curing to cross-linked solvent insoluble polymer by further heating, particularly if additional catalyst is added.

EXAMPLE E

A casting syrup was made from 100 parts of 2-hydroxyethyl acrylate, 0.2 parts of ethylene glycol dimethacrylate and 0.4 parts *t*-butyl peroxoate.

EXAMPLE F

Ten kilograms of 2-hydroxyethyl methacrylate, 150 grams of ethylene glycol dimethacrylate and 4.0 grams of *t*-butyl peroxoate were heated with stirring for 50 minutes at 95° C. to yield a syrup having a viscosity of 420 centipoises at 30° C. To this syrup was added 20 grams of ethylene glycol dimethacrylate and 20 grams of *t*-butyl peroxoate and the syrup stirred until a homogeneous solution was obtained.

Similar results were obtained when replacing the ethylene glycol dimethacrylate by divinyl benzene.

EXAMPLE G

Seventy-five liters of ethanol, 1 kilogram of *t*-butylaminoethyl methacrylate, 1.5 kilograms of N-isopropyl acrylamide and 22.5 kilograms of hydroxyethyl methacrylate (containing 0.3 percent of ethylene glycol dimethacrylate) together with 100 grams of *t*-butyl peroxoate were charged into a vessel and the solution heated at 85° C. for 7 hours to effect polymerization to a 90 percent conversion level.

There can be incorporated with the hydrophilic polymers of the invention to provide coatings to prevent fouling by marine organisms any of the conventional inorganic or organic antifoulants including cuprous oxide, copper powder, mercuric oxide, cuprous oxide-mercuric oxide (e.g. 3:1 mercurous chloride), organotin compounds including triphenyltin chloride, triphenyltin bromide, tri *p*-cresyltin chloride, triethyltin chloride, tributyltin chloride, phenyl diethyltin fluoride, tri (*p*-chlorophenyltin) chloride, tri (*m*-chlorophenyltin) chloride, dibutyl ethyltin bromide, dibutyltin bromide, tricyclohexyltin chloride, triethyltin stearate, tributyltin stearate, triethyltin fluoride, tributyltin fluoride, diphenyl ethyltin, chloride, diphenyl ethyltin fluoride, triphenyltin hydroxide, triphenyltin thiocyanate, triphenyltin trichloroacetate, tributyltin acetate, tributyltin neodecanoate, tributyltin neopentanoate, trioctyltin

neodecanoate, tributyltin oxide, trioctyltin oxide, triphenyltin fluoride, tripropyltin oleate, tripropyltin neodecanoate, tributyltin laurate, tributyltin octanoate, tributyltin dimethyl carbamate, tributyltin resinate, tributyltin chromate, amyldiethyltin neodecanoate, tributyltin naphthenate tributyltin isooctylmercaptoacetate, bis-(tributyltin) oxalate, bis-(tributyltin) malonate, bis-(tributyltin) adipate, bis-(tributyltin) carbonate; organo lead compounds, e.g. triphenyl lead acetate, triphenyl lead stearate, triphenyl lead neodecanoate, triphenyl lead oleate, triphenyl lead chloride, triphenyl lead laurate, triethyl lead oleate, triethyl lead acetate, triethyl lead stearate, trimethyl lead stearate, triphenyl lead bromide, triphenyl lead fluoride, organic compounds including 10,10'-oxybisphenoxazine (SA-546), 1, 2, 3-trichloro-4,6-dinitrobenzene, hexachlorophene, dichlorodiphenyl trichloroethane (DDT), phenol mercuric acetate, tetrachloroisophthalonitrile, bis-(*n*-propylsulfonyl) ethylene, etc.

The quantity of antifouling agent required in the coating as would be expected varies with the particular agent used and the severity of fouling tendency encountered in the particular service to which the coated vessel or static structure is to be used. In general, the amount of antifouling agent employed will range from 2 to 50 percent of the resin, although as little as 0.1 percent of antifoulant can be used based on the resin.

Of course, there can be included in the formulations conventional pigments and fillers such as titanium dioxide, red lead, bone black, red iron oxide, talc, aluminum silicate, fullers earth, pumice, zinc oxide, calcium carbonate, etc.

