

Description

This invention is concerned with anti-fouling marine paints used on surfaces likely to come into contact with aquatic fouling organisms such as algae, seaweed and barnacles, for example on ships or boats, or on the outfalls for cooling water from power stations. More particularly it is concerned with improvements in binders for such paints.

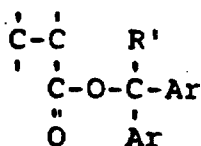
The most successful anti-fouling paints in recent years have been self-polishing anti-fouling paints which use binders which are linear polymers containing pendant side groups (hereinafter called "leaving groups") which are liberated from the polymer by reaction with seawater, the residual polymer being sufficiently dispersible or soluble in seawater to be swept away from the paint surface, exposing a fresh layer of the binder able to undergo a similar reaction with seawater. Such paints are described for example in British patent 1 457 590. The gradual thinning of the paint film controls the release of a biocide active against fouling and present either as a pigment in the paint or as a leaving group. The well-known benefits of such self-polishing paints are that the paint film tends to at least retain its initial smoothness and may even become smoother from the action of relatively moving water and that the biocide contained in the paint tends to be delivered from the surface at a more uniform or constant rate.

The only commercially significant self-polishing paints employ binders which comprise triorganotin ester leaving groups. The triorganotin provides some of the biocidal action of the paints and the triorganotin ester readily undergoes the hydrolysis on which the self-polishing action is dependant. The biocidal activity can be augmented by other anti-fouling substances dispersed or dissolved in the paint film. There may be advantages in replacing some or all of the triorganotin leaving groups by other leaving groups, which are not necessarily biocidal, both for cost reasons and because the powerful biocidal effects of triorganotin may not be desired. There has been concern about the environmental effect of triorganotin biocides released from yachts in particular.

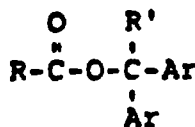
There have been many proposals for a leaving group which substitutes for the triorganotin in forming an easily hydrolysable ester with a polycarboxylic acid polymer, but a commercial self-polishing paint in which the triorganotin moiety has been replaced is still awaited. International patent publication WO 84/02915 suggests a wide range of organic leaving groups for use in antifouling paint binders but these generally do not hydrolyse quickly enough in the conditions of use, that is in contact with natural water, such as seawater, having a pH of from 8 to 8.4.

We have found new binders having a rate of hydrolysis suitable for use in anti-fouling paints.

An anti-fouling marine paint according to the invention comprises a pigment, a marine biocide which may or may not be identical to the pigment, and a film-forming binder which is a hydrolysable polymer containing units corresponding to an ester of an olefinically unsaturated acid. The polymer is characterised by a content of units of the formula



which may be regarded as being derived from an alphaaryl alkyl ester of the formula



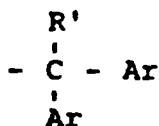
where

R is an alpha, beta-unsaturated organic group,

each Ar independently is an aryl group and

R' is a hydrogen atom or an alkyl or aryl group.

Each aryl group Ar is preferably a phenyl or naphthyl group which may be substituted. The two groups Ar may be identical or different. The unsaturated acyloxy group R-COO- is preferably an acrylate or methacrylate group or a maleate or itaconate group, whose second carboxyl group may be esterified with a further group of the formula



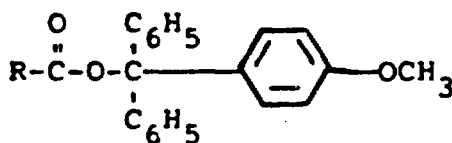
The polymer used in the paints of the present invention generates a water-soluble residue by hydrolysis of the aralkyl carboxylate linkage, releasing aralkyl compounds into the seawater. The aralkyl compounds are generally not toxic to marine life and the paints of the present invention therefore contain a separate marine biocide.

