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PATENT SPECIFICATION

(11) 1 509 250

- (21) Application No. 32150/75 (22) Filed 31 July 1975
(31) Convention Application No. 50/034 541
(32) Filed 24 March 1975 in
(33) Japan (JP)
(44) Complete Specification published 4 May 1978
(51) INT CL² C09D 5/14, 3/38, 3/40, 5/16//C08K 9/10
(52) Index at acceptance

C4A 4D 4L 4R 4X
C3B 1C10 1C11 1C12 1C13M 1C13P 1C13S 1C25 1C26
1C6X 1C9B 1C9N 1L3A 1L6G L
C3L DC
C3R 3C C10 C11 C12 C13M C13P C13S C25 C26 C6X C9B
C9N L3A L6G



(54) IMPROVEMENTS IN OR RELATING TO PAINT

(71) We, KANSAI PAINT CO., LTD., a company of Japan, of 365, Kanzaki, Amagasaki-shi, Hyogo-ken, Japan, 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:—

This invention relates to an antifouling paint of the two component or package type. More particularly, the invention relates to an antifouling paint of two component type which is characterised in that the paint comprises a pair of compositions, that is, a vehicle composition normally containing vehicles, pigments, auxiliary antifouling agents and other additives, and an antifouling composition containing at least one triphenyl tin compound(s) and/or triphenyl lead compound(s) as the principal antifouling agent. Furthermore the present invention relates to an antifouling paint of two package type which is used by mixing together just before use.

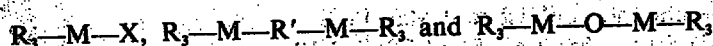
Ships and marine structures generally suffer severe damage from fouling, caused by a variety of marine life. When ships or vessels are fouled with some marine life, the frictional resistance between the hulls and seawater increases, and a decrease of speed and an increase of fuel consumption may occur as a result. Therefore, the fouling brings about serious economical loss and further it also causes an undesirable effect from the standpoint of corrosion inhibition. Thus, in order to prevent or substantially mitigate such fouling by marine life, antifouling paint, the so-called "ship-bottom" paint, is applied to the marine structures. When the antifouling paint is applied to the hulls of vessels or marine structures, the rosin in the coating film dissolves into weakly alkaline seawater and the antifouling agent contained in the paint dissolves simultaneously into the seawater. Therefore, the clinging of sea life such as barnacles, serpulæ, sea lettuces, green leavers and ascidians can be prevented or at least substantially mitigated.

As antifouling paints of this kind, those containing triphenyl or tributyl tin compounds or triphenyl lead compounds are noted because they have an excellent film property and antifouling effect. Such antifouling paint containing triphenyl tin compounds or triphenyl lead compounds, however, suffers the defect that the antifouling effect thereof decreases to a notable degree during storage. It is considered that the cause of the above defect in the conventional single liquid type paint containing the dispersions or rosin as a vehicle and triphenyl tin compounds as an antifouling agent, is that the rosin and triphenyl tin compounds react with each other so that the solubilities of the matrix and antifouling agent to seawater are decreased and those compounds are also decomposed in the paint during storage, resulting in the lowering of antifouling effect.

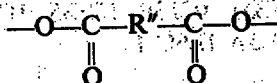
Accordingly, it is an object of the present invention to provide an improved and useful antifouling paint which is substantially free from the above-mentioned disadvantages, to provide an antifouling paint of two package type which is used by mixing just before the application and to provide an antifouling paint which has excellent antifouling property as well as other good film properties.

According to the first aspect of the present invention there is provided an antifouling paint of a Component A and Component B being in separate packages

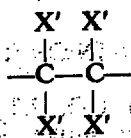
which are mixed just before application, wherein Component A comprises a resin having carboxylic groups and an acid value of from 5 to 250, a pigment and optionally an auxiliary antifouling agent, and wherein Component B comprises a vehicle having an acid value of less than 20; at least one triphenyl tin compound and/or triphenyl lead compound selected from compounds having the following general formulae:



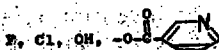
in which M represents a Sn or Pb atom, R represents a phenyl radical, R' represents a



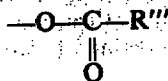
radical (in which R'' represents a



radical and X' represents an H or halogen atom), and X represents



sulphide, thiocarbamate, sulphonamide or



(in which R''' represents an alkyl radical having 1 or 8 to 18 carbon atoms) and optionally auxiliary antifouling agent(s).

