

ABSTRACT

This invention purports to provide a paint composition, an antifouling paint film, a submerged structure, and an antifouling method of a submerged structure. The paint film according to the present invention does not have defects such as separation over time after immersed in water, while the paint composition is eroded at a constant rate, which results in an excellent long-term antifouling property. The paint composition can be applied even onto aluminum-made ships. Furthermore, the paint composition has an excellent long-term antifouling property, and ensures a superior environmental safety.

This invention provides a paint composition, an antifouling paint film, a submerged structure, and an antifouling method of a submerged structure, in which the paint composition is characterized by including both of a component (A) represented by formula (1) and a component (B) including a copolymer derived from a polymeric unsaturated metal-salt compound represented by $R^5-(CH_2)_k-COO-M-L_q$:

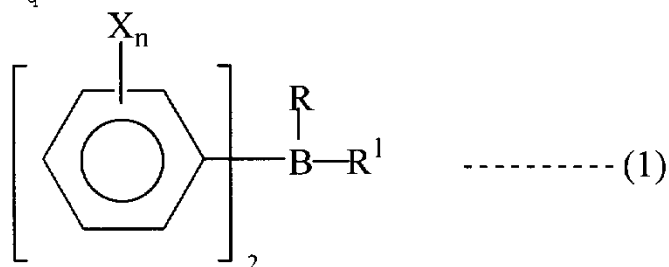


Table 1

Preparation example	Polymer solution 1	Polymer solution 2	Polymer solution 3	Polymer solution 4	Polymer solution 5	Polymer solution 6	Polymer solution 7	Polymer solution 8	Polymer solution 9	Polymer solution 10
Zinc methacrylate		20				25	18	17		
Zinc acrylate	14		14	14	14					
Zinc acetate acrylate				26						
Zinc propionate acrylate										
Zinc oleate acrylate	26									
Zinc oleate methacrylate		20					2			
Zinc versatate methacrylate						2				
Zinc isostearate methacrylate										
Zinc naphthenate acrylate					26					
Methyl methacrylate	15	15	15	15	15	18	20	21	50	
Ethyl acrylate	45		45	45	45	55	60	63	42.8	44.7
i-butyl acrylate		45								
Acrylic acid									7.2	
Methacrylic acid										15.3
Methoxyethyl acrylate										40
Solid content	40	40	40	40	40	40	40	40	49.2	50
Butyl acetate	40	40	40	40	40	40	40	40		46
n-butanol	20	20	20	20	20	20	20	20	5	42
Total (parts by weight)	100	100	100	100	100	100	100	100		
Zinc oxide									8	7.3
Molecular weight of copolymer	about 8,000	about 8,000	about 7,000	about 7,000	about 8,000	about 6,000	about 6,000	about 6,000	about 40,000	about 6,000

Table 2

[illegible]

Table 3

[illegible]

Table 4

		Working Example						
		21	22	23	24	25	26	
Component (B)	Polymer solution 1							
	Polymer solution 2							
	Polymer solution 3							
	Polymer solution 4							
	Polymer solution 5							
	Polymer solution 6							
	Polymer solution 7							
	Polymer solution 8							
	Polymer solution 9							
	Polymer solution 10	46.5	30.0 16.5	46.5	30.0 16.5	46.5	46.5	46.5
Component (C) or other blend polymer Additive	Gum rosin	3.5	3.5	3.5	3.5	3.5	3.5	
	Copper rosinate							
	Zinc rosinate							
	Laroflex MP-45							
Acrylic resin								
	Chlorinated paraffin							
	Tricresyl phosphate							
	TSP-4445	1.0	1.0	1.0	1.0	1.0	1.0	
Component (A) or different antifouling agent	Pyridine-methyl(diphenyl)borane							
	3-methylpyridine-methyl(diphenyl)borane							
	3-bromopyridine-methyl(diphenyl)borane							
	4-isopropylpyridine-methyl(diphenyl)borane							
	4-t-butylpyridine-methyl(diphenyl)borane	25.0	10.0	8.0			20.0	
	4-phenylpyridine-methyl(diphenyl)borane							
	n-octadecylamino-methyl(diphenyl)borane							
	3-(2-ethylhexyloxy)-propylamino-methyl(diphenyl)borane				10.0	10.0		
	Pyridine-trimethylborane							
	n-octylamino-triphenylborane			5.0				
Pigment	n-octadecylamino-triphenylborane							
	3-(2-ethylhexyloxy)-propylamino-triphenylborane							
	2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine							
	N,N-dimethyl-n-octyl-isothiazoline-3-one							
	2,4,6-trichlorophenyl-maleimide							
	2-pyridinethiol-1-oxide-copper salt	2.0		2.0	2.0	2.0	2.0	
	2-pyridinethiol-1-oxide-zinc salt							
	Talc	1.0					1.0	
	Cyanine blue		4.0	4.0	4.0	4.0		
	Zinc oxide		12.0	12.0	12.0	12.0		
Antisagging agent	Red ochre	1.0						
	Titanium dioxide							
	AEROSIL #200						5.0	
	DISPARLON A630-20XN	2.5	2.5	2.5	2.5	2.5	2.0	
Solvent	DISPARLON 4200-20	2.0	2.0	2.0	2.0	2.0		
	BENTON SD-2							
	Xylene	10.5	13.5	8.5	11.5	11.5	9.5	
	Propylene glycol monomethyl ether	5.0	5.0	5.0	5.0	5.0	5.0	
Total	Butyl acetate							
	n-butanol							
	Methyl isobutyl ketone							
		100.0	100.0	100.0	100.0	100.0	100.0	

