

- 1 -

Treatment of Painted Surfaces

Field of the invention

This invention relates to a process and composition for the rehabilitation and/or rejuvenation of the surface of an antifouling paint which has been in service on a ship's hull.

Background of the invention

Antifouling paint traditionally comprises a biocide for aquatic organisms, dispersed in a paint binder. The biocide typically is a sparingly soluble biocide having a solubility in seawater of less than 50 parts per million (p.p.m.) by weight, preferably 0.5-10 p.p.m. The most widely used marine biocide is cuprous oxide, although other sparingly soluble copper and zinc compounds are also used, as are organic compounds of similar solubility which are biocides for barnacles, algae and/or diatoms. When the antifouling paint is applied to a surface such as a ship's hull, which is underwater in use, the sparingly soluble biocide is gradually leached out of the paint, so that the concentration of biocide at the surface of the hull is high enough to prevent settlement of marine organisms such as barnacles, algae or diatoms on the hull.

The antifouling paint binder can be of the soluble matrix or eroding type, in which at least part of the binder is sparingly soluble in seawater and is gradually dissolved in seawater after the biocide has been leached out, or of the insoluble matrix type, in which the binder has lower seawater solubility but the pigment volume concentration of biocidal pigment (such as cuprous oxide) and optionally other pigments is higher. These types of antifouling paint are described in more detail in the book "Marine Fouling and its Prevention" published by Woods Hole Oceanographic Institution in 1952. A further type of antifouling paint binder is the "self-polishing" type in which a polymeric binder is gradually hydrolysed to become

- 2 -

water-soluble. One example of this type is a triorganotin acrylate or methacrylate polymer as described in GB-A-1457590; another example is an acrylate or methacrylate polymer having pendent copper carboxylate groups as described in EP-A-204456.

A potential problem in all antifouling paints, but most particularly with eroding or soluble matrix paints, is the build-up at the paint surface of an outer layer of binder which has not dissolved but from which almost all the biocide has been leached. This "leached layer" may cause several problems. When the hull is repainted, the presence of the leached layer may cause bubbling of the newly applied paint and detachment of the new antifouling from the old leached antifouling. Even before repainting takes place, the leached layer hinders the free release of remaining biocide from underlying intact antifouling paint which still contains the biocide, and it thus retards the rate at which biocide is released from the paint, perhaps eventually to a rate which allows the growth of barnacles, algae and/or diatoms on the surface of the hull.

The object of the present invention is to provide a process and a composition for the removal of a leached layer which has built up on a ship's hull coated with antifouling paint.

25 Summary of the invention

A process according to the invention for removal from a hull of a ship of the outer leached layer of an antifouling paint originally comprising a paint binder and a biocide but from which seawater-soluble material has been leached is characterised in that a water-dispersible composition comprising a solvent for the paint binder remaining in the leached layer is applied to the surface of the antifouling paint, and the surface thus treated is subsequently washed with water to remove the said water-dispersible composition containing dissolved or emulsified

- 3 -

material of the leached layer, thereby exposing a surface of underlying intact antifouling paint, i.e. comprising paint binder and biocide.

The invention also includes the use of a solvent composition to remove from a hull of a ship an outer leached layer of an antifouling paint, originally comprising a paint binder and a biocide but from which seawater-soluble material has been leached, characterised in that the solvent composition used is a thickened water-dispersible composition comprising a solvent for the paint binder remaining in the leached layer and is capable of being removed from the surface of a painted ship's hull by water washing.

A composition according to the invention for facilitating the removal from a hull of a ship of an outer leached layer of an antifouling paint, originally comprising a paint binder and a biocide but from which seawater-soluble material has been leached, is a thickened water-dispersible composition comprising a water-dispersible solvent for the paint binder remaining in the leached layer and a thickening agent so that the composition has a viscosity sufficiently high that the composition can be coated on the surface of the said antifouling paint with the ship in a substantially vertical position substantially without running down the hull.

Detailed Description

In the case of an eroding or soluble matrix antifouling paint the paint binder can for example be rosin or maleinised or fumarised rosin. The paint binder can alternatively be a hydrophilic acrylic polymer, for example a polymer containing units of an alkoxyalkyl acrylate or methacrylate such as methoxyethyl acrylate or a polyoxyalkylene acrylate or methacrylate as described in GB-A-2152947 or units of a hydroxyalkyl acrylate or

- 4 -

methacrylate such as hydroxyethyl methacrylate as described in WO-93/02146. Alternatively, the binder may be a mixture of rosin with such a hydrophilic acrylic polymer or with any other acrylic polymer such as

5 polybutylacrylate or with a vinyl ether polymer such as a copolymer of vinyl methyl ether with vinyl chloride or vinyl acetate. Whilst these binders are intended to be, and usually are, gradually dissolved in seawater, it has been found that a thick leached layer up to 50 or 100

10 microns thick sometimes forms, particularly in the case of soluble matrix paints which contain a hydrophilic acrylic polymer or a vinyl ether polymer as part or all of the paint binder. The binder is often a mixture of resins with different seawater solubility, and the less soluble

15 resins frequently become enriched in the leached layer.