According to the second aspect of the present invention there is provided an antifouling paint ready for application, which comprises, in admixture, Component A and Component B of an antifouling paint in accordance with the first aspect of the present invention.

The present inventors have invented an antifouling paint of two component or package type which comprises a vehicle composition as Component A, preferably containing rosin as a main component, and an antifouling composition as Component B containing triphenyl tin compound(s) and/or triphenyl lead compound(s). The above two compositions, Components A and B, are mixed together prior to the application; therefore the antifouling compounds contained in Component B can remain stable during the storage of the paint and becomes effective when the paint is applied.

As disclosed in the above, the antifouling paint of the present invention comprises Component A and Component B. Component A comprises a resin having carboxy groups and an acid value of from 5 to 250, preferably 10 to 200, such as rosin and other natural resins, petroleum resins (for example coumarone-indene-resin), acrylic resins, alkyd resins, maleinised resins, carboxylated vinyl resin and carboxylated epoxy resin. The Component A further may contain auxiliary antifouling agent(s). These agents are exemplified cuprous oxide, organo-sulphurous compounds (for example zinc dimethyl bithiocarbamate and tetramethylthiuramdisulphide) and other organic compounds other than those containing tin or lead. The Component B contains vehicles having an acid value of less than 20, preferably less than 10, and at least one of triphenyl tin compound(s) and/or triphenyl lead compound(s) as the indispensable antifouling agents.

Examples of the triphenyl tin or lead compounds are triphenyl tin fluoride, triphenyl tin chloride, triphenyl lead chloride, triphenyl tin hydroxide, triphenyl lead hydroxide, triphenyl tin pyridine-3-carboxylate, triphenyl lead pyridine-3-carboxylate, triphenyl tin-sulphide, triphenyl lead

3 sulphide, triphenyl tin thiocarbamate, triphenyl lead thiocarbamate, triphenyl tin
sulphonamide, triphenyl lead sulphonamide, triphenyl tin acetate, triphenyl lead
acetate, triphenyl tin laurate, triphenyl lead laurate, triphenyl tin stearate,
triphenyl lead stearate, bis(triphenyl tin) succinate, bis(triphenyl tin)- α,α' -di-
bromosuccinate, bis(triphenyl lead) succinate, bis(triphenyl lead)- α,α' -dibromo-
succinate, bis(triphenyl tin) oxide and bis(triphenyl lead) oxide. 5

Suitable examples of the vehicles used in the Component B are styrene-
butadiene copolymer, chlorinated rubber, vinyl chloride resin, chlorinated
paraffin, tricresyl phosphate, acryl resin and alkyd resin. The content of the above-
mentioned triphenyl tin or lead compound(s) is preferably from 1 to 30% by weight 10
to the total solids of both the Component A and Component B. Both Component
A and Component B are used by mixing together just before the application.

As compared with the conventional one package or component type paint,
the antifouling paint of two package or component type of the present invention
hardly shows the lowering of antifouling property and excellent results can be 15
thereby obtained. Other film properties of the coating formed according to the
present invention are also excellent.

The following Examples illustrate the present invention, all parts and
percentages being by weight unless otherwise specified.

Examples 1 to 8 and
Comparative Examples 1 to 8.

Paint compositions were prepared according to the following formulae:

Example 1.

Chlorinated rubber antifouling paint

Component A		Component B	
Rosin	12%	Chlorinated paraffin	5%
Chlorinated rubber	3	Triphenyl tin hydroxide	10
Cuprous oxide	35	xylene	5
Red iron oxide	5		
Talc	4		
Zinc oxide	1		
Xylene	20		
	80%		20%

Example 2.