Alpha-aryl alkyl ester groups in which not only Ar but also R' is aryl are generally more readily hydrolysed than groups in which R' is hydrogen or alkyl and only Ar is aryl. One or more of the aryl groups can be substituted by one or more (e.g. two) electron-releasing groups, for example alkoxy, acyloxy, aryl or tertiary amino groups. The effect of electron-releasing groups, which are preferably positioned ortho or para to the alkyl substituent, is to increase the rate of hydrolysis of the ester. Where R' is hydrogen or alkyl at least one of the groups Ar is preferably substituted by an electron-releasing group. Where R' is aryl the three aryl groups are preferably unsubstituted or contain in total only one electron-releasing group; they may alternatively be substituted by one or more other groups, for example alkyl, chloro, NH₂ or nitro groups.

The class of alpha-aryl alkyl esters therefore provides a wide choice of esters from which polymers for use in this invention may be made, with the opportunity to achieve the desired rate of hydrolysis of the polymer by making homopolymers of those esters having relatively slow rates of hydrolysis or copolymers of those having faster rates.

Specific examples of alpha-aryl alkyl esters of ethylenically unsaturated acids are triphenylmethyl acrylate or methacrylate (i.e. R is CH₂=CH or CH₂=C(CH₃), R' and Ar are all phenyl), diphenyl (p-methoxyphenyl)-methyl acrylate or methacrylate (i.e. R is CH₂=CH or CH₂=C(CH₃), R' and one Ar are both phenyl and one Ar is p-methoxyphenyl), tris(p-chlorophenyl)methyl acrylate or methacrylate, phenyl bis(p-methoxyphenyl)methyl acrylate or methacrylate and bis(p-methoxyphenyl)methyl acrylate or methacrylate.

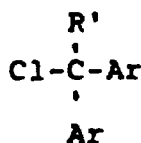
Polymers, particularly copolymers, of a diphenyl (p-methoxyphenyl)methyl ester of the formula:



are particularly preferred as binders for the anti-fouling paints of the invention. Such polymers have not previously been described.

Polymers of triphenylmethyl methacrylate are known from the literature as optically active polymers, for example J. Polymer Sci. (Part B 6 (10), 753 (1968) and Polym. Chem. Ed. 13, 1161 (1975) and Japanese published (unexamined) Patent Application 56.106 907. There has been no suggestion of any use of the polymers as coatings.

The alpha-aryl alkyl esters can generally be prepared by reacting an alpha-aryl alkyl chloride of the formula:



with a metal salt of the unsaturated carboxylic acid RCOOH, for example the potassium or sodium salt, in an organic solvent, for example toluene or xylene. Alternatively, they may be prepared by the process described in European patent Application 134 005.

The film-forming polymers can be prepared by addition polymerisation of the alpha-aryl alkyl ester, with or without one or more comonomers, in an organic solvent such as xylene, toluene, butyl acetate, butanol, butoxyethanol or ethoxyethyl acetate at a temperature of 60 - 100°C using a free radical catalyst such as benzoyl peroxide or azobisisobutyronitrile. Some alpha-aryl alkyl esters, for example triaryl methyl esters such as triphenyl methyl methacrylate, do not polymerise as readily as simpler acrylic monomers such as methyl methacrylate, and care should be taken that the triaryl methyl ester and its comonomer truly copolymerise. The polymerisation can be carried out using a controlled monomer feed, with a higher proportion of the triaryl methyl ester being present in the early stages of polymerisation.

The polymers may alternatively be made by reacting the corresponding alpha-aryl alkanol with a preformed polymer of the ethylenically unsaturated acid or its anhydride obtained by addition polymerisation of an appropriate precursor based on the acid moiety of the ester, referred to as an acidic precursor. The

10

polymer/alpha-aryl alkanol reaction is preferred for making maleate ester polymers. The preformed polymer of the precursor can be obtained in a known manner, for example by addition polymerisation of the monomer with or without one or more comonomers at 60 - 100°C in an organic solvent using a free radical catalyst in the case of maleic anhydride.