The coatings of the present invention can be applied to the surfaces to be subjected to underwater conditions from solution in organic solvents or from aqueous dispersions. Suitable solvents include lower aliphatic alcohols such as methanol, ethanol, propanol and isopropanol or mixtures of these solvents with higher boiling alcohols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diacetone alcohol, *n*-butanol, sec. butanol, isobutanol and mixtures of these solvents with water.

The coatings of the present invention generally exhibit adequate adhesion to marine surfaces protected by corrosion resistant finishes such as epoxy or vinyl-based paints, to previously applied antifouling finishes and to polyester-fiberglass laminates. Typical of such finishes are those shown in Sparmann U.S. Pat. No. 2,970,923, Scott U.S. Pat. No. 3,214,279 and Robins U.S. Pat. No. 3,236,793.

The thickness of the coating applied will vary with the particular formulation employed and the method of application. It can be from 0.1 mil to 250 mils or more in thickness. Usually it will be between 0.3 mil, and 5 mils. The coatings can be applied to the marine surface, e.g. boat bottom or hull or wharf piling by any conventional procedure such as brushing, dipping, spraying, roller coating etc.

Coating applied at boat yards, marinas or similar locations will normally be placed in water soon after drying. These coatings if made from linear, alcohol soluble polymers will remain alcohol soluble. However, as pointed out supra it is also possible to provide cured or cross-linked coatings which exhibit improved mechanical durability. There can be used the peroxide catalysts referred to supra alone or as part of a two-component catalyst system which is mixed into the coating solution immediately prior to application. Alternatively, the coating can be cured by incorporating a free radical initiator and heating the coated surface after drying.

Two-component catalyst systems for effecting cure at ambient conditions, e.g. 20° C., include peroxides of the type referred to supra together with such amine accelerators as *N,N*-dimethylaminoethyl acetate, *N,N*-dimethyl aniline, *N,N*-dimethyl aminoethanol, *N,N*-dimethyl toluidine. The accelerator can be used in an amount of 0.05 to 1 part per part of peroxide, e.g. a mixture of 89 percent benzoyl peroxide and 11 percent dimethylaniline can be employed.

The invention will be understood best in connection with the drawings wherein:

FIG. 1 shows a boat having a coating according to the invention; and

FIG. 2 is a sectional view along the line 2-2 of FIG. 1.

Referring more specifically to the drawings, the boat 2 in water 4 has a coating 6 of hydroxyethyl methacrylate polymer below the water line 8. If desired, the entire boat can be coated with the polymer. The thickness of the coating 6 is greatly exaggerated for illustrative purposes.

EXAMPLE 1

2-hydroxyethyl methacrylate (50 parts) and TiO₂ (30 parts) are ground in a pebble mill to a fine powder (Hegeman 7-8). Additional 2-hydroxyethyl methacrylate (50 parts) is added along with ethylene glycol dimethacrylate (0.2 part), cobalt naphthenate a conventional metallic paint dryer or catalyst (0.1 part) and *t*-butyl peroctoate (0.4 part). The resulting viscous syrup is painted onto a wooden boat hull and cured at 20° to 35° C. The resulting protective marine coating is characterized by its ability to discourage barnacle and algae growth and corrosion on prolonged underwater exposure. Additionally, it reduces the drag on moving the coated hull through water.

EXAMPLE 2

The procedure of example 1 is repeated with the modification that the coating syrup is cast onto a steel hull and cured at 100° C. in the absence of cobalt naphthenate. The drag on moving the coated hull through water was reduced compared to an uncoated hull.

EXAMPLE 3

The procedure of example 1 is repeated employing an isomeric mixture of hydroxy isopropyl methacrylate isomer in place of the hydroxyethyl methacrylate.

EXAMPLE 4

To a glass-lined reactor was charged 800 lbs. of ethanol, 200 lbs. of hydroxyethyl methacrylate and 0.5 lb. of *t*-butyl peroctoate. The reactor was flushed with nitrogen and heated to 80° C. over a period of 1 hour. The reactor was stirred at 80° C. for 7 hours, wherein 90 percent conversion of hydroxyethyl methacrylate to polymer was attained.

