

PATENT SPECIFICATION

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(54) SYSTEM FOR PROTECTING A SUB-AQUEOUS STRUCTURES AGAINST FOULING AND CORROSION

(71) I, ØYSTEIN RASMUSSEN, a Norwegian citizen of Hoslevej 119, Bekkestua, Norway, do hereby declare the invention, for which I pray that a Patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The invention relates to a system for protecting a sub-aqueous structure (e.g. a ship's hull) against fouling and normally also against corrosion, comprising a primer layer and an antifouling outer layer which contains a substance toxic to marine life.

One conventional system for protecting ship's hulls against fouling and corrosion comprises one or more coats of substantially water impermeable anti-corrosion paint, hereafter called the "primer coating", and one or two coats of at least somewhat water permeable fouling-preventive paint, hereafter designated the "anti-fouling coating".

The purpose of the primer coating is to reduce the diffusion of water to the structure surface as much as possible and the primer coating typically contains anti-corrosion constituents. The anti-fouling coating, however, has to have a significantly higher degree of water absorption, so that the conventional anti-fouling constituents, e.g. cuprous oxide and/or tributyl tin fluoride, can be dissolved by the water and thus be present in sufficiently high concentrations in the outermost layer of the anti-fouling coating to prevent fouling of the exposed surface.

Illustrative of the difference between the two types of coatings is the fact that the water absorption in an anti-fouling coating is desirably greater than 6%, while the water absorption in the primer coating ought to be less than 2% and is preferably less than 1%.

Cuprous oxide is a satisfactory anti-fouling constituent effective against algae as well as molluscs and the like, but a higher concentration of ionic copper must be present in the boundary layer between the anti-fouling coating and the sea water in order to provide effective protection against algae than is necessary to be effective against molluscs, i.e., 20 micrograms/cm²/24 hours as opposed to 10 micrograms/cm²/24 hours. Experience has shown, therefore, that algae fouling often starts less than one year after the protective system has been applied. It is therefore desirable to use other anti-fouling constituents in conjunction with cuprous oxide, for example, organic tin compounds, which provide effective protection against algae fouling in a concentration of only 1—2 micrograms/cm²/24 hours in the boundary layer of the system.

Among the most effective organic tin compounds are tributyl tin oxide (hereafter designated (TBTO) tributyl tin sulfide (TBTS) and tributyl tin chloride (TBTCI), all of which are liquid, oily substances. However, the water solubility of these substances is too high for their effective use in combination with cuprous oxide, which requires a high absorption of water in the anti-fouling coating, because the TBTO and/or TBTS and/or TBTCI is washed out of the anti-fouling coating so rapidly that it does not provide any significant extension of the period of protection against the growth of algae.

Because TBTO, TBTS and TBTCI are liquid, oily substances, they will act as plasticizers in a film of paint, and, like most plasticizers, will migrate up to the surface of the paint film.

This property is utilized in the method disclosed in the Specification of British Patent No. 1,175,978, where a coating of rubber to which TBTO was added is vulcanized in the form of sheets and glued to the underwater surface of a ship, or

alternatively vulcanised directly onto the ship. However, this method has not found much practical application, owing to the purely practical problems and high costs which it involves.

The present invention relates to a method for obtaining an extension of the period of anti-fouling protection, especially against algae, in a paint system comprising a primer coating and an anti-fouling coating and is characterized by the use of TBTO, TBTS and/or TBTCI (e.g. as a plasticizer) in the primer coating. Conveniently a thickening agent, (e.g. "Aerosil" (RTM) or "Bentone 27" (RTM), is incorporated in the primer coating, for the purpose of avoiding a gummy surface caused by too-rapid sweating of TBTO, TBTS and/or TBTCI when these are present in amounts greater than 3% by weight of the composition of the primer coating as applied. Other thickening agents which could be used, are for example, carbon black or "Dicalite WB-5" (RTM) (a type of diatomaceous earth).

"Aerosil" is a special colloidal silicic acid, and "Bentone 27" is a modified *montmorillonite*. Both are conventionally-used additives in paint compositions, and it is known that a fouling-preventive paint which includes TBTO combined with one of these thickening agents adheres well to different types of surfaces, see German Patent Publication No. 2,240,487.

The achievement of the present invention is that liquid, organic tin compounds having relatively high water solubility provide extended protection against fouling because they are incorporated in the primer coating having a low degree of water absorption, while anti-fouling substances having low water solubility, e.g. cuprous oxide and tributyl tin fluoride, are incorporated in the anti-fouling coating having a relatively high water absorption, and, by combining these two coatings in this manner, one obtains the optimal utilization of both types of anti-fouling compositions in one practical, economic system.

Anti-fouling coatings utilizing cuprous oxide are based on the fact that cuprous oxide particles will be dissolved by the sea water and become ionized. When the cuprous oxide particles have been dissolved down to a depth of approximately 40—50 microns, the supply of ionic copper at the boundary layer of the coating will normally have fallen below the critical limit of 20 micrograms/cm²/24 hours, which is the amount necessary to provide effective prevention of algae fouling. There is therefore little purpose in applying an anti-fouling coating in a thickness greater than 60—70 microns, unless one reactivates the anti-fouling coating by brushing away the binder skeleton remaining after the cuprous oxide particles have been washed out.

