

Marine paint

This invention relates to marine anti-fouling paints generally used as top-coat paints for ships' hulls.

The growth of marine organisms on the sub-marine parts of a ship's hull increases the frictional resistance of the hull to passage through water, leading to increased fuel consumption and/or a reduction in the speed of the ship. Marine growths accumulate so rapidly that the remedy of cleaning and repainting as required is impractical. In general, the extent of fouling is limited by applying to the hull a top-coat incorporating anti-fouling agents. The anti-fouling agents are biocides which are freed from the surface of the paint over a period in concentrations lethal to marine organisms on the hull's surface. The anti-fouling paint fails only when the concentration of biocide available at the paint surface falls below the lethal concentrations, and with marine paints up to two years of useful life can be expected. The better anti-fouling paints are thus effective in dealing with gross infestation of hulls for considerable periods but a top-coat paint of a ship's sub-marine surface has irregularities from its method of application and is furthermore subject to breakdown and delamination during service, increasing the roughness of the hull so that the performance of the ship falls off even when fouling is prevented.

According to the present invention, a marine paint comprises a film-forming copolymer which is a copolymer containing 20 to 80 per cent by weight of units of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, the balance of the copolymer being units of at least one olefinically unsaturated comonomer, and a metalliferous pigment which is sparingly soluble in sea-water.

The paint of the present invention has the remarkable

property that relatively moving sea-water smooths the surface of the paint, removing excrescences composed of the paint. When it is painted on a ship, the painted sub-marine surface of the ship at least preserves its initial smoothness and may become smoother during the ordinary traffic of the ship, leading to improved efficiency. Our British patent specification 1,457,590 describes and claims a paint having this remarkable property and Figures 2A - 2D in particular of the drawings accompanying British patent specification 1,457,590 illustrate the smoothing effect of the relatively moving sea-water. A similar smoothing effect is achieved with the paint of the present invention. The paint described and claimed in British patent specification 1,457,590 is based on a film-forming copolymer containing units of a triorgano tin salt of an olefinically unsaturated carboxylic acid. Upon contact with sea-water it loses triorgano tin ions by ion exchange with sea-water. This generates a water-soluble resin which essentially is a copolymer salt formed as a result of the depletion in the copolymer organotin content and exchange with metal ions present in sea-water. The smoothing of paint described in British patent specification 1,457,590 is thus inevitably accompanied by the release of organotin ions into the surrounding sea-water. In most circumstances this is useful, because the triorgano tin ions are effective anti-fouling agents. However, triorgano tin ions are expensive to employ and are strongly biocidal and there are some circumstances where the release of triorgano tin ions is preferably avoided or reduced whilst still obtaining the benefits of smoothing of the paint in service. The present invention provides a self-smoothing paint which does not release such strongly biocidal ions.

35 The paint of the present invention generates a water-soluble residue by exchange of quinolinyl (or substituted

quinolinyl) groups in the polymer for metal ions present in the sea-water. The quinolinyl groups are released into the sea-water. These are generally not toxic to animal life, although they have some effect in inhibiting fouling by algae and seaweed. Generally, the metalliferous pigment is chosen to have biocidal activity or a separate anti-fouling agent is used in paints according to the invention. This can be chosen for the particular waters which a ship is likely to encounter.

10 If desired, the film-forming copolymer can also contain units of a triorgano tin salt of an olefinically unsaturated carboxylic acid and these units can replace a part of the units of the quinolinyl (or substituted quinolinyl) ester.

15 The invention therefore also provides a marine paint which comprises a film-forming copolymer and a metalliferous pigment which is sparingly soluble in sea-water, and in which the copolymer comprises 10-80 per cent by weight of (a) units of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, up to 60 per cent by weight of (b) units of a triorgano tin salt of an olefinically unsaturated carboxylic acid, (a) and (b) together forming 20-80 per cent by weight of the copolymer, and the balance of the copolymer being (c) units of at least one olefinically unsaturated comonomer.