The resulting solution, containing 18 percent polymer by weight was used for the formulation of coatings for sailboats and motorboats below the waterline. The boats were made of wood, metal and fiberglass (i.e. polyester impregnated fiberglass).

EXAMPLE 5

Example 4 was repeated using 20 lbs. of methyl methacrylate and 180 lbs. of hydroxyethyl methacrylate as the monomer charge. A conversion of 95 percent was attained in 7 hours. The resulting solution was used for the formulation of marine coatings in a similar fashion to example 4.

EXAMPLE 6

Example 4 was repeated using 80 lbs. of methyl methacrylate and 120 lbs. of hydroxyethyl methacrylate as the monomer charge. A conversion of 90 percent was attained in 6 hours. The resulting solution was used for the formulation of marine coatings in a similar fashion to example 4.

EXAMPLE 7

A 22-foot polyester fiberglass boat (Aqua Sport) equipped with a 100-horsepower outboard engine was operated at two different throttle settings between two buoys approximately 1 mile apart. Average times required to travel between buoys going in both directions were determined at each throttle setting. The boat was then removed from the water, the bottom was washed with fresh water and dried. The polymer solution of example 4 was applied with a roller to provide a dry coating thickness of 0.75 to 1.0 mil.

The boat was replaced in the water and the speed at the same throttle settings between the buoys was determined. The following results were obtained.

Throttle setting:	Speed, knots before coating	Speed, knots after coating
Low.....	10.5	12.0
Medium.....	17.2	19.8

The results show a 13 percent reduction in drag resistance at a speed of about 10 knots and a 15 percent reduction at the higher speed.

EXAMPLE 8

The "apparent viscosity" of water at 23° C. was measured using a Brookfield RVT Synchroelectric viscosimeter employing a 01 spindle at 100 r.p.m. The value obtained was 11.1 centipoises. The spindle was removed, dried, and was coated with the solution prepared in example 4 by dipping and allowing the spindle to drain and dry. The coating thickness was approximately 0.5 mil. The "apparent viscosity" of water at 23° C. was again measured at 100 r.p.m. using the coated spindle. A value of 10.7 centipoises was obtained. The peripheral speed of the 01 spindle at 100 r.p.m. is approximately 0.6 mile per hour. At this speed approximately 4 percent reduction in frictional resistance or drag was obtained.

EXAMPLE 9

A 9-foot polyester-fiberglass dinghy was towed behind a motor launch with a rope attached to a spring scale having a capacity of 10 kilograms. The dinghy was towed at 25 knots. An average force of 8 kilograms was noted on the scale. The dinghy was then removed from the water, rinsed with fresh water and dried. The dinghy was then brush coated with the polymer solution of example 4 to provide a 1.5 mil coating, after drying, the dinghy was again towed at 25 knots. An average force of 6.5 kilograms was recorded on the scale. Thus, at 25 knots approximately 18 percent reduction in drag resistance was obtained.

EXAMPLE 10

Using a high-shear mixer, 200 grams of triphenyl lead acetate and 50 grams of titanium dioxide were dispersed in 8 kilograms of the polymer solution prepared in example 4. To the dispersion was added 2 kilograms of sec-butyl alcohol. A 01 spindle of a Brookfield viscosimeter was coated with the dispersion by dipping and allowing to dry. An average coating thickness of 0.6 mil was obtained. The "apparent viscosity" of water was measured as in example 8. A value of 10.5 centipoises was obtained. The coating was removed from the spindle and the "apparent viscosity" was again determined. A value of 11.0 centipoises was obtained.

The coating composition prepared in example 10 was employed on sailing craft, both of the wood hull type and polyester-fiberglass laminate type to provide a fouling resistant drag-reducing coating.