Chlorinated rubber antifouling paint

Component A		Component B	
Rosin	12%	Chlorinated paraffin	5%
Chlorinated rubber	12	Triphenyl tin hydroxide	13
Red iron oxide	10	xylene	15
Talc	8		
Zinc oxide	10		
Xylene	15		
	67%		33%

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Comparative Example 1.
Chlorinated rubber antifouling paint

	Rosin	12%	
	Chlorinated rubber	3	
5	Chlorinated paraffin	5	5
	Cuprous oxide	35	
	Triphenyl tin hydroxide	10	
	Red iron oxide	5	
	Talc	4	
10	Zinc oxide	1	10
	Xylene	25	
		100%	

Comparative Example 2.
Chlorinated rubber antifouling paint

15	Rosin	12%	15
	Chlorinated rubber	12	
	Chlorinated paraffin	5	
	Triphenyl tin hydroxide	13	
	Red iron oxide	10	
20	Talc	8	20
	Zinc oxide	10	
	Xylene	30	
		100%	

Example 3.
Chlorinated rubber antifouling paint

25	Component A		Component B		25
	Rosin	12%	Chlorinated <i>n</i> -paraffin	5%	
	Chlorinated rubber	3	Triphenyl tin chloride	10	
	Cuprous oxide	35	Xylene	5	
	Talc	4			
	Red iron oxide	5			
	Zinc oxide	1			
	Xylene	20			
		80%		20%	

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Example 4.
Chlorinated rubber antifouling paint

Component A		Component B	
Rosin	12%	Chlorinated <i>n</i> -paraffin	5%
Chlorinated rubber	12	Triphenyl tin fluoride	10
Red iron oxide	10	Xylene	5
Talc	23		
Zinc oxide	10		
Xylene	13		
	80%		20%

Example 5.
Vinyl chloride antifouling paint

Component A		Component B	
Rosin	10%	Vinyl chloride resin	5%
Organosulphurous compound	20	Tricresyl phosphate	5
Red iron oxide	10	Triphenyl tin acetate	10
Talc	15		
Zinc oxide	5		
Toluene	10		
Methyl isobutyl ketone	10		
	80%		20%

Example 6.
Vinyl chloride antifouling paint

Component A		Component B	
Rosin	10%	Tricresyl phosphate	5%
Copolymer of vinyl chloride and vinyl acetate	5	Bis(triphenyl tin)- α,α' -dibromosuccinate	20
Red iron oxide	10	Toluene	3
Talc	15	Methyl isobutyl ketone	2
Zinc oxide	5		
Toluene	12		
Methyl isobutyl ketone	13		
	70%		30%

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Example 7.
Vinyl chloride antifouling paint

Component A		Component B	
Rosin	10%	Tricresyl phosphate	5%
Copolymer of vinyl chloride and vinyl acetate	5	Bis(triphenyl tin) oxide	20
Red iron oxide	10	Toluene	3
Talc	15	Methyl isobutyl ketone	2
Zinc white	5		
Toluene	12		
Methyl isobutyl ketone	13		
	70%		30%

Example 8.
Vinyl chloride antifouling paint

Component A		Component B	
Rosin	10%	Tricresyl phosphate	5%
Copolymer of vinyl chloride and vinyl acetate	5	Triphenyl lead acetate	10
Red iron oxide	10	Toluene	3
Talc	15	Methyl isobutyl ketone	2
Zinc oxide	5		
Toluene	12		
Methyl isobutyl ketone	13		
	70%		30%

Comparative Example 3.
Chlorinated rubber antifouling paint

	Rosin	12%	
	Chlorinated rubber	3	
	Chlorinated- <i>n</i> -paraffin	5	5
	Cuprous oxide	35	
	Triphenyl tin chloride	10	
	Red iron oxide	5	
	Talc	4	
10	Zinc oxide	1	10
	Xylene	25	

100%

Comparative Example 4.
Chlorinated rubber antifouling paint

15	Rosin	12%	15
	Chlorinated rubber	12	
	Chlorinated <i>n</i> -paraffin	5	
	Triphenyl tin fluoride	10	
	Red iron oxide	10	
20	Talc	23	20
	Zinc	10	
	Xylene	18	

100%

Comparative Example 5.
Vinyl chloride antifouling paint

25	Rosin	10%	25
	Copolymer of vinyl chloride and vinyl acetate	5	
	Tricresyl phosphate	5	
30	Zinc dimethyl bithiocarbamate	20	30
	Triphenyl tin acetate	10	
	Red iron oxide	10	
	Talc	15	
	Zinc oxide	5	
35	Toluene	10	35
	Methyl isobutyl ketone	10	