30 The quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid preferably has the formula $\text{CHR}' = \text{CR}-\text{COO}-\text{Q}$ (I) where R is a hydrogen atom or methyl group, R' is hydrogen or $-\text{COOQ}$ and Q is a 8-quinolinyl group optionally substituted by one or more alkyl or alkoxy groups having 1 to 4 carbon atoms, halogen atoms, nitro, cyano or substituted acid amide groups. Compounds of formula (I) can be made by reaction

of the corresponding 8-hydroxy quinoline with acrylyl or methacrylyl chloride. The ester (I) is preferably unsubstituted quinolinyl acrylate or methacrylate; halogenated derivatives such as 7-bromo-5-chloro-quinolinyl-8 acrylate are an alternative.

The olefinically unsaturated comonomer can be an acrylic monomer, for example methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, the corresponding esters of methacrylic acid, acrylonitrile or methacrylonitrile, or a vinyl monomer, for example vinyl acetate, vinyl butyrate, vinyl chloride, styrene or vinyl pyridine. The polymer can also contain monomer units conferring increased water-reactivity, particularly when the polymer contains a relatively low proportion of monomer units (a) or monomer units (a) and (b). For example, the polymer can contain up to 20 per cent by weight of maleic or itaconic anhydride, acrylamide, methacrylamide or N-vinyl pyrrolidone units or up to 5 per cent by weight, preferably 2 per cent or less, of acrylic, methacrylic or itaconic acid units. Care must be taken to avoid gelation of the paint when using a copolymer containing free acid monomer units.

The monomer units (b) are preferably of the formula $R_3SnOCCCR' = CHR''$ where each R is an alkyl radical containing 2 to 8 carbon atoms or an aryl or aralkyl radical, R' is H or CH_3 and R'' is H or $-COOSnR_3$. The groups R attached to the tin atom can be different but are preferably the same, for example R_3Sn can be tributyl tin, tripropyl tin, tribenzyl tin, triphenyl tin, tritolyl tin or trihexyl tin. The carboxylate group $-OCCCR' = CHR''$ is preferably acrylate, methacrylate or maleate.

If triorgano tin salt units are not present the film-forming copolymer preferably comprises 20-60 per cent by weight of the quinolinyl (or substituted quino-

- linyl) ester units and 40-80 per cent by weight of units of the comonomer, for example at least one alkyl acrylate or methacrylate. If triorgano tin salt units are present the copolymer preferably comprises 15-40 per cent by weight of the quinolinyl (or substituted quinolinyl) ester units (a), 20-45 per cent by weight of the triorgano tin salt units (b), for example tributyl tin methacrylate units, and 30-50 per cent by weight of units of at least one alkyl acrylate or methacrylate.
- 10 The film-forming copolymers can be prepared by free radical polymerisation under polymerisation conditions, generally using a catalyst such as benzoyl peroxide or azobisisobutyronitrile in an organic solvent such as xylene, toluene, butyl acetate, 2-ethoxyethanol, 2-methoxyethanol, 2-ethoxyethyl acetate, methyl isobutyl ketone, butanol and/or cyclohexanone or in aqueous emulsion. For solvent polymerisation mixtures of xylene with minor amounts, for example up to 20 per cent by volume, of 2-ethoxyethanol, 2-ethoxyethyl acetate or methyl isobutyl ketone may be preferred. Polymerisation is preferably carried out at a temperature in the range 70-100°C.
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The metalliferous pigment sparingly soluble in sea-water may alternatively be described as a substantially water-insoluble metalliferous pigment capable of reacting with sea-water. It is exemplified by cuprous thiocyanate, cuprous oxide, zinc oxide, zinc chromate, cupric acetate metaarsenate, and zinc ethylene bis(dithiocarbamate). These pigments produce water-soluble metal compounds on reaction with sea-water so that the pigment particles do not survive at the paint surface. Preferably, the sparingly soluble pigment has a solubility in sea-water of from about 1 to about 10 parts per million by weight. The pigment has the effect of inducing the overall smoothing which the relatively moving sea-water exerts on the paint film, minimising localised erosion and preferen-

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tially removing excrescences formed during application of the paint. Mixtures of such pigments can be used, for example zinc oxide, which is most effective at inducing the gradual dissolution of the paint, can be mixed
5 with cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate), which are more effective marine biocides. The ratio of zinc oxide to cuprous oxide or thiocyanate can for example be 1:1 to 9:1 by weight.