EXAMPLE 11

Example 4 was repeated using a monomer charge of 40 lbs. of hydroxypropyl acrylate and 160 lbs. of hydroxyethyl methacrylate. A conversion of 85 percent was achieved after 7 hours. The procedure of example 8 was repeated using this solution. Similar results were obtained. The solution of example 11 was also coated on the bottom of a metal-bottomed motor launch to provide a drag-reducing coating.

EXAMPLE 12

The procedure of example 11 was repeated replacing the hydroxypropyl acrylate by 40 lbs. of acrylamide. Similar results were obtained.

EXAMPLE 13

To 500 grams of the coating dispersion of example 10 was added 2 grams of ethylene dimethacrylate (ethylene glycol dimethacrylate), 1 gram of benzoyl peroxide and 0.4 gram of N,N-dimethyl aniline. The coating was immediately applied to a polyester-fiberglass laminated boat hull surface. After drying and standing at 75° F. (about 24° C.) for 2 hours the coating merely swelled but did not dissolve in alcohol. The resulting coating was tougher when water swollen than the coating of example 10. It was also effective as a fouling-resistant drag-reducing coating for the boat bottom.

A number of antifouling experiments were carried out using the hydrophilic polymers of the present invention. After 6 months of testing on polyester resin panels the best results were obtained using triphenyl lead acetate as the active antifouling ingredient. The results were also superior to using the antifouling agent in formulations which did not include the hydrophilic polymer.

Most antifouling compositions now used on oceangoing vessels are based on the use of cuprous oxide pigment, a relatively inert material. A large proportion of the cuprous oxide is not effectively used because it is encapsulated in the resin and is unavailable unless the resin itself breaks down. A second disadvantage of cuprous oxide is that it can induce galvanic corrosion. In addition, because of its dark color, it is unsatisfactory as an antifouling ingredient for decorative finishes.

The U.S. Navy is, of course, interested in antifouling finishes. It would like to have a 2½ year minimum, but finds that cuprous oxide coatings last from 12—18 months. Another market for effective systems is on tankers and large freighters. The operators are constantly seeking ways to decrease fouling because even a small amount of extra drag on the hull makes an appreciable difference to the efficiency of the vessel, which has an important effect on the economics, particularly in tanker operations. In addition, there is a need for periodic removal from service for bottom cleaning.

During the past decade a number of organometallic and organic pesticides have been found to exhibit high activity against a broad spectrum of marine fouling organisms. Economic utilization of these chemical antifoulants in shipbottom formulations has not been successfully accomplished, however, primarily because of the encapsulation problem. The new antifoulants are all several time more potent than cuprous oxide, but their relatively high cost dictates that they be employed at a fraction of the normal concentration of the latter cuprous oxide. Continuous contact between toxicant particles in the paint film is not maintained at these relatively low concentrations, so that the toxicants are not even utilized as efficiently as cuprous oxide, which in turn is also partially inactivated by encapsulation. Modification of the paints with inert extender pigments or water-soluble resin constituents improves the efficiency of toxicant utilization, but degrades the physical integrity of the paint films to an intolerable degree. To date, the most successful comprise is represented by blends of organometallic antifoulants with cuprous oxide to obtain durability and high potency. However, such blends eliminate the two major benefits offered by organic and organometallic antifoulants: freedom from the galvanic corrosion hazard of cuprous oxide, and flexibility of decorative pigmentation.

The use of hydrophilic water insoluble polymers of the present invention reduces the problem of encapsulation of active antifoulants in impermeable resin systems due to the water-swellaible nature of the hydrophilic film. In other acrylic resins and in other types of resin systems, solid organic and organometallic antifoulants do not demonstrate any significant activity unless their concentration in the film exceeds a threshold of about 25 percent by weight of the resin. In the systems of the present invention activity at much lower concentrations is noticed indicating that the hydrophilic resin does not impermeably encapsulate the toxicant particles.

In the following examples, Hydron-S is hydroxyethyl methacrylate homopolymer. Hema is an abbreviation for hydroxyethyl methacrylate.

