a chemical structure containing a polyfunctional group having 2 to 6 functional groups. Further, the antifouling coating composition has Michael addition reactivity to undergo conjugate addition reaction with carbanion such as amine or other nucleophiles.

[0022]

Examples of bifunctional compounds having an ether structure among the above compounds include:

diethylene glycol diacrylate, tetraethylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, dipropylene glycol diacrylate, alkoxylated hexanediol diacrylate, polyethylene glycol dimethacrylate, ethoxylated (3) bisphenol A diacrylate, ethoxylated (4) bisphenol A dimethacrylate and ethoxylated (4) bisphenol A diacrylate;

examples of trifunctional compounds include:

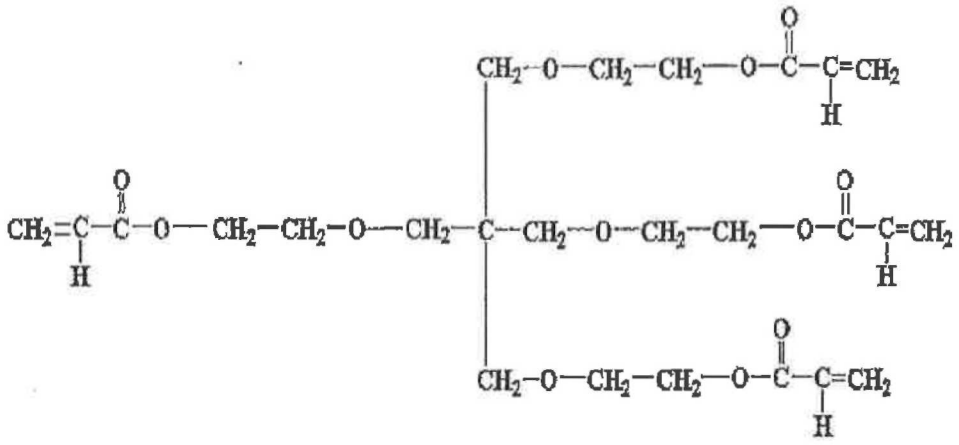
ethoxylated (9) trimethylolpropane triacrylate, ethoxylated (20) trimethylolpropane triacrylate, ethoxylated (6) trimethylolpropane triacrylate, propoxylated (6) trimethylolpropane triacrylate, propoxylated (3) glyceryl triacrylate and ethoxylated (15) trimethylolpropane triacrylate; and

examples of tetrafunctioanl compounds include:

ethoxylated (4) pentaerythritol tetraacrylate.

Typical examples of commercial products thereof include SR230 (diethylene glycol diacrylate, bifunctional), SR502 (ethoxylated (9) trimethylolpropane triacrylate, trifunctional) and SR494

(ethoxylated (4) pentaerythritol tetraacrylate, tetrafunctional)



On the other hand, examples of bifunctional compounds having no ether structure include:

1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexanedimethanol diacrylate, tricyclodecanedimethanol diacrylate, ethylene glycol dimethacrylate, dioxane glycol diacrylate, dipropylene glycol diacrylate, and dodecane diacrylate;

examples of trifunctional compounds include:

trimethylolpropane triacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate and pentaerythritol triacrylate;

examples of tetrafunctioanl compounds include:

pentaerythritol tetraacrylate, ditrimethylolpropane tetraacrylate and tetraacrylate;

examples of pentafunctional compounds include dipentaerythritol pentaacrylate; and

It is desirable that the plasticizer (I) is used in an amount of 0.1 to 40% by weight, preferably 0.5 to 30% by weight, more preferably 1.0 to 20% by weight, in the antifouling coating (solid component).

<Anti-sagging agent (J) (also referred to as "anti-running agent")>

Examples of the anti-sagging agents (J) include amide wax, a hydrogenated castor oil wax-based anti-sagging agent, a polyamide wax-based anti-sagging agent, a mixture of these agents, and synthetic finely divided silica. Preferable are polyamide wax and synthetic finely divided silica. Examples of commercial products thereof include "Disparlon A603-20X" manufactured by Kusumoto Chemicals, Ltd. and "ASAT-250F" manufactured by Itoh Oil Chemicals Co., Ltd. The antifouling coating composition of the present invention containing the anti-sagging agent is preferable because anti-sagging properties, etc. in the coating process can be controlled. It is desirable that the anti-sagging agent (J) is used in an amount of 0.1 to 30% by weight, preferably 0.5 to 20% by weight, more preferably 1.0 to 10% by weight, based on the antifouling coating (solid component).