In the case of an insoluble matrix antifouling paint the paint binder can for example be a vinyl chloride polymer such as a vinyl chloride/vinyl acetate copolymer. Such a paint can form a thick leached layer, particularly

20 if the pigment volume concentration of the paint is below the critical pigment volume concentration.

Antifouling paints of the "self-polishing" type generally have a thin outer leached layer, typically 10 to 30 microns thick, of paint binder which is at least partly

25 hydrolysed but which has not yet dissolved. Such a thin leached layer does not spoil the antifouling efficiency of the paint, but in some cases it may be desired to remove the leached layer before overcoating with further antifouling.

30 The solvent composition which is applied to the leached layer of antifouling paint should dissolve the paint binder remaining in the leached layer or emulsify it sufficiently that it can be washed off with water. The solvent composition must be at least water-dispersible,

35 that is to say it must at least disperse in water and may

- 5 -

be water-miscible or dissolve in water. It may itself be an aqueous composition containing for example at least 20 or 40% up to 80 or 90% water, by weight.

In many cases, particularly for removing leached
5 layers based at least partly on a rosin binder, the solvent composition contains a hydrocarbon solvent which dissolves or disperses the paint binder remaining in the leached layer. A solvent which is particularly useful for dissolving leached rosin layers is a terpenic hydrocarbon
10 such as limonene, for example D-limonene, or pinene. The hydrocarbon solvent can alternatively be a "white spirit", which is a predominantly aliphatic, especially paraffinic, hydrocarbon mixture. The white spirit is preferably one having some aromatic content, for example 10 to 30% by
15 weight aromatics, although entirely aromatic hydrocarbon solvents are less effective than white spirit. White spirit is itself less effective than D-limonene as a solvent for leached rosin layers, that is to say it may need to be used at a higher concentration in the solvent
20 composition or with a longer contact time between application of the composition and water washing, but white spirit may be preferred because of lower cost. Alternatively, a mixture of white spirit and a terpenic hydrocarbon may be used. The proportion of hydrocarbon
25 solvent in the solvent composition is preferably at least 5 and may be up to 50 or even 80% by weight, with the most preferred proportion being in the range 8 or 10 to 30% by weight for many leached layers.

When a hydrocarbon solvent is used the solvent
30 composition preferably contains sufficient of a surfactant to ensure that the hydrocarbon solvent is stably dispersed in the solvent composition and/or that the solvent composition is itself water-dispersible on washing with water. The surfactant can be an anionic, nonionic or
35 cationic surfactant; an example of a suitable anionic surfactant is an ammonium, amine or alkali metal salt of a

- 6 -

long-chain sulphonic acid such as dodecylbenzenesulphonic acid. The surfactant can be present at up to 30% by weight of the solvent composition, most preferably at 5 to 25%, particularly 15 to 25%, by weight.

5 An example of a solvent which is miscible with water and which can be used in the solvent composition is an ether alcohol for example methoxypropanol, ethoxyethanol, butoxyethanol or ethoxyethoxyethanol. The ether alcohol acts as a solvent for hydrophilic acrylic polymers and for
10 vinyl ether polymers. Esters of such ether alcohols, for example methoxypropyl acetate, can also be used. Other alcohols or carboxylate esters may also be useful. The proportion of water-miscible solvent, for example ether alcohol, in the solvent composition can be up to 50% by
15 weight, preferably up to 25%, for example 1 to 20%, by weight. The presence of such a water-miscible organic solvent in the solvent composition may aid in the solution or dispersion of a hydrocarbon solvent.

The solvent composition is preferably thickened before
20 application to the leached layer on the ship's hull, for example by incorporation of a thickening agent which makes the composition thixotropic or pseudoplastic. The solvent composition may even be gelled, provided it is capable of being applied to the hull. The thickening agent used is
25 preferably a fine-particle silica gel such as that sold under the Trade Mark "Aerosil 200", which can for example be used at 2 to 6% by weight of the composition, and/or a bentonite clay. The thickened solvent composition most preferably has a viscosity at low or zero shear higher
30 than is usual for paint; this allows application of a thick layer of the solvent composition, preferably at least 100 microns, for example 150 or 200 microns up to 250 or even 500 microns thick (wet film thickness), and it inhibits the penetration of the solvent composition into
35 the intact antifouling paint below the leached layer. The thickened solvent composition is preferably applied by

- 7 -

spray, for example airless spray, especially when treating big ships, but it can alternatively be applied by brush or roller. The thickened composition is preferably able to be applied to a ship's hull when the ship is in a substantially vertical position, for example in a dry dock, substantially without the composition running down the hull.