EXAMPLE 14

This series of experiments was designed as an attempt to determine whether or not one of a variety of toxicants showed any activity against marine organisms when incorporated into unmodified Hydron-S films. Accordingly, ethanol solutions of Hydron-S containing concentrations of 2-32 percent of the active ingredients were applied to panels and immersed at a Miami Beach test facility. Three toxicants of different chemical type were selected; hexachlorophene (G11), tetrachloroisophthalonitrile (DAC-2787) and triphenyl lead

TABLE 2.—SUMMARY OF BEHAVIOR REPORTS OF EXPERIMENTAL SURFACES
(Plates Immersed March 15—Hydron-S Brush Coatings Containing Triphenyl Lead Acetate)

Antifoulants	Code	Overall rating, percent				
		May	June	July	August	September
None	A	37	0	0	0	0
TPLA, 2%	3B	100	71	42	36	36
TPLA, 4%	3C	100	92	90	90	84
TPLA, 8%	3D	100	95	93	92	92
TPLA, 16%	3E	100	100	100	100	100
TPLA, 32%	3F	100	100	100	94	100

¹ Attributed to green algae which attached during prolific growth period but which did not persist.
Note: Physical condition of all coatings was rated "good", without physical defects, at time of September report.

TABLE 3.—TPLA IN HYDRON S AND 2 COPOLYMERS
(Grams per liter of paint)

Ingredient:	Paint Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Hydron-S	153	153	153	153								
90% Hema-10% Me methacrylate					153	153	153	153				
60% Hema-40% Me methacrylate									153	153	153	153
Triphenyllead acetate	11	21	42	81	11	21	42	81	11	21	42	81
Iron oxide	240	240	240	240	240	240	240	240	240	240	240	240
Talc	130	115	85	30	130	115	85	30	130	115	85	30
Ethanol	614	614	614	614	614	614	614	614	614	614	614	614
Total	1,148	1,143	1,134	1,118	1,148	1,143	1,134	1,118	1,148	1,143	1,144	1,118
Percent TPLA	2	4	8	16	2	4	8	16	2	4	8	16

NOTE: All paints: Pigments volume content=39.6%; non-volatiles volume=24.5%

acetate (TPLA). These solutions, which contained 14 percent Hydron, were applied by brush to panels of glass-reinforced polyester laminate which has been sanded to give a clean surface. The details of the formulations are given in Table 1.

These panels were observed at monthly intervals. After the first period, all three of the formulations showed some activity against marine organisms. The resin itself was inactive, as demonstrated by the control sample which rapidly became fouled. The G11-containing series showed good protection with the exception of the panel containing the 2 percent active ingredient (the lowest level). DAC-2787 was described as moderately active while TPLA exhibited a degree of control described as "startling." The films were completely free of slimes and silt, as well as macrofouling. In all cases, the physical integrity of the film was good. This was highly encouraging, since organolead compounds have not demonstrated useful levels of protection in coatings even though they are known to have broad-spectrum activity in sea water when leached out of porous blocks.

After five months' immersion, the G11 and DAC-2787 panels were removed because all had fouled extensively. However, the TPLA series was still performing well, and after 6 months the two films containing the most concentrated quantity of active ingredient (16 to 32 percent) were still rated as 100 percent effective at this time, the film containing 8 percent TPLA was rated 92 percent, the 4 percent film 84 percent, and the 2 percent coating, 36 percent. Complete results are summarized in Table 2.

TABLE 1.—HYDRON-S FORMULATIONS, FIRST SERIES

Formulation No.	Hydron-S	G 11	DAC-2787	TPLA	E+OH
A (Control)	13.8				86.2
1B	13.7	0.3			86.0
1C	13.7	0.6			85.7
1D	13.6	1.2			85.2
1E	13.4	2.6			84.0
1F	13.0	6.1			80.9
2B	13.7		0.3		86.0
2C	13.7		0.6		85.7
2D	13.6		1.2		85.2
2E	13.4		2.6		84.0
2F	13.0		6.1		80.9
3B	13.7			0.3	86.0
3C	13.7			0.6	85.7
3D	13.6			1.2	85.2
3E	13.4			2.6	84.0
3F	13.0			6.1	80.9

EXAMPLE 15

Triphenyl lead acetate (TPLA) tests were also carried out at four concentrations from 2 to 16 percent by weight in Hydron-S and also in two copolymers (90 percent Hema-10 percent methyl methacrylate and 60 percent Hema-40 percent methyl methacrylate). The copolymers have lower levels of sea water permeability than Hydron-S. These coatings were applied by both brush and doctor-blade techniques. 8 inches x 10 inches aluminum alloy panels were employed in the testing of effectiveness against fouling. After one month the Hydron-S formulations performed better than the copolymers. Pigmentation of the Hydron-S did not detract from its performance.