<Anti-settling agent (K)>

Examples of the anti-settling agents (K) include organic clay-based amine salts of Al, Ca or Zn, polyethylene wax and oxidized polyethylene-based wax, and preferable is oxidized polyethylene-based wax. An example of a commercial product of the anti-settling agent is "Disparlon 4200-20" manufactured by Kusumoto

Production of side-chain end metal salt bond copolymer (a1)

Production of side-chain end metal salt bond copolymer (a1)		Production Example 1 (a1)
Monobasic acid metal (meth)acrylate: monomer (a11)	Versatic acid zinc methacrylate	35
Other unsaturated monomer copolymerizable with monomer (a11): monomer (a12) *	2-Methoxyethyl acrylate	10
	3-Methoxybutyl acrylate	30
	Ethyl acrylate	25
Polymerization initiator	t-Butyl peroxide	6
Property value	Viscosity (mPa·s)	1880
	Solid content (wt%)	45.7

* The units of the values of the monomer (a11), the monomer (a12) and the polymerization initiator are each part(s) by weight.

[Production Example 2]

Production of metal salt bond-containing monomer (a21)

Into a four-neck flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer, 85.4 parts by weight of propylene glycol methyl ether (PGM) and 40.7 parts by weight of zinc oxide were introduced, and with stirring, they were heated to 75°C.

[0104]

Subsequently, from the dropping funnel, a mixture consisting of 43.1 parts by weight of methacrylic acid (MAA), 36.1 parts by weight of acrylic acid (AA) and 5 parts by weight of water was dropped at a constant rate over a period of 3 hours. After the dropping was completed, the reaction solution turned into transparent from an opaque white state. After stirring for 2 hours, 36 parts by weight of propylene glycol methyl ether (PGM) were added, to thereby obtain a transparent metal salt bond-containing monomer solution (a21). The solid content in the mixture solution of the resulting metal salt bond -containing monomer solution (a21) was 44.8% by weight.

[Production Example 3]

Production of metal salt bond-containing copolymer (a2)

Into a four-neck flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer, 15 parts by weight of propylene glycol methyl ether (PGM), 57 parts by weight of xylene and 4 parts by weight of ethyl acrylate were introduced, and with stirring, they were heated to 100°C.

[0105]

Subsequently , from the dropping funnel, a transparent mixture consisting of 1 part by weight of methyl methacrylate (MMA), 70.2 parts by weight of ethyl acrylate (EA), 5.4 parts by weight of 2-methoxyethyl acrylate (2-MEA), 52 parts by weight of the metal salt bond-containing monomer solution (a21) obtained in Production Example 2, 10 parts by weight of xylene, 1 part by weight of a chain transfer agent ("Nofmer MSD", manufactured by Nippon Oil & Fats Co., Ltd.), 2.5 parts by weight of azobisisobutyronitrile (AIBN, manufactured by Japan Hydrazine Company Inc.) and 7 parts by weight of 2,2'-azobis(2-methylbutyronitrile) (AMBN) was dropped at a constant rate over a period of 6 hours. (Dropping step 1)

After the dropping was completed, 0.5 part by weight of t-butyl peroctoate (TBPO) and 7 parts by weight of xylene were dropped over a period of 30 minutes. After stirring for 1 hour and 30 minutes, 4.4 parts by weight of xylene were added, to thereby obtain a light yellow, transparent crosslinked metal salt bond-containing copolymer (a2). Property values of the resulting crosslinked metal salt

for 1 hour. A list of the raw materials is shown in Table 7.

[0112]

The resulting dispersion was filtered through a 60-mesh filtering net, to thereby prepare a first component of an antifouling coating composition.

(Second component)

An amino group-containing compound having composition described in Table 4-1 was prepared as a second component.

<Property evaluation of antifouling coating composition>

The first component and the second component prepared above were mixed in a given ratio shown in Table 4-1, and an antifouling coating film was produced and evaluated.

Examples 2 to 27, Comparative Examples 1 to 17

Antifouling coating composition were prepared in the same manner as in Example 1, except that the blending components of the first component containing (A) and the second component containing (B), another resin component, and the blending amounts of them were changed as shown in Tables 4-1 and 4-2 (Examples) and Tables 5-1 and 5-2 (Comparative Examples).

Comparative Examples 18 to 23

Coatings of one-component composition were intended to be prepared in blending amounts shown in Table 6, but gelation took place during the preparation of each of the coatings, so that a coating film could not be formed.

dried at 23°C for 7 days and statically immersed in Nagasaki Bay of Nagasaki Prefecture, and the area of adhesion of aquatic organisms was measured by visual observation every month, and the static antifouling properties were evaluated based on the following evaluation criteria.