The solvent composition can contain one or more additional ingredients, for example it may contain a colouring pigment to aid visibility so that there is an easy check that the solvent composition has been removed before re-painting.

After the solvent composition has been applied to the leached layer on the ship's hull, it is washed off by water. A light wash (hosing down with water at a normal pressure of up to 10.5 MPa (1500 psi) is usually adequate in the case of treated layers of "self-polishing" antifouling paints and may be sufficient for layers of other antifouling paints. For treated soluble matrix and insoluble matrix antifouling paints a high-pressure water wash at at least 10.5 MPa (1500 psi) and preferably at 14 MPa (2000 psi) or more, particularly 14 to 35 MPa (2000-5000 psi), is usually preferred to ensure removal of all the treated leached layer. In general, water washing can take place any time from 5 minutes to 5 days or more after the solvent composition has been applied; but it is preferred to carry out washing 1 to 24 hours after application of the solvent composition, most preferably at least 2 or 3 hours, for example 4 to 16 hours, after application. Water washing should be continued until all the solvent composition has been washed from the hull before applying further antifouling paint.

The removal of the leached layer provides a surface of intact paint to which newly applied antifouling paint, for example a self-polishing organotin antifouling paint or an

- 8 -

eroding soluble matrix antifouling paint, will adhere securely without bubbling. If there is a substantial layer of old intact paint beneath the leached layer, this will be revealed and biocide will subsequently be leached 5 from the paint at the intended rate. Moreover, removal of the leached layer restores the colour of the painted surface from a faded appearance to an appearance more like a freshly painted surface.

The invention is illustrated by the following
10 Examples:-

Example 1

A ship's hull painted with a soluble matrix antifouling paint having a pigment volume concentration of 40% and whose binder comprised 59% by weight rosin and 41% 15 by weight vinyl ether polymer was found after 24 months in service to have developed a leached layer up to 60 microns thick which was starting to foul with barnacles and weed. The presence of the leached layer could be detected visually, as the paint had a pale frosted appearance, and 20 by light finger-rubbing, which removed a chalky deposit.

95% by weight degreasing composition sold under the name "Citrisolve Concentrate", believed to consist by weight of 64% water, 8-10% limonene, up to 5% methoxypropanol, 20-25% surfactants (including an alkyl 25 benzene sulphonate as the main surfactant) and 1% 2,6-di-t-butyl cresol, was mixed with 4% by weight "Aerosil 200" fumed silica thickener and 1% by weight of a tinter comprising 20 wt% black pigment in a 40% solution of rosin in trimethyl benzenes, to give a thixotropic solvent 30 composition.

This thickened solvent composition was sprayed on the leached layer on the ship's hull at an average wet film thickness of 150 microns. After 3 hours the hull was

- 9 -

washed by high-pressure water (3000 psi = 20.5 MPa). The water washing removed substantially all the leached layer and the solvent composition, exposing a fresh surface of intact antifouling paint. This could be seen to have a darker clearer colour than the leached layer before treatment, and after water washing no chalky deposit could be removed by finger rubbing.

Examples 2 to 4

The process of Example 1 was repeated except for the use of the following solvent compositions (% by weight based on liquid ingredients) in place of the composition used in Example 1:

	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4
15 Water	50	50	60
D-Limonene	30	-	20
White Spirit (18-20% aromatic content)	-	30	-
Methoxypropanal	5	5	-
20 Dodecylbenzene sulphonic acid amine salt	15	15	20
Aerosil 200	4	4	4
Tinter	1	1	1

In each case the leached layer was completely removed.

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Example 5

64% by weight "Citrisolve Concentrate" as described in Example 1 was mixed with 3% by weight "Aerosil 200" and 1% by weight of the tinter used in Example 1 in a high speed disperser for 15 minutes. A further 32% by weight "Citrisolve Concentrate" was mixed into the mixture for 5 minutes before any gel formation occurred. A thixotropic gel then formed about 12 hours after manufacture.