TABLE 4.—TPLA IN HYDRON-S AND 2 COPOLYMERS
IMMERSION TEST RESULTS

Polymer	Percent TPLA	Paint Panel number number ¹	One month		
			Physical condition	Percent rating O.P. ²	
Hydron-S	2	1	1-1/c	Good	95
			1-1/b	do	100
			1-2/c	do	100
			1-2/b	do	100
	4	2	2-1/c	do	100
			2-1/b	do	100
			2-2/c	do	100
			2-2/b	do	100
	8	3	3-1/c	do	100
			3-1/b	do	100
			3-2/c	do	100
			3-2/b	do	100
16	4	4-1/c	do	100	
		4-1/b	do	100	
		4-2/c	do	100	
		4-2/b	do	100	
90/10	2	5	5-1/c	Blistering	98
			5-1/b	Good	100
			5-2/c	do	100
			5-2/b	Blistering	80

Polymer	Percent TPLA	Paint Panel number number ¹	One month	
			Physical condition	Percent rating O.P. ²
	4	6	6-1/c	95
			6-1/b	70
			6-2/c	100
			6-2/b	65
	8	7	7-1/c	100
			7-1/b	40
			7-2/c	90
			7-2/b	20
90/10	16	8	8-1/c	70
			8-1/b	35
			8-2/c	50
			8-2/b	30
60/40	2	9	9-1/c	25
			9-1/b	95
			9-2/c	35
			9-2/b	100
	4	10	10-1/c	70
			10-1/b	100
			10-2/c	25
			10-2/b	100
	8	11	11-1/c	85
			11-1/b	100
			11-2/c	25
			11-2/b	100
	16	12	12-1/c	Not prepared
			12-1/b	100
			12-2/c	Not prepared
			12-2/b	75

¹ c=cast; b=brushed.
² O.P.=Overall Performance.
³ Corrosion eruptions on portions of bare aluminum.

EXAMPLE 16

In another series of experiments, aluminum panels were prepared from Hydron-S solutions containing the following antifoulants:

Test panel designation	Antifoulant
A	Bis(tri-n-butyltin) oxide; "TBTO".
B	Triphenyltin chloride; "TPTCl".
C	Tributyltin fluoride; "TBTF".
E	Triphenyllead chloride; "TPLC".
F	Triphenyllead laurate; "TPLL".
G	1,2,3-trichloro-4,6-dinitrobenzene; "Vancide PB".
H	Saturated solution of Vancide PB in TBTO; "PBTO" (ca. 20.5% PB).
I	10,10'-oxybisphenoxarsine; "SA-546".
J	Mercurous chloride; Powder.
K	Cuprous oxide; Grade AA.

The formulations containing these antifoulants are shown in Table 5, and the results after one month's immersion in Table 6. Again, these results are from tests in sea water at Miami, Florida.

Panels K4 and K16, each with cast and brushed films containing cuprous oxide on aluminum, were expected to show galvanic corrosion. Since cuprous oxide is of importance for comparison, additional K4 and K16 films were applied to glass-reinforced polyester panels. K4 replicates were brushed, and K16 cast because only the latter panels were flat enough to permit accurate film draw-down.

A number of the formulations show considerable interest, not only because of the protection afforded, but also because of the sizeable content of pigments.