100%

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Comparative Example 6.
Vinyl chloride antifouling paint

	Rosin	10%	
5	Copolymer of vinyl chloride and vinyl acetate	5	
	Tricresyl phosphate	5	
	Bis(triphenyltin)- α,α' -dibromosuccinate	20	
	Red iron oxide	10	
10	Talc	15	10
	Zinc oxide	5	
	Toluene	15	
	Methyl isobutyl ketone	15	
		100%	

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Comparative Example 7.
Vinyl chloride antifouling paint

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	Rosin	10%	
	Vinyl chloride resin	5	
	Tricresyl phosphate	5	
20	Bis(triphenyl tin) oxide	20	20
	Red iron oxide	10	
	Talc	15	
	Zinc oxide	5	
	Toluene	15	
25	Methyl isobutyl ketone	15	25
		100%	

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Comparative Example 8.
Vinyl chloride antifouling paint

	Rosin	10%	
	Copolymer of vinyl chloride and vinyl acetate	5	5
	Tricresyl phosphate	5	
	Triphenyl lead acetate	10	
	Red iron oxide	10	
	Talc	15	
10	Zinc oxide	5	10
	Toluene	15	
	Methyl isobutyl ketone	15	
		100%	

15 According to the above formulae, paint compositions were prepared and applied to steel plates. Each steel plate was 10×30×0.5 cm in size and was previously coated with anticorrosive paint. The test pieces coated with the antifouling paints were then hung under rafts and immersed in the seawater of Toba Bay, Mie-ken, Japan. 15

20 In the meantime, the compositions of component A and component B were preserved without mixing for 2 months and 5 months. After such periods, the components A and B were mixed together and applied to the similar steel plates, and immersion tests were additionally carried out. The compositions for Comparative Examples were prepared by mixing the ingredients together from the beginning and the mixtures were likewise stored for the same periods of 2 months and 5 months, and used for the comparative immersion tests. The temperature for preserving the above paint compositions was room temperature. 20 25

The results of seawater immersion tests and tin-dissolving rates are shown in the following Tables 1 and 2.

30 The tin-dissolving rates of the antifouling paint of the present invention were not less than the antifouling limit ($\mu\text{g}/\text{cm}^2/\text{day}$); therefore, it was understood that the antifouling paint of the present invention is superior to the conventional single liquid type paint containing triphenyltin compound. 30

35 Table 3 shows the acid values of rosin and residual rates of carbonyl group ($-\text{C}=\text{O}$) after storage of rosin/triphenyl tin compound systems. The composition of this system was 25% of rosin, 25% of triphenyl tin compound and 50% of xylene. It was recognised from the results that the reactions of rosin and triphenyltin compound proceeded which correspond to the results of the antifouling property. 35

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TABLE 1
Seawater Immersion Test

Property	Antifouling Property (Fouled area with barnacles, %)					
	Just after Preparation		2 months		5 months	
	6	12	6	12	6	12
Compositions						
Example 1	0	0	0	0	0	0
Example 2	0	0	0	0	0	0
Example 3	0	0	0	0	0	0
Example 4	0	0	0	0	0	0
Example 5	0	0	0	0	0	0
Example 6	0	0	0	0	0	0
Example 7	0	0	0	0	0	0
Example 8	0	0	0	0	0	0
Comparative Example 1	0	0	50	90	70	90
Comparative Example 2	0	0	40	90	90	90
Comparative Example 3	0	0	40	90	70	90
Comparative Example 4	0	0	60	80	70	90
Comparative Example 5	0	0	60	80	90	90
Comparative Example 6	0	0	60	90	90	90
Comparative Example 7	0	0	60	90	90	90
Comparative Example 8	0	0	30	70	90	100

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TABLE 2

Dissolving Rate of Tin
($\mu\text{g}/\text{cm}^2/\text{day}$)

