

PATENT SPECIFICATION

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(54) METHOD OF COMBATTING AQUATIC PARASITES AND COMPOSITION FOR USE IN THE METHOD

(71) We, RHONE-PROGIL, a French Body Corporate of 6, Rue Piccini, Paris (16^{eme}), France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of combatting aquatic parasites and to an anti-fouling composition for use in the method.

It is known that all objects under seawater are subject to fouling due to the proliferation of marine parasites, especially algae, molluscs and crustaceans. Civil engineering works such as port installations, piles, landing-stages, lock gates, well-drilling stations and sea-water treatment installations are overrun by deposits due to numerous marine organisms which are very difficult to remove. The harmful action of the various aquatic parasites is particularly critical on cellulosic materials such as timber; thus a heavy crust forms on the hulls of ships, which resists the smooth gliding of the keel through the water and causes a reduction in speed which can sometimes be as much as 25%.

Examples of the parasites which can be responsible for the above disadvantages are molluscs, for example stone borers, xylophages and shipworms, crustaceans for example Limnoria, Chelura and Cirripedia, and algae for example Annelida, Hydroids, Bryozoa and Ascidiace.

In order to overcome these disadvantages, it is usual in the shipping industry to protect the keels of ships by several layers of coatings which generally consist of a wash primer, an anti-corrosion coating and then an anti-fouling paint containing substances which are toxic towards marine micro-organisms. Of the toxic substances usually employed, copper compounds are the most

important. Cuprous oxide is in practice recommended as one of the most efficient constituents of the above paint.

It has now been found that if the conventional copper compounds in these paints are replaced by cuprous alkylthiocarbamates or alkylene-bis-dithiocarbamates, the copper content in the anti-fouling paints can be much lower (generally down to 1/10th) than that required when cuprous oxide is employed.

The above cuprous carbamates can be obtained by reacting, while stirring, an alkali metal dithiocarbamate with cuprous chloride in an aqueous alkali chloride.

The carbamates can be employed in conjunction with other metal alkylthiocarbamates or alkylene-bis-dithiocarbamates, for example those of manganese, cadmium, zinc, nickel and iron. The cuprous carbamate can be either mixed with the other metal carbamates, for example by co-precipitation, or can be deposited on granules of the latter in the form of a coating; these processes and the products thereof are disclosed in British Patent Application No. 37048/68 (Serial No. 1 199 677).

The invention therefore provides a method of combatting aquatic parasites, the method comprising applying, to the habitat of the parasites, a cuprous salt which is cuprous alkylthiocarbamate or alkylene-bis-dithiocarbamate.

The invention also provides an anti-fouling composition comprising the above cuprous salts and at least one ingredient conventionally used in anti-fouling compositions; suitably containing 25-50% of the salts.

It has already been proposed to use metal thiocarbamates containing copper in marine anti-fouling compositions. However the copper in these compositions has always been in the cupric form. The cupric (generally called "copper" in the literature) alkyl-

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dithiocarbamates or alkylene-bis-dithiocarbamates have very much lower chemical stability and heat stability than the corresponding cuprous compounds. Furthermore, their pigment properties and their resistance to ultraviolet rays are mediocre compared with those of the cuprous carbamates. Finally they are difficult to disperse in the components, especially the solvents, usually employed in the formulation of paints and varnishes.

The anti-fouling compositions of the invention, on the other hand, possess all the pigment properties generally desired for paint formulations for timber, steel or other substrates to be protected against parasitic animals. The cuprous carbamates can be obtained according to known processes in the form of fine powders of uniform particle size, which improves their penetrating power in ligneous media. Furthermore, they are very stable to atmospheric agents and are in particular resistant to sunlight. Finally, they can, depending on the nature and/or the relative proportions of the metals which they contain, provide a wide range of shades, varying from yellow to black-brown, which shades are not affected even if accidental partial sedimentation of the pigment occurs.

Furthermore, the cuprous dithiocarbamates which are obtained *in situ* during the preparation of the well known dithiocarbamates of zinc ("zineb"), manganese ("maneb") and iron ("ferreb") are very stable and non-inflammable even when exposed to high temperatures, as has already been shown in the Patent Application mentioned above.