TABLE 5.—HYDRON-S SYSTEM CONTAINING 4 AND 16% OF VARIOUS ANTIFOULANTS

[Grams per liter of paint]

Ingredient	Paint Number																					
	A/4	A/16	B/4	B/16	C/4	C/16	E/4	E/16	F/4	F/16	G/4	G/16	H/4	H/16	I/4	I/16	J/4	J/16	K/4	K/16		
Hydron-S	160	139	163	163	163	163	163	163	153	153	163	163	150	140	153	153	153	153	163	163	163	
TBTO	22	100																				
TPTCl																						
TBTF			21	75																		
TPLC					20	70																
TPLL							21	81														
Vancide PB									21	81	21	78										
"PBTO"										21	81	21	78									
Dow SA-546													22	100	21	74						
Mercurous chloride																	22	95				
Cuprous oxide																						
Iron oxide	240	240	240	240	214	240	240	240	240	240	240	240	240	240	240	240	240	240	240	240	240	240
Talc	146	146	105	1	99	115	30	115	30	115	30	110	15	145	103	145	136	107	136	107	136	101
Ethanol	601	566	614	614	614	614	614	614	614	614	614	614	614	602	614	560	614	614	614	614	614	614
Total	1,188	1,180	1,133	1,083	1,126	1,051	1,143	1,118	1,143	1,118	1,138	1,100	1,169	1,185	1,131	1,165	1,165	1,209	1,164	1,204	1,164	1,204

TABLE 6.—HYDRON-S SYSTEM CONTAINING 4 AND 16% OF VARIOUS ANTIFOULANTS IMMERSION TEST RESULTS

Antifoulant	Paint Number	Panel Number ¹	One month	
			Physical condition	Percent rating O.P.
TBTO	A/4	A4.1/c	Good	95
		A4.1/b	do	95
		A4.2/c	do	95
		A4.2/b	do	95
	A/16	A16.1/c	Soft	95
		A16.1/b	do	98
		A16.2/c	do	95
		A16.2/b	do	98
TPT Cl.	B/4	B4.1/c	Good	100
		B4.1/b	do	100
		B4.2/c	do	100
		B4.2/b	do	100
	B/16	B16.1/c	Soft	98
		B16.1/b	do	98
		B16.2/c	do	98
		B16.2/b	do	98
TBTF	C/4	C4.1/c	Good	95
		C4.1/b	do	95
		C4.2/c	do	95
		C4.2/b	do	95
	C/16	C16.1/c	do	100
		C16.1/b	do	100
		C16.2/c	do	100
		C16.2/b	do	100
TPLC	E/4	E4.1/c	do	95
		E4.1/b	do	95
		E4.2/c	do	100
		E4.2/b	do	100
	E/16	E16.1/c	Soft	98
		E16.1/b	do	98
		E16.2/c	Good	100
		E16.2/b	Soft	98
TPLL	F/4	F4.1/c	Good	95
		F4.1/b	do	95
		F4.2/c	do	95
		F4.2/b	Soft	95
	F/16	F16.1/c	do	98
		F16.1/b	Good	100
		F16.2/c	Soft	98
		F16.2/b	Good	100
Vanicide PB	G/4	G4.1/c	do	91
		G4.1/b	do	90
		G4.2/c	do	89
		G4.2/b	do	91
	G/16	G16.1/c	do	95
		G16.1/b	do	95
		G16.2/c	do	95
		G16.2/b	do	95
PBTO	H/4	H4.1/c	do	95
		H4.1/b	do	95
		H4.2/c	do	100
		H4.2/b	do	95
	H/16	H16.1/c	do	100
		H16.1/b	do	100
		H16.2/c	do	100
		H16.2/b	Soft	95
Dow SA-546	I/4	I4.1/c	Good	100
		I4.1/b	do	100
		I4.2/c	do	100
		I4.2/b	do	100
	I/16	I16.1/c	do	100
		I16.1/b	do	100
		I16.2/c	do	100
		I16.2/b	do	100
Mercurous chloride	J/4	J4.1/c	do	100
		J4.1/b	do	95
		J4.2/c	do	100
		J4.2/b	do	100
	J/16	J16.1/c	Blistering	90
		J16.1/b	do	99
		J16.2/c	do	90
		J16.2/b	do	99
Cuprous oxide	K/4	K4.1/c	Corr. eruption	95
		K4.1/b	Good	95
		K4.2/c	do	95
		K4.2/b	do	95
	K/16	K16.1/c	Corr. eruption	99
		K16.1/b	do	99
		K16.2/c	do	99
		K16.2/b	do	90

¹ b, brushed; c, cast.

