

"Marine coatings, production and use thereof"

5 This invention relates to marine coatings and to the production and use thereof .

There are known marine coatings in which an essential component is a copolymer containing units of alkyl acrylates and methacrylates and units of triorganotin esters of acrylic and methacrylic acid. The alkyl acrylate and methacrylate units impart hardness to the film obtained when the marine coating is applied to a substrate, and the triorganotin ester units impart biocidal as well as self-polishing effect. During use the triorganotin units are split off from the polymer by hydrolysis and/or ion exchange, whereby the film of the marine coating exerts a desired biocidal effect. At the same time the film is degraded, and this results in the self-polishing effect.

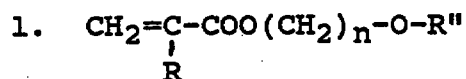
Thus, to obtain a satisfactory self-polishing effect, a certain amount of triorganotin units must be present in the copolymer used in the marine coating, since the self-polishing effect is a consequence of the cleavage of said units. On the other hand, it is desired to keep the amount of triorganotin units as low as possible, with due regard to the desired biocidal and self-polishing effect, since the triorganotin monomers are rather expensive and also have a softening effect on the copolymer.

Copolymers of the above type are disclosed i.a. in British Patent No. 1 457 590.

In Norwegian Patent Application 81.3553 it is suggested to replace some or all of the triorganotin ester units by methyl acrylate and/or ethyl acrylate units. The marine coating may contain some additional

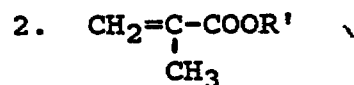
biocide, particularly if the copolymer does not
5 contain any triorganotin ester units. Said methyl
acrylate and ethyl acrylate units will to some extent
be hydrolysed in water, and will impart a self-
polishing effect to the final coating. However, due to
10 the low rate of hydrolysis of the resulting copolymer,
the self-polishing effect will not be entirely
satisfactory.

According to the present invention there is
provided a marine coating which in addition to
ordinary paint components, such as pigments, dyes,
15 solvents, etc., contains a copolymer of units of the
following monomers:



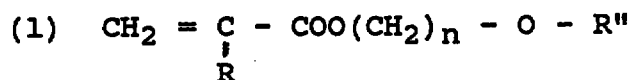
R = H or CH₃, R'' = CH₃ or C₂H₅, n = 1 or 2,

20 and



R' = C₁₋₄ alkyl

Hence, in one embodiment, the present invention
25 provides a method for preparing a marine coating
composition which hydrolyses under marine conditions,
which method comprises mixing a film-forming acrylic
polymer comprising units of the following monomers:



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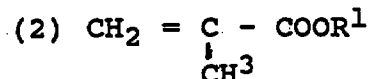
wherein

R represents H or CH₃

R'' represents CH₃ or C₂H₅;

and

35 n represents 1 or 2;



wherein

R¹ represents C₁₋₄ alkyl;

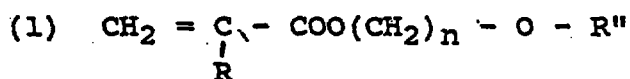
and, optionally,

- 5 (3) triorganotin methacrylate or acrylate;
with one or more conventional marine paint components.

In another embodiment, the present invention provides a process for the production of a marine coating which hydrolyses under marine conditions,
10 which process comprises applying to a marine surface a film-forming acrylic polymer comprising units as defined above or a marine coating composition prepared according to the above method.

Basically, the present invention relates to the
15 use of a film-forming acrylic polymer comprising units as defined above in a marine coating composition.

The present invention further provides a coating composition which hydrolyses under marine conditions and which comprises a film-forming acrylic polymer
20 comprising units of the following monomers:



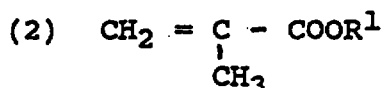
wherein

R represents H or CH₃;

25 R'' represents CH₃ or C₂H₅;

and

n represents 1 or 2;



30 wherein

R¹ represents C₁-C₄ alkyl;

and

(3) triorganotin methacrylate or acrylate.