The paint composition can additionally contain a
10 pigment which is highly insoluble in sea-water (solubility below 1 ppm by weight), such as titanium dioxide or ferric oxide. Such highly insoluble pigments can be used in proportions up to 40 per cent by weight of the total pigment component of the paint, but preferably are used
15 in proportions of less than 20 per cent by weight. The highly insoluble pigment has the effect of retarding the dissolution of the paint.

The proportion of pigment to copolymer is preferably such as to give a pigment volume concentration which
20 is above 25 per cent in the dry paint film but below the critical pigment volume concentration; most preferably the pigment volume concentration is 35-50 per cent.

Polymers containing the quinolinyl (or substituted quinolinyl) ester may be somewhat brittle, particularly
25 those containing a high proportion of a quinolinyl methacrylate. The paints according to the invention may therefore include a plasticiser, for example tritolyl phosphate, diisooctyl phthalate, tributyl phosphate, butyl benzyl phthalate, 'Lutenal A25' polyether or dibutyl
30 tartrate. Alternatively, the olefinically unsaturated comonomer can be chosen to reduce the brittleness of the copolymer. Examples of comonomers which reduce brittleness are alkyl acrylates containing three or more carbon atoms in the alkyl group, for example butyl acryl-

ate, hexyl acrylate or 2-ethylhexyl acrylate.

If the rate of dissolution in relatively moving sea-water of a combination of the polymer containing quinolinyl (or substituted quinolinyl) ester units and a pigment sparingly soluble in sea-water is undesirably rapid, for example when the polymer contains a relatively high proportion of quinolinyl (or substituted quinolinyl) ester and triorgano tin salt units, the rate of dissolution can be retarded by including in the paint a hydrophobic organic compound which retards the dissolution of the paint. Examples of such hydrophobic organic retarders are methyl phenyl silicone fluids, for example silicone fluid DC550 sold by Dow Corning Ltd., chlorinated diphenyl, for example Aroclor^(RTM) 1254 sold by Monsanto Ltd., chlorinated paraffin wax, for example Cereclor^(RTM) 48 and Cereclor 70 sold by I.C.I. Ltd., diphenyl ether, dichlorodiphenyl-trichloroethane and low molecular weight polybutenes, for example Hyvis^(RTM) 05 sold by B.P. Ltd. The hydrophobic organic retarder, for example chlorinated diphenyl or chlorinated paraffin wax, may also be a plasticiser for the paint.

Many of the sparingly sea-water soluble metalliferous pigments have some biocidal activity, particularly zinc ethylene bis(dithiocarbamate) and copper compounds such as cuprous thiocyanate, cupric acetate metaarsenate and cuprous oxide but also zinc oxide to a lesser extent. Even when the copolymer contains no triorgano tin salt units (b), the biocidal effect of the sparingly sea-water-soluble pigments, particularly zinc ethylene bis(dithiocarbamate) and cuprous oxide, may be sufficient so that the paint needs no further biocide, for example in the case of paint for use on the flat bottom of very large tankers, where fouling is less likely to occur. We believe that the self-smoothing action of the paint increases its resistance to fouling compared to a conven-

tional paint releasing biocide at the same rate. This effect is more marked with increasing rate of dissolution of the paint.

The paint can contain an added biocide effective
5 against seaweed and barnacles. Triorgano tin salts and oxides such as triphenyltin fluoride, tributyl tin fluoride, tributyl tin dibromosuccinate, triphenyltin chloride, triphenyltin hydroxide and tributyltin oxide are effective
10 marine biocides and can be used in paints according to the invention, particularly where the polymer contains no monomer units (b). A paint according to the invention comprising a tin-free polymer, a pigment such as cuprous oxide and a small proportion of a triorgano tin salt (up to 25 per cent by volume based on the pigment) may
15 have antifouling and smoothing properties equal to an organo tin copolymer paint of much higher total organo tin content. Alternatively a mixture of organo tin-free and organo tin-containing polymers can be used.

In some cases it will be desired to avoid completely
20 the release of triorgano tin ions. Examples of other biocides effective as antifouling agents are dithiocarbamate derivatives such as cuprous ethylene bis(dithiocarbamate) or 2-(N,N-dimethyl thiocarbamyl thio)-5-nitro
thiazole, substituted isothiazolones particularly halo-
25 genated N-substituted isothiazolones, tetramethyl thiuram disulphide and dichlorodiphenyltrichloroethane (which also acts as a hydrophobic organic retarder).