In example 14 through 16, the formulations containing pigments were prepared on a paint mill. All were applied (with the few exceptions indicated) to 6061-T6 anodized aluminum alloy by doctor-blade coating or brushing.

I claim:

1. A marine structure which is a watercraft having an adherent coating consisting essentially of either (1) a water-insoluble hydrophilic acrylic polymer which is swellable to an extent of at least 20 percent in water wherein the coating is sufficient to reduce the drag of the watercraft when in water or (2) said hydrophilic acrylic polymer having encapsulated therein at least one member of the group consisting of antifouling agents and pigment.

2. A marine structure having a coating film consisting essentially of a water-insoluble hydrophilic acrylic resin which is swellable to an extent of at least 20 percent in water and containing in the coating film an antifouling agent.

3. A marine structure according to claim 1 wherein the coating polymer is a polymer of a hydrophilic hydroxyalkyl or hydroxyalkoxyalkyl acrylate or methacrylate or acrylamide, alkyl acrylamide, methacrylamide, alkyl methacrylamide or diacetone acrylamide.

4. A marine structure according to claim 3 wherein the coating polymer is a polymer of hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate or hydroxypropyl methacrylate.

5. A marine structure according to claim 4 wherein the polymer is a linear polymer.

6. A marine structure according to claim 5 wherein the polymer is a homopolymer.

7. A marine structure according to claim 4 wherein the polymer is a copolymer of said acrylate or methacrylate with a minor amount up to 20 percent of a cross-linking agent.

8. A marine structure according to claim 2 wherein the antifouling agent is an organolead compound.

9. A marine structure according to claim 2 wherein the coating polymer is a polymer of hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate or hydroxypropyl methacrylate.

10. A method of increasing the speed of watercraft comprising moving said watercraft through water while having on the watercraft below the waterline the coating set forth in claim 1.

11. A method according to claim 10 wherein the coating polymer is a polymer of a hydrophilic hydroxyalkyl or hydroxyalkoxyalkyl acrylate or methacrylate or acrylamide, alkyl acrylamide, methacrylamide, alkyl methacrylamide or diacetone acrylamide.

12. A method according to claim 11 wherein the coating is a linear polymer.

13. A method according to claim 11 wherein the coating is a homopolymer of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate or hydroxypropyl methacrylate.

14. A method providing continuous availability of an antifouling agent comprising placing in water a marine structure having the coating composition of claim 2 applied thereto, the swelling of the hydrophilic acrylic resin in water rendering the antifouling agent readily available for its intended purpose.

15. A marine structure according to claim 2 wherein the swellability of the polymer is not over 120 percent.

16. A marine structure according to claim 1, wherein the swellability of the polymer is not over 120 percent.

17. A marine structure according to claim 2 including a pigment.

18. A marine structure which is a watercraft having an adherent coating film of a water-insoluble hydrophilic acrylic resin which is swellable to an extent of at least 20 percent in water wherein the film is sufficient to reduce the drag of the watercraft when in water,

19. A marine structure according to claim 18 wherein the film has a thickness of 0.3 to 5 mils and the resin is a polymer of hydroxyethyl acrylate, hydroxyethyl methacrylate,

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hydroxypropyl acrylate or hydroxypropyl methacrylate.

20. A marine structure according to claim 19 wherein the film consists essentially of said polymer having releasably encapsulated therein an organometallic antifoulant, said film being characterized by the fact that said antifoulant is still effective after at least 6 months of use of the marine structure in water.

21. A marine structure according to claim 19 wherein the polymer is a linear polymer.

22. A marine structure according to claim 1 wherein the adherent coating consists essentially of (1) and the hydrophilic acrylic polymer is linear polymer of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate or hydroxypropyl methacrylate.

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