5 The polymer of the present invention preferably contains at least 20 mole per cent of units corresponding to the alpha-aryl alkyl ester. For reasons explained above, the polymer may be a homopolymer of a slowly hydrolysing species of the ester, so that the polymer preferably contains from 20 to 100 mole per cent of units corresponding to the alpha-aryl alkyl ester. Most preferably it is a copolymer containing 25 to 40 mole per cent of units corresponding to the alpha-aryl alkyl ester with at least one ethylenically unsaturated comonomer. The
10 comonomer is copolymerised with the alpha-aryl alkyl ester or the acid or acid anhydride precursor of such an ester. The comonomer is selected to be innocuous to the ester, acid or acid anhydride as appropriate. Such comonomers include, but are not limited to, acrylic esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate or 2-ethyl hexyl methacrylate, styrene, acrylonitril, vinyl acetate, vinyl butyrate, vinyl chloride or vinyl pyridine. The polymer may include a minor proportion, preferably less than 25 per cent by
15 weight, of units corresponding to a triorganotin ester of an unsaturated carboxylic acid to provide a paint having a reduced emission of triorganotin groups but having the self-polishing property of known organotin copolymer paints.

Polymers of alpha-aryl alkyl methacrylates, particularly triaryl methyl methacrylate, may be brittle. Copolymers of such methacrylates preferably use a plasticising monomer, for example butyl acrylate, 2-ethylhexyl acrylate or ethyl acrylate, as at least part of the ethylenically unsaturated comonomer content. Polymers of alpha-aryl alkyl acrylates are less brittle.

To form the paint, the hydrolysable polymer binder is mixed with the pigment or pigments used in the paint and with the marine biocide if this is different from the pigment(s). Conventional blending procedures can be used. The pigment generally has a solubility in seawater of below 10 parts per million by weight and is
25 preferably a sparingly soluble pigment having a solubility in seawater of from 0.5 to 10 parts per million, for example cuprous oxide, cuprous thiocyanate, zinc oxide, zinc chromate, zinc ethylene bis(dithiocarbamate), zinc dimethyl dithiocarbamate or zinc diethyl dithiocarbamate. These sparingly soluble copper and zinc compounds are generally marine biocides. These sparingly soluble pigments produce water-soluble metal compounds on reaction with seawater so that the pigment particles do not survive at the paint surface; this
30 aids the smooth dissolution of the paint in relatively moving seawater. Mixtures of sparingly soluble pigments can be used, for example cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate) which are the most effective biocidal pigments can be mixed with zinc oxide which dissolves slightly more rapidly in seawater and is more effective at inducing the smooth dissolution of the paint.

The paint composition can additionally or alternatively contain a pigment which is not reactive with seawater and may be highly insoluble in seawater (solubility below 0.5 ppm by weight) such as titanium dioxide or ferric oxide. Such highly insoluble pigments are preferably used in proportions up to 40 per cent by weight of the total pigment component of the paint, most preferably less than 20 per cent by weight.

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

Paints according to the invention, particularly if based on polymers of an alpha-aryl alkyl methacrylate, may contain a plasticiser, for example tritolyl phosphate, dioctyl phthalate, dibutyl phthalate, tributyl phosphate, butyl benzyl phosphate or dibutyl tartrate.

If it is desired to retard the rate of dissolution of the paint as well as plasticising it, a hydrophobic retarder which also acts as a plasticiser, such as chlorinated paraffin wax, can also be used.

The biocidal effect of the sparingly seawater-soluble pigments, particularly cuprous oxide, cuprous thiocyanate and zinc ethylene bis(dithiocarbamate), may be sufficient so that the paint needs no further biocide. For encountering severe fouling the paint may contain an added biocide. Triorganotin salts and oxides
50 such as triphenyltin fluoride, tributyltin fluoride, tributyltin dibromosuccinate, triphenyltin chloride, triphenyltin hydroxide and tributyltin oxide are effective marine biocides and can be used in paints according to the invention. A paint according to the invention comprising a triorganotin salt (up to 25 per cent by volume of the pigments) may have anti-fouling and smoothing properties equal to a triorganotin copolymer paint of much higher triorganotin content. In some cases it will be desired to avoid completely the release of triorganotin ions. Examples of other biocides effective as marine anti-fouling agents are dithiocarbamate derivatives such
55 as cuprous ethylene bis(thiocarbamate) or tetramethyl thiuram disulphide, methylene bis(thiourea), 4-butyl catechol and captan.