The units of monomer no. 1 are readily hydrolysed to
35 form free carboxyl groups, resulting in a polymer which is gradually degraded to provide a self-polishing effect.

Monomer no. 2 is present to impart sufficient hardness to the film.

Preferably, the acrylic polymer comprises 1 - 80
5 percent by weight of (1), 20 - 85 percent by weight of
(2) and up to 60 percent by weight of (3); more
preferably from 15 to 80 percent by weight of monomer
No. 1. In one particular embodiment, the acrylic
polymer comprises 5 - 40 percent by weight of (1), 20
10 - 70 percent by weight of (2) and 1 - 55 percent by
weight of (3).

A preferred representative of monomer No. 1 is 2-
methoxyethyl acrylate, a preferred representative of
monomer No. 2 is methyl methacrylate and a preferred
15 triorganotin component is tributyltin methacrylate.

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As pointed out above, a marine coating which
5 comprises a copolymer containing units of the above
two monomers No. 1 and No. 2, may also contain
biocidal components to obtain the desired biocidal
effect, such as cuprous oxide, dithiocarbamates and
triorganotin compounds as known in the state of the
10 art.

In addition to the two types of monomer disclosed
above, the copolymers used in the marine coatings of
the present invention may also contain units of
triorganotin acrylates and methacrylates. Examples of
15 such triorganotin monomers are tributyltin
methacrylate and acrylate, tripropyltin methacrylate
and acrylate and triphenyltin methacrylate and
acrylate. The triorganotin monomers may constitute up
to 60, particularly 1 - 55, percent by weight of the
20 copolymer (terpolymer). Monomer No. 1 is then normally
present in an amount of 1 - 80 percent by weight,
particularly 5 - 40 percent by weight, and monomer No.
2 is then normally present in an amount of 20 - 85,
particularly 20 - 70 percent by weight.

25 The copolymers containing monomers No. 1 and 2
may be prepared by ordinary polymerisation of the
suitable monomers, using suitable initiators and
polymerisation conditions. When it is desired to
prepare a copolymer (terpolymer) which also contains
30 triorganotin methacrylate or acrylate units, this may
be done either by polymerising monomers No. 1 and 2
together with the desired triorganotin methacrylate or
acrylate monomer, or monomers No. 1 and 2 may be
polymerised with methacrylic or acrylic acid, and the
35 carboxyl groups on the resulting polymer are then
esterified with triorganotin groups in a per se known
manner.

Example 1

Methyl methacrylate (300 g; 3.00 mole) and 2-methoxyethyl acrylate (200 g; 1.54 mole) were dissolved in xylene (750 g). Azobisisobutyronitrile (4 g; 0.024 mole) was added and the solution heated to 75°C, with stirring and under nitrogen.

The polymerisation was carried out at the above temperature for a period of 5 hours and was monitored by the change in refractive index.

The temperature was raised to 100°C for 30 minutes to destroy any residual activity of the initiator.

The solution obtained was that of a copolymer of methyl methacrylate - 2-methoxyethyl acrylate (60:40 by weight).

Example 2

Tributyltin methacrylate (150 g; 0.40 mole), methyl methacrylate (250 g; 2.50 mole) and 2-methoxyethyl acrylate (100 g; 0.77 mole) were dissolved in xylene (750 g).

Azobisisobutyronitrile (4 g; 0.02 mole) was added and polymerisation was carried out in a similar manner as in example 1.

The solution obtained was that of a terpolymer of tributyltin methacrylate - methyl methacrylate - 2-methoxyethyl acrylate (30:50:20 by weight).

Example 3

Tributyltin methacrylate (275 g; 0.73 mole), methyl methacrylate (210 g; 2.10 mole) and 2-methoxyethyl acrylate (15 g; 0.12 mole) were dissolved in xylene (750 g).

Azobisisobutyronitrile (4 g; 0.02 mole) was added and polymerisation was carried out in a similar manner

as in example 1.

The solution obtained was that of a terpolymer of tributyltin methacrylate - methyl methacrylate - 2-methoxyethyl acrylate (55:42:3 by weight).