The invention is illustrated by the following
Examples:-

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Example 1

Preparation of 8-Quinolinyl Acrylate

8-Hydroxyquinoline (58.0 g : 0.40 mole) was dissolved in a mixture of toluene (500 ml) and triethylamine

- (41.4 g ; 0.41 mole). Acrylyl chloride (38.0 g ; 0.42 mole) was added slowly, while stirring, the reaction temperature being kept under 30°C. When the addition was complete the mixture was stirred for another 1 hour.
- 5 The solution was then filtered and washed with a solution of sodium hydrogen carbonate in water followed by water only, and finally the toluene layer was dried with anhydrous sodium sulphate. Some toluene was evaporated off using a rotary evaporator under low pressure. The
- 10 solution was left in a refrigerator overnight and the solid formed was filtered off. This was identified by infra-red and N.M.R. spectroscopy and microanalysis to be 8-quinolinyl acrylate. Yield 48.6 g (61 per cent of the theoretical yield).
- 15 It was recrystallised from toluene to give crystals with m.p. : 50-52°C.

Copolymerisation

- 8-Quinolinyl acrylate (12.3 g ; 0.054 mole) was dissolved in cyclohexanone (63 g). Butyl acrylate (28.7
- 20 g ; 0.224 mole) was added, followed by azobisisobutyronitrile (1.0 g). The solution was heated to 75°C and the polymerisation reaction was conducted with stirring at this temperature. A mild exotherm was observed in the first 15 minutes of the reaction. The course of
- 25 the polymerisation was followed by observing the change in the refractive index. No further change was observed after 5 hours and the solution was heated to 100°C for a period of 30 minutes to destroy any residual activity of the azobisisobutyronitrile. The product was a solution
- 30 of a 30:70 by weight copolymer of 8-quinolinyl acrylate and butyl acrylate.

Paint Preparation

64.3 g of the quinolinyl acrylate butyl acrylate copolymer solution was diluted with 20.3 g cyclohexanone

to give 84.6 g of a 29.5 per cent by weight solution. This was mixed with zinc oxide (67.5 g) and Aerosil(ATM) colloidal silica (1.3 g) and milled overnight.

The paint obtained had a pigment volume concentration of 35 per cent and a solids content of 37 per cent by volume.

Example 2

Copolymerisation

8-Quinolinyll acrylate prepared as described in Example 1 (16.4 g ; 0.072 mole) was dissolved in cyclohexanone (63 g). Butyl acrylate (24.6 g ; 0.192 mole) was added, followed by azobisisobutyronitrile (1.0 g). The solution was heated to 75°C and the polymerisation reaction was conducted as described in Example 1. The product was a solution of a 40:60 by weight copolymer of 8-quinolinyll acrylate and butyl acrylate.

Paint Preparation

66.7 g of the quinolinyll acrylate butyl acrylate copolymer solution was diluted with 18.7 g cyclohexanone to give 85.4 g of a 30.1 per cent by weight solution. This was mixed with zinc oxide (67.5 g) and Aerosil colloidal silica (1.3 g) and milled overnight.

The paint obtained had a pigment volume concentration of 35 per cent and a solids content of 37 per cent by volume.

The smoothing performance of paints in relatively moving sea-water can be tested in the apparatus described in British patent specification 1,457,590 with reference to Figures 7A and 7B. A mild steel disc 31 having a diameter of 23 cm is coated overall with a conventional anti-corrosive paint and overcoated in radial stripes

with the paints under test. The stripes are applied by a standardised applicator adapted to deposit a film 20 μ thick (wet thickness).

The disc is immersed in flowing sea-water and rotated
5 at a peripheral speed of 33 knots.

During this test the paint films under test are planed away, eventually to the extent that the underlying substrate (the anti-corrosive paint) is revealed. There is always some variation in the thickness of the paint
10 film within each stripe so that the stripe of paint does not suddenly vanish; an increasing proportion of the substrate is revealed over time. When the substrate is revealed over 50 per cent of the area of the stripe it is a good approximation to say that the paint film
15 in the stripe has lost by planing the original average dry thickness of the paint film in the stripe. The time in days to achieve this ("D⁵⁰") is a measure of the rate of planing of the paint in relatively moving sea-water.