Storage Period	Just after Preparation		2 months		5 months	
Immersion (months)	6	12	6	12	6	12
Composition						
Example 1	3.9	2.0	3.2	1.9	4.0	1.2
Example 2	5.0	3.1	2.9	2.0	3.3	2.5
Example 3	3.2	1.9	4.0	1.2	3.1	1.2
Example 4	2.6	2.0	3.0	4.2	2.1	1.2
Example 5	3.4	1.5	2.0	2.3	1.5	1.3
Example 6	6.0	4.0	6.1	3.9	5.4	4.0
Example 7	4.2	4.1	4.5	3.1	3.2	4.0
Comparative Example 1	2.8	1.5	0.5	0.3	0.2	0.0
Comparative Example 2	4.2	2.0	0.2	0.0	0.0	0.0
Comparative Example 3	3.9	2.0	0.9	0.1	0.0	0.0
Comparative Example 4	2.9	1.5	0.1	0.1	0.0	0.0
Comparative Example 5	3.0	1.0	0.3	0.1	0.0	0.0
Comparative Example 6	5.5	4.0	0.0	0.0	0.0	0.0
Comparative Example 7	4.1	4.1	0.6	0.0	0.2	0.1

Note: The dissolving rate of tin was determined by absorptiometry with phenylfluorone.

TABLE 3

Storing of Rosin/Phenyl tin or Phenyl lead Compound System
(Changes in acid value and residual -C=O)

Item	Acid Value					Residual Rate (%) of -C=O				
	Start	1	2	5	Start	1	2	5		
Storage Period (month)										
Phenyl tin or Phenyl lead Compounds										
Triphenyl tin hydroxide	165	80	80	60	100	70	70	40		
Triphenyl tin fluoride	165	150	120	80	100	90	50	40		
Triphenyl tin chloride	165	90	70	50	100	80	30	10		
Triphenyl tin acetate	163	70	65	72	100	40	20	10		
Triphenyl tin monochloroacetate	159	72	72	60	100	40	20	10		
Triphenyl tin dimethyldithiocarbamate	160	90	80	80	100	35	30	10		
Triphenyl tin	165	100	80	70	100	80	40	30		
Triphenyl tin nicotinate	165	60	50	50	100	30	20	10		
Bis triphenyltin α, α' -dibromosuccinate	163	95	80	80	100	30	10	10		
Bis (triphenyl tin) oxide	165	90	60	40	100	70	20	10		
Triphenyl lead acetate	165	90	80	50	100	75	30	100		
Rosin, alone	164	165	165	163	100	100	100	100		

Note: The acid value was determined according to the method of item 8.5 of JIS K 5400.

Example 9.

Component A		Component B	
Acryl resin K146*	10.0	Tricresyl phosphate	5.0
Red iron oxide	10.0	Triphenyltin hydroxide	20.0
Talc	25.0	Toluene	3.0
Toluene	12.0	Methyl isobutyl ketone	2.0
Methyl isobutyl ketone	13.0		
	70.0%		30.0%

*The resin was prepared by polymerising methyl methacrylate (55% by wt.), butyl methacrylate (10.2% by wt.), ethyl methacrylate (10% by wt.), butylacrylate (15% by wt.) and methylacrylate (9.8% by wt.)

Example 10.

Component A		Component B	
Alkyd resin Becozol No. 1341 (Dainihoninki Co., Ltd.)	10.0	Tricresyl phosphate	5.0
Red iron oxide	10.0	Triphenyltin chloride	20.0
Talc	25.0	Toluene	3.0
Toluene	12.0	Methyl isobutyl ketone	2.0
Methyl isobutyl ketone	13.0		
	70.0%		30.0%

The word "Becozol" is a Trade Mark.

Comparative Example 9.

5	Acryl resin K-146 (Mitsubishi Gass Chemical Co. Ltd.)	10.0	5
	Tricresyl phosphate	5.0	
	Triphenyl tin hydroxide	20.0	
	Red iron oxide	10.0	
10	Talc	25.0	10
	Toluene	15.0	
	Methylisobutylketone	15.0	
		100.0	

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Comparative Example 10.