The invention is illustrated by the following Examples, in which parts and percentages are by weight unless otherwise stated:

Example 1

65 1 mole triphenylchloromethane was stirred with 1.2 moles potassium methacrylate in 998 g dimethyl formamide in the presence of 0.14 g hydroquinone. The mixture was maintained at room temperature and

arged with nitrogen gas. Heterogeneous condensation occurred between the two reactants and solid potassium chloride was precipitated. The potassium chloride was removed by filtration and the triphenylmethyl methacrylate solution produced was concentrated by rotary evaporation at 65 to 100°C at reduced pressure. The concentrate was left to cool to 20°C and crystals of triphenylmethyl methacrylate separated out. The product was isolated by filtration, washed with 60/80 petroleum ether and dried at 50°C at reduced pressure. The yield of triphenylmethyl methacrylate was 85 per cent.

55 parts triphenylmethyl methacrylate, 40 parts butyl acrylate and 5 parts methyl methacrylate were dissolved in xylene at a total solids content of 45 per cent. 1 part azobisisobutyronitrile was added and polymerisation was carried out for 3 hours at 80°C followed by 15 minutes at 100°C.

The copolymer solution produced was milled with cuprous oxide at a pigment volume concentration of 35 per cent together with a small amount of anti-settling agents to produce a self-smoothing marine anti-fouling paint.

Examples 2 to 13

Triphenylmethyl methacrylate prepared as described in Example 1 was copolymerised using the procedure of Example 1 with various proportions of comonomers as set out in Table 1 below. In each case the copolymer solution obtained could be pigmented with cuprous oxide as described in Example 1 to produce an anti-fouling paint.

Examples 14 to 17

1 mole triphenylchloromethane was stirred with 1.5 moles potassium acrylate in 998 g dimethyl formamide in the presence of 0.14 g hydroquinone under the conditions described in Example 1. The precipitated potassium chloride was filtered off and the triphenyl methyl acrylate solution was concentrated by rotary evaporation at 65 to 100°C and reduced to produce liquid triphenylmethyl acrylate. This was dissolved at 70 per cent in xylene and filtered.

Copolymers of triphenylmethyl acrylate were prepared using the procedure of Example 1 using the proportions of comonomers set out in Table 2. The copolymer solutions produced could be milled with cuprous oxide as described in Example 1 to produce a marine anti-fouling paint.

Table 1
Per Cent By Weight of Each Monomer

	<u>Triphenylmethyl Methacrylate</u>	<u>Methyl Methacrylate</u>	<u>Ethyl Acrylate</u>	<u>Butyl Acrylate</u>	<u>2-Ethylhexyl Acrylate</u>	<u>Tributyltin Methacrylate</u>
Example 2	60	-	-	40	-	-
Example 3	50	20	30	-	-	-
Example 4	50	20	15	15	-	-
Example 5	45	20	-	35	-	-
Example 6	55	10	-	-	35	-
Example 7	50	20	-	-	30	-
Example 8	55	20	10	-	15	-
Example 9	50	20	20	-	10	-
Example 10	53	15	-	30	-	2
Example 11	49	15	-	30	-	6
Example 12	48	20	-	30	-	2
Example 13	44	20	-	30	-	6

Table 2
Per Cent By Weight of Each Monomer

<u>Monomer % Wt ratio</u>	<u>Triphenylmethyl Acrylate</u>	<u>Methyl Methacrylate</u>	<u>Triphenylmethyl Methacrylate</u>
Example 14	52	48	-
Example 15	55	45	-
Example 16	50	45	5
Example 17	10	45	45

(12)

Example 18

Diphenyl (p-methoxyphenyl)methyl chloride was reacted with potassium methacrylate using the procedure of Example 1 to produce diphenyl(p-methoxyphenyl)methyl methacrylate (hereinafter abbreviated to MTMA).