Examples of the conventional ingredients used in anti-fouling compositions are natural binders or synthetic polymers such as drying oils, colophony and its derivatives, polyvinyl and polyacrylic compounds, epoxy resins, alkyd resins which may or may not be oil-modified and polyurethanes, as well as solvents such as aromatic hydrocarbons, for example toluene or xylene, aliphatic hydrocarbons, for example the crude cuts from the distillation of petroleum, ketones such as methyl ethyl ketone or methyl isobutyl ketone, and polymer plasticisers such as the highly chlorinated diphenyls or dialkylphthalates. The binders can also be in the form of aqueous emulsions of polyvinyl or polyacrylic compounds. These compositions can also contain other known adjuvants such as dispersing agents for example alkali pyrophosphates or soya lecithin, anti-foaming agents such as silicones or pigments and supplementary biocidal agents, especially fungicides.

The amount of metal dithiocarbamate to be used depends on the viscosity and the amount of paint to be deposited on the

substrates to be protected. As a result, it can vary within wide limits but, as a general rule, amounts which give a coating weight on a substrate of 30 and 60 g. of cuprous copper/m² of surface area of the substrate, are sufficient to achieve the desired molluscicidal and algicidal effect.

The invention is illustrated by the following Examples wherein, unless otherwise indicated, all the parts are parts by weight.

EXAMPLE 1

The following formulation was prepared by mixing in a ball mill:

Cuprous ethylene-bis-dithiocarbamate	35 parts	
Colophony glycerin ether	30 "	
Pentachlorodiphenyl	5 "	85
Xylene	30 "	

This paint, which contained 11.5% of cuprous copper, was applied to steel sheet previously coated with a conventional anti-corrosion protective layer, to give a coating weight of 330 g. of paint per m² (or 38 g/m² of Cu).

After a test of 1 year carried out in the sea on the keel of a boat, the protection obtained was equivalent to that obtained with an anti-fouling paint of the same composition, but in which a coating weight of 380 g. of cuprous copper per m² was applied in the form of cuprous oxide.

EXAMPLE 2

A paint of the following composition was manufactured:

Cuprous ethylene-bis-dithiocarbamate	30 parts	
Red iron oxide	10 "	
Polyvinyl chloride resin	8 "	110
Colophony glycerine ether	6 "	
Dibutyl phthalate	1.5 "	
Methyl isobutyl ketone	13.5 "	
Toluene	31 "	

The paint was applied to sheet metal in 3 successive layers so as to provide a total coating weight of 350 g. per m² (or 35 g/m² of cuprous copper). The protection system proved equivalent, in its anti-fouling action, to one consisting of 3 layers (providing a cuprous copper coating weight of 300 g/m²) of a paint of identical composition but based on cuprous oxide.

EXAMPLE 3

300 G/m² (or 40 g/m² of cuprous copper) of a molluscicidal paint of the following composition were applied to a timber raft

immersed in the sea:

	Cuprous monomethyldithiocarbamate	35 parts
5	Colophony glycerine ether	30 "
	Pentachlorodiphenyl	5 "
	Xylene	30 "

- 10 After one year, it was found that the protection was equivalent to that of a paint of the same composition but in which 300 g. of copper (in the form of cuprous oxide) per m² had been deposited.

15 EXAMPLE 4

An anti-fouling marine paint was made up from the following constituents:

20	Ferrous and cuprous ethylene-bis-dithiocarbamate	40 parts
	Colophony glycerine ether	30 "
	Hexachlorodiphenyl	5 "
25	Organic solvent	25 "

- 30 On applying 350 g/m² (or 29 g/m² of cuprous copper) of this paint to a substrate exposed to the action of marine micro-organisms for one season, the protection obtained was equivalent to that obtained with the same paint except that cuprous oxide was used as the pigment at a coating weight of 300 g/m² of copper.

- 35 The mixed dithiocarbamate was prepared in accordance with the Patent Application mentioned above, by reacting ferrous sulphate heptahydrate (0.5 mol) and cuprous chloride (1 mol.) in a sodium chloride brine (200 g./l.) with 25% aqueous sodium ethylene-bis-dithiocarbamate (1 mol.) at 26°C and pH 2. After filtration and washing with water, a paste containing about 40% solids was obtained.

45 EXAMPLE 5

- A paint obtained by replacing the ferrous and cuprous dithiocarbamate of Example 4 by granules of a mixed ethylene-bis-dithiocarbamate of zinc and cadmium coated with cuprous ethylene-bis-dithiocarbamate by precipitation *in situ* had the same anti-fouling properties.