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Alkyd resin Becozol No. 1341 (Dainihoninki Co. Ltd.)	10.0
Tricresylphosphate	5.0
Triphenyltin chloride	20.0
Red iron oxide	10.0
Talc	25.0
Toluene	15.0
Methylisobutylketone	15.0
	100.0

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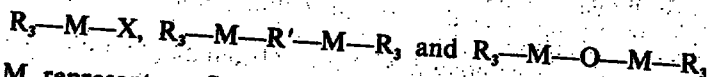
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Storage Period	Just after preparation		2 months		5 months	
Immersion (months)	6	12	6	12	6	12
Compositions						
Example 9	3.3	2.0	4.2	1.8	2.9	1.2
Example 10	5.2	3.0	3.0	2.0	6.7	1.8
Comparative Example 9	3.5	1.2	0.3	0.0	0.0	0.0
Comparative Example 10	2.6	2.3	0.5	0.4	0.2	0.3

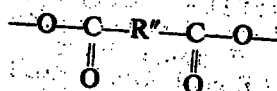
Property	Antifouling Property (Fouled area with barnacles, %)					
Storage Period	Just after preparation		2 months		5 months	
Immersion (months)	6	12	6	12	6	12
Compositions						
Example 9	0	0	0	0	0	0
Example 10	0	0	0	0	0	0
Comparative Example 9	0	0	60	100	90	100
Comparative Example 10	0	0	70	100	90	100

WHAT WE CLAIM IS:—

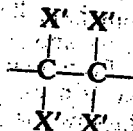
1. An antifouling paint of a Component A and Component B being in separate packages which are mixed just before application, wherein Component A comprises a resin having carboxylic groups and an acid value of from 5 to 250, a pigment and optionally an auxiliary antifouling agent; and wherein Component B comprises a vehicle having an acid value of less than 20, at least one triphenyl tin compound and/or triphenyl lead compound selected from compounds having the following general formulae:



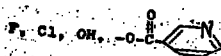
in which M represents a Sn or Pb atom, R represents a phenyl radical, R' represents a



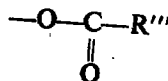
radical (in which R'' represents a



radical and X' represents an H or halogen atom), and X represents



sulphide, thiocarbamate, sulphonamide or



(in which R''' represents an alkyl radical having 1 or 8 to 18 carbon atoms) and optionally auxiliary antifouling agent(s).

2. An antifouling paint according to Claim 1, wherein the acid value of the vehicle in Component B is less than 10.

3. An antifouling paint according to Claim 1 or 2, wherein Component A comprises a resin having carboxyl groups and an acid value of from 10 to 200.

4. An antifouling paint according to Claim 3, wherein the vehicle of Component A is at least one of rosin and other natural resins, petroleum resin, acrylic resin, alkyd resin, maleinized resin, carboxylated vinyl resin and carboxylated epoxy resin.

5. An antifouling paint according to any one of the preceding claims, wherein the vehicle in Component B is at least one of styrene-butadiene copolymer, chlorinated rubber, vinyl chloride resin, chlorinated paraffin, tricresyl phosphate, acrylic resin and alkyd resin.

6. An antifouling paint according to any one of the preceding claims, wherein the auxiliary antifouling agent(s) is at least one of cuprous oxide, organosulphurous compounds and other organic compounds other than those containing tin or lead.

7. An antifouling paint according to Claim 6, wherein the auxiliary antifouling agent(s) is at least one of zinc dimethyl bithiocarbamate and tetramethylthiuram disulphide.

8. An antifouling paint according to any one of the preceding claims, wherein Component B contains from 1 to 30% by weight of triphenyl tin compound(s) and/or triphenyl lead compound(s), based on the total solids of both Component A and Component B.

9. An antifouling paint, substantially as described in foregoing Example 1.

10. An antifouling paint, substantially as described in foregoing Example 2.

11. An antifouling paint, substantially as described in foregoing Example 3.



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- 10
12. An antifouling paint, substantially as described in foregoing Example 4.
13. An antifouling paint, substantially as described in foregoing Example 5.
14. An antifouling paint, substantially as described in foregoing Example 6.
15. An antifouling paint, substantially as described in foregoing Example 7.
16. An antifouling paint, substantially as described in foregoing Example 8.
17. An antifouling paint, substantially as described in foregoing Example 9.
18. An antifouling paint, substantially as described in foregoing Example 10.
19. An antifouling paint ready for application, which comprises, in admixture,
Component A and Component B of an antifouling paint in accordance with any
one of the preceding claims.
20. A surface whenever coated with the antifouling paint of any one of the
preceding claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.



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