5 50 parts MTMA, 30 parts methyl methacrylate and 20 parts butyl acrylate were dissolved in xylene at a solids content of 50 per cent. 2 parts 'Vazo 67' (Trade Mark) azo compound initiator was added and polymerisation was carried out at 90°C for 5 hours followed by 30 minutes at 110°C.

The copolymer solution produced was milled with cuprous thiocyanate at a pigment volume concentration of 35 per cent to produce a self-smoothing marine antifouling paint.

Examples 19 and 20

15 MTMA prepared as described in Example 18 was copolymerised using the procedure of Example 18 with various proportions of methyl methacrylate and butyl acrylate as set out in Table 3 below. In each case the copolymer solution produced could be pigmented with cuprous thiocyanate as described in Example 18 to produce an antifouling paint.

Table 3

	Per Cent By Weight of Each Monomer		
	MTMA	Methyl Methacrylate	Butyl Acrylate
Example 19	60	20	20
Example 20	70	10	20

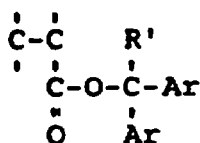
Example 21

30 Phenyl bis(p-methoxyphenyl) methyl chloride was reacted with potassium methacrylate using the procedure of Example 1 to produce phenyl bis(p-methoxyphenyl) methyl methacrylate (DMTMA).

50 parts DMTMA and 50 parts methyl methacrylate were copolymerised at 50 per cent solids in xylene using the procedure of Example 18. The copolymer solution produced could be pigmented with cuprous thiocyanate as described in Example 18 to produce an anti-fouling paint.

Claims

40 1. An anti-fouling marine paint comprising a pigment, a marine biocide which may or may not be identical to the pigment and a film-forming binder which is a hydrolysable polymer containing units corresponding to an ester of an olefinically unsaturated acid, characterised in that the polymer contains units of the formula:



50 where each Ar independently is an aryl group and R' is a hydrogen atom or an alkyl or aryl group.

2. An anti-fouling marine paint according to claim 1, characterised in that R' and each Ar are all independently aryl groups.

3. An anti-fouling marine paint according to claim 2, characterised in that the polymer contains units corresponding to triphenylmethyl acrylate or methacrylate.

4. An anti-fouling marine paint according to claim 1 or claim 2, characterised in that at least one of the groups Ar is a phenyl group substituted by one or two electron-releasing groups.

5. An anti-fouling marine paint according to claim 4, characterised in that the polymer contains units corresponding to diphenyl (p-methoxyphenyl)methyl acrylate or methacrylate.

6. An anti-fouling marine paint according to any of claims 1 to 5, characterised in that the polymer contains 25 - 40 per cent of units of the formula given in claim 1.

7. An anti-fouling marine paint according to any of claims 1 to 6, characterised in that the polymer also contains units of an alkyl acrylate having at least two carbon atoms in the alkyl group.

8. A film-forming hydrolysable polymer of an ester of an olefinically unsaturated acid, the polymer being useful as a binder for a self-polishing anti-fouling marine paint, characterised in that the polymer contains at



(12)

Example 18

Diphenyl (p-methoxyphenyl)methyl chloride was reacted with potassium methacrylate using the procedure of Example 1 to produce diphenyl(p-methoxyphenyl)methyl methacrylate (hereinafter abbreviated to MTMA).

5 50 parts MTMA, 30 parts methyl methacrylate and 20 parts butyl acrylate were dissolved in xylene at a solids content of 50 per cent. 2 parts 'Vazo 67' (Trade Mark) azo compound initiator was added and polymerisation was carried out at 90°C for 5 hours followed by 30 minutes at 110°C.

The copolymer solution produced was milled with cuprous thiocyanate at a pigment volume concentration of 35 per cent to produce a self-smoothing marine antifouling paint.

Examples 19 and 20

15 MTMA prepared as described in Example 18 was copolymerised using the procedure of Example 18 with various proportions of methyl methacrylate and butyl acrylate as set out in Table 3 below. In each case the copolymer solution produced could be pigmented with cuprous thiocyanate as described in Example 18 to produce an antifouling paint.