Example 4

409.2 g of the copolymer solution from example 1 was mixed with cuprous oxide (365.4 g), zinc oxide (151.2 g), Aerosil® (colloidal silica) (4.0 g), Bentone® (thickening agent) (8.0 g), denaturated ethanol (4.8 g) and xylene (57.4 g), and milled overnight to produce a paint with a cuprous oxide - zinc oxide ratio of 70:30 by volume.

Example 5

409.2 g of the terpolymer solution from example 2 was mixed with cuprous oxide (365.4 g), zinc oxide (151.2 g), Aerosil® (4.0 g), Bentone® (8.0 g), denaturated ethanol (4.8 g) and xylene (57.4 g) and milled overnight to produce a paint with a cuprous oxide - zinc oxide ratio of 70:30 by volume.

Example 6

As Example 4, with the exception that the polymer of Example 1 was replaced by that of Example 3.

The paints described in Example 4, 5 and 6 were tested for polishing using a rotor apparatus with a peripheral speed of 17 knots (about 31 km/h), in sea water, at an average temperature of 23°C.

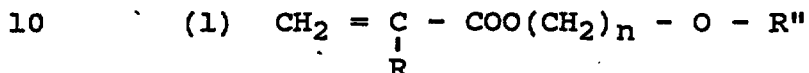
A commercially successful selfpolishing paint containing organotin polymer (X) was used as reference. The test was carried out over a period of 90 days and the thickness of the paint film was determined by electromagnetic induction.

Paint	Polishing Rate ($\mu\text{m}/\text{year}$)
X	60
Example 4	52
Example 5	72
Example 6	80

Claims

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1. A method for preparing a marine coating composition which hydrolyses under marine conditions, which method comprises mixing a film-forming acrylic polymer comprising units of the following monomers:



wherein

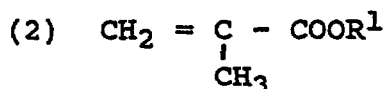
R represents H or CH₃;

R'' represents CH₃ or C₂H₅;

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and

n represents 1 or 2;



wherein

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R¹ represents C₁-C₄ alkyl;

and, optionally,

(3) triorganotin methacrylate or acrylate;

with one or more conventional marine paint components.

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2. A process for the production of a marine coating which hydrolyses under marine conditions, which process comprises applying to a marine surface a film-forming acrylic polymer comprising units as defined in claim 1 or a marine coating composition prepared according to claim 1.

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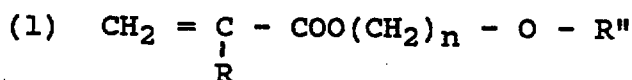
3. The use of a film-forming acrylic polymer comprising units as defined in claim 1 in a marine coating composition.

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4. The invention as claimed in any of claims 1 to 3 substantially as herein described.



5. A coating composition which hydrolyses under
5 marine conditions and which comprises a film-forming
acrylic polymer comprising units of the following
monomers:



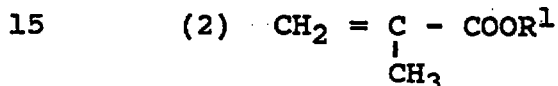
10 wherein

R represents H or CH₃;

R'' represents CH₃ or C₂H₅;

and

n represents 1 or 2;



wherein

R¹ represents C₁-C₄ alkyl;

and

20 (3) triorganotin methacrylate or acrylate.

6. A composition as claimed in claim 5 wherein the
acrylic polymer comprises:

(1) 2-methoxyethyl acrylate;

25 (2) methyl methacrylate;

and

(3) tributyltin methacrylate.

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7. A composition as claimed in claim 5 or claim 6
5 wherein the acrylic polymer comprises 1 - 80 percent
by weight of (1), 20 - 85 percent by weight of (2) and
up to 60 percent by weight of (3).

8. A composition as claimed in claim 7 wherein the
10 acrylic polymer comprises 15 - 80 percent by weight of
(1).

9. A composition as claimed in any of claims 5 to 7
wherein the acrylic polymer comprises 5 - 40 percent
15 by weight of (1), 20 - 70 percent by weight of (2) and
1 - 55 percent by weight of (3).

10. A composition as claimed in claim 5 substantially
as herein described with particular reference to the
20 Examples.