- 10 -

The resulting gel was applied by airless spray to the underwater hull area of a ferry at a thickness of 200 microns. The hull had previously been coated with a rosin-based soluble matrix antifouling paint and had a pale
5 "patina" or leached layer-of antifouling on about 50% of its underwater area, which layer could not be removed by water washing at 4,000 psi (28 MPa) . The gel composition was left in contact with the leached layer for 2 hours. The treated hull was then water washed at 4000 psi (28
10 MPa) followed by a wash at 2000 psi (14 MPa) to remove any traces of foam caused by the surfactant in the gel composition. The leached layer was completely removed and the colour of the hull reverted back to the original red colour of the soluble matrix antifouling paint.

15 The treated hull was overcoated the next day with a rosin-based soluble matrix antifouling paint. No problems of bubbling or adhesion were encountered during coating or subsequently in service.

In another application, the gel was sprayed by airless
20 spray onto the underwater hull of a container ship which had a pale leached layer of soluble matrix antifouling paint resulting from excessive time spent stationary in harbour between newbuilding and pre-delivery drydocking. The ambient temperature was 2°C, but no problems were
25 encountered during spraying. The gel was applied to the whole starboard side and the bow and stern of the port side, and was left in contact with the leached layer for about 12 hours. The starboard broadside was water-washed at 24.5 MPa (3500 psi) using a hydroblasting machine and
30 the bow and stern (both sides) were water washed at 17.5 MPa (2500 psi) with high-pressure water lances. The port broadside (which had not been treated according to the invention) was water washed at 35 MPa (5000 psi) using the hydroblasting machine. In the areas treated according to
35 the invention, the leached layer was removed and the underlying antifouling remained in its active state and

- 11 -

original red colour. The leached layer was not removed from the port broadside.

The treated hull was overcoated with an organotin self-polishing antifouling paint. The areas which had been 5 treated according to the invention showed no bubbling or detachment of the overcoating.



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- 12 -

CLAIMS

1. A process for the removal from a hull of a ship of an outer leached layer of an antifouling paint originally comprising a paint binder and a biocide but
5 from which seawater-soluble material has been leached, characterised in that a water-dispersible composition comprising a solvent for the paint binder remaining in the leached layer is applied to the surface of the antifouling paint, and the surface thus treated is subsequently washed
10 with water to remove the said water-dispersible composition containing dissolved or emulsified material of the leached layer, thereby exposing a surface of underlying intact antifouling paint.

2. A process according to claim 1, characterised in
15 that the water-dispersible composition is thixotropic.

3. A process according to claim 2, characterised in that the water-dispersible composition is applied at a wet film thickness of at least 100 microns.

4. A process according to any of claims 1 to 3,
20 characterised in that the washing with water is carried out 2 to 24 hours after the water-dispersible composition has been applied to the surface of the antifouling paint.

5. A process according to any of claims 1 to 4, characterised in that the washing with water is carried
25 out at a pressure of at least 10.5 MPa (1500 psi).

6. A process according to claim 5, characterised in that the washing with water is carried out at a pressure of from 14 to 35 MPa (2000 to 5000 psi).

7. The use of a solvent composition to remove from a
30 hull of a ship an outer leached layer of an antifouling paint originally comprising a paint binder and a biocide

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- 13 -

but from which seawater-soluble material has been leached, characterised in that the solvent composition used is a thickened water-dispersible composition comprising a solvent for the paint binder remaining in the leached
5 layer and is capable of being removed from the surface of a painted ship's hull by water washing.

8. A composition for facilitating the removal from a hull of a ship of the outer leached layer of an antifouling paint originally comprising a paint binder and
10 a biocide but from which seawater-soluble material has been leached, characterised in that the composition is a thickened water-dispersible composition comprising a water-dispersible solvent for the paint binder remaining in the leached layer and sufficient of a thickening agent
15 so that the composition can be coated on the surface of the said antifouling paint on the hull when the ship is in a substantially vertical position substantially without running down the hull.

9. A composition according to claim 8, characterised
20 in that the composition is an aqueous composition containing at least 40% by weight water.

10. A composition according to claim 8 or claim 9, characterised in that the composition contains a hydrocarbon solvent and sufficient of a surfactant to
25 render the composition water-dispersible.

11. A composition according to claim 10, characterised in that the hydrocarbon solvent comprises a terpenic hydrocarbon.

12. A composition according to claim 11,
30 characterised in that the composition contains 5 to 50% by weight of the terpenic hydrocarbon.

13. A composition according to any of claims 10 to

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- 14 -

12, characterised in that the composition contains 5 to 25% by weight of the surfactant.

14. A composition according to any of claims 8 to 13, characterised in that the composition contains an ether 5 alcohol.

15. A composition according to any of claims 8 to 14, which is thixotropic.

16. A composition according to any of claims 8 to 15, characterised in that the composition contains a silica 10 gel thickener.

17. A process according to claims 1 to 6, characterised in that the water-dispersible composition is as defined in any of claims 8 to 16.

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