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Per Cent By Weight of Each Monomer

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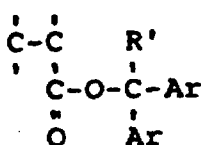
Example 21

30 Phenyl bis(p-methoxyphenyl) methyl chloride was reacted with potassium methacrylate using the procedure of Example 1 to produce phenyl bis(p-methoxyphenyl) methyl methacrylate (DMTMA).

50 parts DMTMA and 50 parts methyl methacrylate were copolymerised at 50 per cent solids in xylene using the procedure of Example 18. The copolymer solution produced could be pigmented with cuprous thiocyanate as described in Example 18 to produce an anti-fouling paint.

Claims

40 1. An anti-fouling marine paint comprising a pigment, a marine biocide which may or may not be identical to the pigment and a film-forming binder which is a hydrolysable polymer containing units corresponding to an ester of an olefinically unsaturated acid, characterised in that the polymer contains units of the formula:



50 where each Ar independently is an aryl group and R' is a hydrogen atom or an alkyl or aryl group.

2. An anti-fouling marine paint according to claim 1, characterised in that R' and each Ar are all independently aryl groups.

55 3. An anti-fouling marine paint according to claim 2, characterised in that the polymer contains units corresponding to triphenylmethyl acrylate or methacrylate.

4. An anti-fouling marine paint according to claim 1 or claim 2, characterised in that at least one of the groups Ar is a phenyl group substituted by one or two electron-releasing groups.

5. An anti-fouling marine paint according to claim 4, characterised in that the polymer contains units corresponding to diphenyl (p-methoxyphenyl)methyl acrylate or methacrylate.

60 6. An anti-fouling marine paint according to any of claims 1 to 5, characterised in that the polymer contains 25 - 40 per cent of units of the formula given in claim 1.

7. An anti-fouling marine paint according to any of claims 1 to 6, characterised in that the polymer also contains units of an alkyl acrylate having at least two carbon atoms in the alkyl group.

65 8. A film-forming hydrolysable polymer of an ester of an olefinically unsaturated acid, the polymer being useful as a binder for a self-polishing anti-fouling marine paint, characterised in that the polymer contains at



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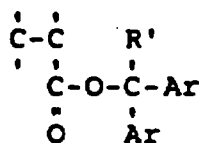
st 20 mole per cent of units of diphenyl (p-methoxyphenyl)methyl acrylate or methacrylate.

9. A paint according to any of claims 1 to 7, characterised in that the pigment is a sparingly soluble copper or zinc compound having a solubility in seawater of from 0.5 to 10 parts per million by weight and forms the marine biocide of the paint.

5 10. A paint according to claim 9, characterised in that the pigment comprises cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate).

10 Patentansprüche

1. Bewuchsverhindernder Schiffsanstrich, bestehend aus einem Marinbiozid, das gegebenenfalls mit dem Pigment identisch sein kann, und einem filmbildenden Bindemittel, welches ein hydrolysierbares, einem Ester einer olefinisch ungesättigten Säure entsprechende Einheiten enthaltendes Polymerisat ist, dadurch gekennzeichnet, daß das Polymerisat Einheiten der Formel



20 worin die Ar jeweils unabhängig voneinander eine Arylgruppe und R' ein Wasserstoffatom oder eine Alkyl- oder Arylgruppe bedeuten, enthält.

2. Bewuchsverhindernder Schiffsanstrich nach Anspruch 1, dadurch gekennzeichnet, daß R' und die Ar jeweils sämtlich unabhängig von einander Arylgruppen bedeuten.

3. Bewuchsverhindernder Schiffsanstrich nach Anspruch 2, dadurch gekennzeichnet, daß das Polymerisat Triphenylmethylacrylat oder -methacrylat entsprechende Einheiten enthält.

30 4. Bewuchsverhindernder Schiffsanstrich nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß mindestens eine der Gruppen Ar eine einfach oder zweifach durch elektronenabgebende Gruppen substituierte Phenylgruppe darstellt.

5. Bewuchsverhindernder Schiffsanstrich nach Anspruch 4, dadurch gekennzeichnet, daß das Polymerisat Diphenyl-(p-methoxyphenyl)methyl-acrylat oder -methacrylat entsprechende Einheiten enthält.