Table 16

[illegible]

Table 17

		Working Example															
		49	50	51	52	53	54	55	56	57	58	59	60				
Polymer Solution	Polymer solution S ₁			30								30					
	Polymer solution S ₂	20			40		20	20									
	Polymer solution S ₃	20				35			10	30	30	20	30				
	Polymer solution S ₄		30					15									
	Polymer solution S ₅			20													
	Polymer solution S ₆																
	Polymer solution S ₇								10				20				
Other hydrolytic resin	Resin A	10			5		30					5					
	Resin B		5			5		10	20	5			5				
	Resin C			5							5						
	Rosin				5	5	5	10	10			5	5				
Organism-Adhesion Inhibitor	4-isopropylpyridine-diphenyl(methyl)borane	10	10	10	10	10	5	7	5			2	2				
	4-phenylpyridyl-diphenylborane									10	2		2				
	Diphenyl(methyl)borane-n-octadecyl-amine										5						
	Triphenylborane-3-ethoxypropyl-amine																
	Pyridine-triphenylborane																
	2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine																
	2,4,5,6-tetrachloro-isophthalonitrile						5		7				1				
	N,N-dimethyl-N'-octyl-isothiazoline-3-one																
	N-(fluorodichloro-methylthio)phthalimide																
	N,N-dimethyl-N'-phenyl-N'-fluorodichloro-methylthio-sulfamide										1						
	N,N-dimethyl-N'-dichlorophenylurea																
	2,4,6-trichlorophenyl-maleimide								2								
	2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine																
	2-pyridinethiol-1-oxide-copper salt																
2-pyridinethiol-1-oxide-zinc salt								5	3			1					
Pigment	Talc	2	2	1	2	2	2	2	2	2	2	2	2				
	Zinc oxide	5	5		10	12			2	3		5	5				
	Red ochre		3				7				7	3	3				
	Cyanine blue	5			5					5							
	Titanium dioxide	1		5		5		20									
Antisagging agent	DISPARLON A630-20XN	2	2		2	2	1	1	2	2	1	2	2				
	BENTON SD-2			1				1			1						
Solvent	Xylene	25	23	20	21	24	34	7	20	43	46	12	11				
	Butyl acetate			8					9			23					

Table 18

		Comparative Example						
		8	9	10	11	12	13	14
Polymer solution	S ₁ S ₂ S ₃ S ₄ S ₅	40	20 20	20	35	35	30	
Other resin and plasticizer	Rosin Zinc rosinate TSF-4445 Chlorinated paraffin				5	5	5	
Organism-adhesion inhibitor	4-isopropylpyridine-diphenyl(methyl)borane 4-phenylpyridyl-diphenylborane Diphenyl(methyl)borane-n-octadecylamine Triphenylborane-3-ethoxypropylamine Pyridine-triphenylborane 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine 2,4,5,6-tetrachloro-isophthalonitrile N,N'-dimethyl-N''-octyl-isothiazoline-3-one N'-(fluorodichloromethylthio)phthalimide N,N'-dimethyl-N''-phenyl-N''-fluorodichloromethylthio-sulfamide N,N'-dimethyl-N''-dichlorophenylurea 2,4,6-trichlorophenyl-maleimide 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine 2-pyridinethiol-1-oxide-copper salt 2-pyridinethiol-1-oxide-zinc salt	10	10	10	10	2 	5 	1 2 2 2
Pigment	Talc Zinc oxide Red ochre Cyanine blue Titanium dioxide	3	3	3	3 10	2 12	1	
Antisagging agent	DISPARLON A630-20XN BENTON SD-2	5 10	5 10	5 10	5 2	5	5	5
Solvent	Xylene Butyl acetate	2	2	2	2	2	1	1
Total		30	30	30	23	20	10 11	17
		100	100	100	100	100	100	100