The surface of the paint film in each stripe should
20 be examined during the test to note whether it is smooth and firm. Paint films according to the invention which at least retain their initial smoothness must be distinguished from paint films which are removed over at least a portion of the stripe by flaking or localised erosion
25 causing roughening or by separation from the disc.

The above test can be used to give an absolute rate of planing of the paint film, but the temperature, composition and flow rate of the sea-water can affect the result. The test is preferably used as a comparison
30 in which one of the stripes painted on the disc is an anti-fouling paint known to have the desired rate of dissolution in relatively moving sea-water. The paint described in Example 1 of British patent specification

1,457,590, using copolymer C and 30 per cent by weight dichlorodiphenyl trichloroethane based on the organotin content of the copolymer, is a paint which has been found to be successful in use on ships in service and
5 can be used as a reference stripe in tests.

A disc was prepared having 2 stripes each of the paints of Examples 1 and 2, and 2 stripes of the above described paint of Example 1 of British patent specification 1,457,590.

10 All the paints were observed to be planed away during rotation in sea-water. The stripes of paint according to Example 1 of British patent specification 1,457,590 both had a D^{50} of 12 days. The stripes of the paint of Example 1 of the present application had a D^{50} of
15 15 and 16 days and the stripes of the paint of Example 2 both had a D^{50} of 16 days. These results indicate a rate of dissolution in relatively moving sea-water which would be sufficient to give appreciable smoothing of the paint film without its being dissolved away too
20 fast and compatible with the release of sufficient of an added biocide without forming a leached inactive outer layer of paint.

Example 3

25 48.9 g of the copolymer solution prepared in the copolymerisation stage of Example 1 was mixed with 20.9 g zinc oxide, 22.2 g cuprous oxide, 0.8 g Aerosil^(ATM), 1.5 g bentonite, 0.5 g n-butanol and 8.0 g cyclohexanone and milled overnight to produce a paint of pigment volume concentration 35 per cent and solids content 38 per cent
30 by volume.

The paints of Examples 1 and 3 were both applied to a test panel. The panels were fixed to the bilge keel of a ferry operating in the Mediterranean. The panels were examined after 14 months in service, including

2 months in which the ferry was laid up in the Mediterranean. Areas around the test panels which were not coated with antifouling paint showed very heavy weed and animal fouling.

5 The paint of Example 1 which contained no biocide apart from zinc oxide and the copolymer, showed no fouling by seaweed and no adherent algal slime, although there was some fouling by tube worms. (Tube worms are known to be susceptible to many marine biocides such as cuprous
10 oxide, zinc ethylene bis(dithiocarbamate) or triphenyl tin fluoride and a small amount of one of these could be added to the paint to boost its resistance to animal fouling.) The paint of Example 1 was smoothed away from the panel at 5 microns per month which is about the ideal
15 rate to obtain a decrease in roughness of the paint film without using up the paint too fast; the commercially successful self-polishing organo tin copolymer paint used on the hull of the ship was smoothed away at 6 microns per month.

20 The paint of Example 3 showed no weed or animal fouling and only a little algal slime. This paint was smoothed away at 1 to 2 microns per month; this may be rather slow to obtain any significant decrease in roughness.

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Example 4

8-quinolinyl acrylate (12.3 g) and methyl methacrylate (28.7 g) were copolymerised under the conditions described in Example 1 to prepare a 39 per cent by weight solution of a 30:70 by weight copolymer of 8-quinolinyl
30 acrylate and methyl methacrylate. 48.9 g of the copolymer solution was milled with 41.1 g zinc oxide, 0.8 g Aerosil^(ATM), 1.5 g bentonite, 0.5 g n-butanol and 8.0 g cyclohexanone to produce a paint of pigment volume concentration 35 per cent and solids content 38 per cent by volume.

Example 5

14.35 g 8-quinolinyl methacrylate and 26.65 g methyl methacrylate were copolymerised under the conditions described in Example 1 to prepare a 39 per cent by weight solution of a 35:65 by weight copolymer of 8-quinolinyl methacrylate and methyl methacrylate. A paint was prepared using the formulation of Example 4 except that 18 per cent of the copolymer was replaced with an equal volume of tritolyl phosphate plasticiser.