- 50 The granules were prepared as follows. 55 Zinc chloride (0.85 mol.) and cadmium chloride (0.10 mol.) in water (1.8 l.) were reacted at about 25°C and pH 3.5, with sodium ethylene-bis-dithiocarbamate (0.95 mol.) in water (1.8 l.). After filtration and 60 washing with water, the filter cake was suspended in a solution of cuprous chloride (0.5 mol.) in brine (50 g. sodium chloride per litre of water). The mixture was reacted with sodium ethylene-bis-dithiocarbamate (0.25

mol.) in water (1.8 l.) at 25°C and pH 2. 65 After filtration and washing with water, a paste (about 40% solids) of the desired orange-yellow pigment was obtained. The dry powder had a colour similar to that of the so-called "Oregon" pine. 70

WHAT WE CLAIM IS:—

1. A method of combatting aquatic parasites, the method comprising applying, to the habitat of the parasites, a cuprous salt which is cuprous alkylthiocarbamate or alkylene-bis-dithiocarbamate. 75
2. A method according to Claim 1 wherein the cuprous salt is employed in the substantial absence of cupric alkylthiocarbamate or alkylene-bis-dithiocarbamate. 80
3. A method according to Claim 1 or 2 wherein the parasite is an alga or mollusc.
4. A method according to any one of the preceding claims wherein cuprous ethylene-bis-dithiocarbamate or cuprous monomethyldithiocarbamate is employed. 85
5. A method according to any one of the preceding claims wherein the cuprous salt is employed in conjunction with a zinc, manganese, iron, cadmium or nickel alkylthiocarbamate or alkylene-bis-dithiocarbamate. 90
6. A method according to any one of the preceding claims wherein the cuprous salt is applied to timber. 95
7. A method according to Claim 1 substantially as described herein.
8. An anti-fouling coating composition comprising a cuprous salt as defined in Claim 1 or 4, and at least one ingredient 100 conventionally used in anti-fouling coating compositions.
9. A composition according to Claim 8 wherein cupric alkylthiocarbamate and alkylene-bis-dithiocarbamate are substantially 105 absent.
10. A composition according to Claim 8 or 9 in the form of a paint.
11. A composition according to Claim 10 which contains such an amount of the cuprous salt that, when the paint is applied to a substrate, a coating weight of 30 to 60 g. of cuprous copper per square metre of substrate is obtained. 110
12. A composition according to any one of Claims 8 to 11 which contains at least one of a drying oil, colophony or a derivative thereof, a polyvinyl or polyacrylic compound, an epoxy resin, an alkyd resin or a polyurethane. 115
13. A composition according to any one of Claims 8 to 12 comprising also a zinc, manganese, iron, cadmium or nickel alkylthiocarbamate or alkylene-bis-dithiocarbamate. 120
14. A composition according to Claim 13 wherein granules of the zinc, manganese, iron, cadmium or nickel alkylthiocarbamate. 125

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	Pentachlorodiphenyl	5 "
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2. A method according to Claim 1 wherein the cuprous salt is employed in the substantial absence of cupric alkylthio- 80 carbamate or alkylene-bis-dithiocarbamate.

3. A method according to Claim 1 or 2 wherein the parasite is an alga or mollusc.

4. A method according to any one of the preceding claims wherein cuprous ethylene-bis-dithiocarbamate or cuprous mono- 85 methyldithiocarbamate is employed.

5. A method according to any one of the preceding claims wherein the cuprous salt is employed in conjunction with a zinc, man- 90 ganese, iron, cadmium or nickel alkylthiocarbamate or alkylene-bis-dithiocarbamate.

6. A method according to any one of the preceding claims wherein the cuprous salt is applied to timber. 95

7. A method according to Claim 1 substantially as described herein.

8. An anti-fouling coating composition comprising a cuprous salt as defined in Claim 1 or 4, and at least one ingredient 100 conventionally used in anti-fouling coating compositions.

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13. A composition according to any one of Claims 8 to 12 comprising also a zinc, manganese, iron, cadmium or nickel alkylthiocarbamate or alkylene-bis-dithiocarbamate. 125

14. A composition according to Claim 13 wherein granules of the zinc, manganese, iron, cadmium or nickel alkylthiocarba-



mate or alkylene-bis-dithiocarbamate are coated with the cuprous salt.

15. A composition according to Claim 8 substantially as described in any one of the 5 Examples.

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