35 6. Bewuchsverhindernder Schiffsanstrich nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Polymerisat 25 - 40 Prozent Einheiten der in Anspruch 1 angegebenen Formel enthält.

7. Bewuchsverhindernder Schiffsanstrich nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Polymerisat ferner Einheiten eines Alkylacrylats mit mindestens zwei Kohlenstoffatomen in der Alkylgruppe enthält.

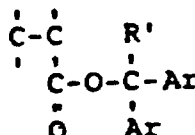
40 8. Filmbildendes hydrolysierbares Polymerisat aus einem Ester einer olefinisch ungesättigten Säure, wobei das Polymerisat als Bindemittel für einen Selbstpolierenden, bewuchsverhindernden Schiffsanstrich verwendbar ist, dadurch gekennzeichnet, daß das Polymerisat mindestens 20 Mol Prozent Diphenyl-(p-methoxyphenyl)-methyl-acrylat- oder methacrylateinheiten enthält.

45 9. Anstrich nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß das Pigment eine schwerlösliche Kupfer- oder Zinkverbindung mit einer Löslichkeit in Meerwasser von 0,5 bis 10 Gewichtsteilen pro Million ist und das Marinbiozid des Anstrichs bildet.

10. Anstrich nach Anspruch 9, dadurch gekennzeichnet, daß das Pigment aus Kupfer(I)-oxyd, Kupfer(I)-rhodanid oder Zink-ethylen-bis(dithiocarbamat) besteht.

Revendications

55 1. Peinture marine antisalissure comprenant un pigment, un biocide marin qui peut ou non être identique au pigment et un liant filmogène qui est un polymère hydrolysable contenant des motifs correspondant à un ester d'un acide à insaturation oléfinique, caractérisée en ce que le polymère contient des motifs de formule:



dans laquelle chaque Ar est indépendamment un groupe aryle et R' est un atome d'hydrogène ou un groupe alkyle ou aryle.

2. Peinture marine antisalissure selon la revendication 1, caractérisée en ce que R' et chaque Ar sont tous indépendamment des groupes aryle.

3. Peinture marine antisalissure selon la revendication 2, caractérisée en ce que le polymère contient des motifs correspondant à l'acrylate ou au méthacrylate de triphénylméthyle.

4. Peinture marine antisalissure selon la revendication 1 ou 2, caractérisée en ce qu'au moins un des groupes Ar est un groupe phényle substitué par un ou deux groupes donneurs d'électrons.

5. Peinture marine antisalissure selon la revendication 4, caractérisée en ce que le polymère contient des motifs correspondant à l'acrylate ou au méthacrylate de diphenyl(p-méthoxyphényl)méthyle.

6. Peinture marine antisalissure selon l'une quelconque des revendications 1 à 5, caractérisée en ce que le polymère contient 25 - 40 % de motifs de formule indiqués dans la revendication 1.

7. Peinture marine antisalissure selon l'une quelconque des revendications 1 à 6, caractérisée en ce que le polymère contient aussi des motifs d'un acrylate d'alkyle comportant au moins 2 atomes de carbone dans le groupe alkyle.

8. Polymère hydrolysable filmogène d'un ester d'un acide à insaturation oléfinique, le polymère étant utile comme liant pour une peinture marine antisalissure autolissante, caractérisé en ce que le polymère contient au moins 20 pour cent en moles de motifs d'acrylate ou de méthacrylate de diphenyl (p-méthoxyphényl)méthyle.

9. Peinture selon l'une quelconque des revendications 1 à 7, caractérisée en ce que le pigment est un composé du cuivre ou du zinc peu soluble, ayant une solubilité dans l'eau de mer de 0,5 à 10 parties par million en poids, et forme le biocide marin de la peinture.

10. Peinture selon la revendication 9, caractérisée en ce que le pigment comprend de l'oxyde cuivreux, du thiocyanate cuivreux ou de l'éthylène-bis(dithiocarbamate) de zinc.