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Example 6

18.45 g 8-quinolinyl methacrylate was copolymerised with 22.55 g methyl methacrylate using the conditions described in Example 1 to produce a 39 per cent by weight solution of a 45:55 by weight copolymer of 8-quinolinyl methacrylate and methyl methacrylate. A paint was prepared from the copolymer solution using the procedure of Example 5, including the plasticising by tritolyl phosphate.

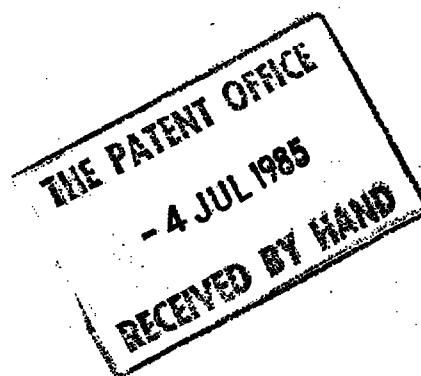
Example 7

20 24.6 g 7-bromo-5-chloro-quinolinyl-8 acrylate was copolymerised with 16.4 g methyl methacrylate using the conditions of Example 1 to produce a 39 per cent by weight solution of a 60:40 by weight copolymer of 7-bromo-5-chloro-quinolinyl-8 acrylate and methyl methacrylate.
25 A paint was prepared from the copolymer solution using the procedure of Example 4.

The smoothing performance of the paints of Examples 4 to 7 was tested using the test apparatus described in British patent specification 1,457,590 with reference to Figures 7A and 7B. The paints of Examples 4 to 7 were tested by comparison with a commercially successful organo tin copolymer paint. The results obtained were as follows:-

	<u>Average D⁵⁰ (Individual readings)</u>
Paint of Example 4	35 days (31, 39)
Paint of Example 5	20 days (only one stripe applied)
Paint of Example 6	14 days (only one stripe applied)
5 Paint of Example 7	13.5 days (14, 13)
Commercial paint for comparison	18 days (16, 18, 20, 17, 17)

The paints of Examples 4 to 7 all had a rate of dissolution similar to that of the commercial paint which has been successfully used in service, indicating that
10 these paints would give appreciable smoothing of the paint film in service without its being dissolved away too fast.





- 16 -

CLAIMS

1. A marine paint comprising a film-forming copolymer which is a copolymer containing 20 to 80 per cent by weight of units of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, the balance of the copolymer being units of at least one olefinically unsaturated comonomer, and a metalliferous pigment which is sparingly soluble in sea-water.
2. A marine paint according to claim 1 in which the copolymer comprises 20 to 60 per cent by weight of the quinolinyl ester units.
3. A marine paint comprising a film-forming copolymer and a metalliferous pigment which is sparingly soluble in sea-water, in which the copolymer comprises 10 to 80 per cent by weight of units (a) of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, up to 60 per cent by weight of units (b) of a triorgano tin salt of an olefinically unsaturated carboxylic acid, the units (a) and (b) together forming 20 to 80 per cent by weight of the copolymer and the balance of the copolymer being units of at least one olefinically unsaturated comonomer.
4. A marine paint according to claim 3 in which the copolymer comprises from 15 to 40 per cent by weight of (a), from 20 to 45 per cent by weight of (b) and from 30 to 50 per cent by weight of units of at least one alkyl acrylate or methacrylate.
5. A marine paint according to any of claims 1 to 4 in which the quinolinyl ester units are 8-quinolinyl acrylate units.
6. A marine paint according to any of claims 1



- 17 -

to 4 in which the quinolinyl ester units are 8-quinolinyl methacrylate units.

7. A marine paint according to any of claims 1 to 6 in which the comonomer is an alkyl acrylate or meth-
5 acrylate ester.

8. A marine paint according to any of claims 1 to 7 in which the metalliferous pigment is a mixture of zinc oxide with cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate).

10 9. A marine paint according to claim 7 in which the metalliferous pigment is a mixture of zinc oxide with cuprous oxide or cuprous thiocyanate in a ratio of 1:1 to 9:1 by weight.

10. A marine paint according to claim 1 or claim
15 3 and substantially as described in any of the foregoing Examples.

11. A ship at least part of the sub-marine surface of which has been painted with a marine paint according to any of claims 1 to 10.