In the present invention, TBTO, TBTS and/or TBTCI will appear at the boundary layer of the system gradually, as it/they migrate(s) from the primer coating through the anti-fouling coating, and will gradually take over the protective function as the cuprous oxide particles or other toxic particles in the anti-fouling coating are washed out.

This principle of protection is known *per se* from US Patent No. 3,426,473. Compared to the method described therein, however, the present invention has the advantage that TBTO and/or TBTCI is/are mixed into a conventional primer coating which is not to be vulcanized thus avoiding a process which is both complicated and expensive to carry out.

Two examples of the composition of a primer coating as used in a system according to the invention, and two examples of an anti-fouling coating for use in such a system will now be given.

Primer Coating Composition

EXAMPLE 1

Component	% by weight
Chlorinated rubber and chlorinated paraffins	27.3
Anti-corrosion pigments (aluminum flakes, zinc-chromate)	16.0
Fillers (mica)	5.7
TBTO ((bis) tributyl tin oxide)	4.7
"Aerosil" and/or "Bentone 27"	1.0
Solvents	45.3

EXAMPLE 2

Vinyl rosin ("Vinglite VROH" (RTM) (Union Carbide)	5.4
Acrylic rosin (Elvacite (2013 (RTM) (Du Pont))	6.4
Coal tar	13.9
Fillers (iron oxide and mica)	36.6

EXAMPLE 2 (contd.)

TBTO	6.5
"Aerosil"	1.4
Solvents	29.8

5 In both these examples the TBTO can be partly or fully substituted by TBTCI. 5

Anti-Fouling Coating Composition

EXAMPLE 3

Component	% by weight	
Chlorinated rubber, plasticizers and rosin	13.0	
Cuprous oxide (Cu(I)oxide)	46.0	10
Other pigments (zinc chromate and iron oxide)	11.0	
Filler (mica)	3.0	
Solvents	27.0	

EXAMPLE 4

Chlorinated rubber	8.0	15
Plasticizers	4.0	
Natural rosin	8.0	
Metallo-organic toxic substances (TBTF)	15.0	
Pigments and fillers (zinc oxide and "Microdol" (RTM) (Norw. Talc.))	40.0	20
Solvents	25.0	

25 Either primer coating can be used with either anti-fouling coating. Other compositions are also possible. The primer coating ought to have a thickness of between 50 to 80 microns. It has been found that the period of effective protection can be extended by at least 3 to 6 months by the system of this invention. 25

TBTCI, TBTO and TBTS have different solubilities in water. TBTCI has the highest solubility and TBTS the lowest. By using a combination of at least two of these organic tin compounds effective migration rates of toxic substances over an extended period can be obtained.

30 WHAT I CLAIM IS:— 30

1. A system for protecting a sub-aqueous structure against fouling by applying a primer coating and an anti-fouling coating (both as hereinbefore defined) to the structure to be protected characterised in that TBTO, TBTS and/or TBTCI is/are used in the primer coating.

35 2. A system as claimed in claim 1, in which a thickening agent is incorporated in the primer coating and the tin compound or tin compounds is (are) present in an amount greater than 3% by weight of the composition of the primer coating as applied. 35

40 3. A system as claimed in claim 2, in which the thickening agent is a colloidal silicic acid, a modified *montmorillonite*, a diatomaceous earth or carbon black. 40

4. A system as claimed in claim 2 or claim 3, in which the thickening agent is present in amount of not more than 2% by weight of the composition of the primer coating as applied.

45 5. A system as claimed in any preceding claim, in which the anti-fouling coating contains cuprous oxide and/or a solid organometallic toxic substance. 45

6. A system as claimed in any preceding claim, in which the water absorption of the anti-fouling coating is greater than 6% and the water-absorption of the primer coating is less than 2%.

50 7. A system for protecting a ship's hull which comprises applying primer and anti-fouling coatings as hereinbefore defined, the coatings being produced by first 50

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EXAMPLE 2 (contd.)

TBTO	6.5
"Aerosil"	1.4
Solvents	29.8

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Anti-Fouling Coating Composition

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Solvents	25.0

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2. A system as claimed in claim 1, in which a thickening agent is incorporated in the primer coating and the tin compound or tin compounds is (are) present in an amount greater than 3% by weight of the composition of the primer coating as applied.

3. A system as claimed in claim 2, in which the thickening agent is a colloidal silicic acid, a modified *montmorillonite*, a diatomaceous earth or carbon black.

4. A system as claimed in claim 2 or claim 3, in which the thickening agent is present in amount of not more than 2% by weight of the composition of the primer coating as applied.

5. A system as claimed in any preceding claim, in which the anti-fouling coating contains cuprous oxide and/or a solid organometallic toxic substance.

6. A system as claimed in any preceding claim, in which the water absorption of the anti-fouling coating is greater than 6% and the water-absorption of the primer coating is less than 2%.

7. A system for protecting a ship's hull which comprises applying primer and anti-fouling coatings as hereinbefore defined, the coatings being produced by first



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applying a composition selected from Examples 1 and 2 as given herein and then a composition selected from Examples 3 and 4 as given herein.

8. A ship whose hull is protected by a system as claimed in any preceding claim.

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