[0116]

0: There is no adhesion of aquatic organisms.

0.5: The area of adhesion of aquatic organisms is more than 0% but not more than 10%.

1: The area of adhesion of aquatic organisms is more than 10% but not more than 20%.

2: The area of adhesion of aquatic organisms is more than 20% but not more than 30%.

3: The area of adhesion of aquatic organisms is more than 30% but not more than 40%.

4: The area of adhesion of aquatic organisms is more than 40% but not more than 50%.

5: The area of adhesion of aquatic organisms is more than 50%.

[Table 4-1] (continued)

			Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
First component	Ether structure-free (meth)acrylic ester	SR295 (pentaerythritol tetraacrylate, tetrafunctional) SR351S (trimethylolpropane triacrylate, trifunctional)							
	Ether structure-containing (meth)acrylic ester	SR502 (ethoxylated (9) trimethylolpropane triacrylate, trifunctional) SR494 (ethoxylated (4) pentaerythritol tetraacrylate, tetrafunctional) SR230 (ethylene glycol diacrylate, bifunctional) SR508 (dipropylene glycol diacrylate, bifunctional)	18	14	22	19	29	14	18
	Another resin component	Laropal A-81 Epikote 828	0 3	6 0	0 0	0 0	0 8	6 0	0 3
	Plasticizer	TCP (tricresyl phosphate) Benzyl alcohol	1 0	1 0	1 0	1 0	0 8	1 0	1 0
	Pigment component	Zinc oxide TTK talc Red iron oxide No. 404 Novoperm Red F5RK	30 12 1 0.5	30 12 1 0.5	30 12 1 0.5	30 12 1 0.5	12 8.5 1 0.5	30 12 1 0.5	30 12 1 0.5
	Pigment dispersing agent	Disperbyk-101	0.3	0.3	0.3	0.3	0	0.3	0.3
	Antifoulant component	Zinc Omadine Sea-Nine 211 ECONEA Irgarol 1051 Medetomidine Copper Omadine Cuprous oxide NC-803	7 0 0 0 0 1.5 0	7 0 0 0 0 1.5 0	7 5 0 0 0 0 0	7 5 0 0 0 0 0	10 0 0 0 0 3 0	7 5 0 0 0 0 0	7 4 0 0 0 0 0
	Thixotropic agent	Disparlon A603-20X	1	1	1	1	0	1	1
	Solvent	Xylene	15.7	15.7	12.2	12.2	0	12.2	12.2
(Subtotal)			91	90	92	89	80	90	90
Second component	Polyether structure-containing amine	Jeffamine D-230 Jeffamine T-403							
	Polyether structure-free amine	Ancamine 2074	10	10	8	11	20	10	10
(Subtotal)			10	10	8	11	20	10	10
[Total]			100	100	100	100	100	100	100

[Table 4-2] (continued)

			Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27
First component	Ether structure-free (meth)acrylic ester	SR295 (pentaerythritol tetraacrylate, tetrafunctional)			18	18	15	13
	Ether structure-containing (meth)acrylic ester	SR502 (ethoxylated (9) trimethylolpropane triacrylate, trifunctional)						
		SR494 (ethoxylated (4) pentaerythritol tetraacrylate, tetrafunctional)	24	15				
	Another resin component	Laropal A-81	0	0	0	0	0	0
		Epikote 828	0	0	0	0	0	0
		Side-chain end metal salt bond-containing copolymer (a1)			6.5			
		Metal salt bond-containing copolymer (a2)				6.5		
		Silyl ester copolymer (a3)					5.5	5.5
		WW rosin						2
	Plasticizer	TCP (tricresyl phosphate)	5	3	1	1	1	1
		Benzyl alcohol	0	0	0	0	0	0
	Pigment component	Zinc oxide	8	9	30	30	6	6
		TTK talc	4	4	12	12	4	4
		Red iron oxide No. 404	1	1	1	1	1	1
		Novoperm Red F5RK	0.5	0.5	0.5	0.5	0.5	0.5
	Pigment dispersing agent	Disperbyk-101	0	0	0.3	0.3	0.3	0.3
	Antifoulant component	Zinc Omadine	0	0	7	7	0	0
		Sea-Nine 211	0	5	0	0	0	0
		ECONEA	0	0	3	3	0	0
		Irgarol 1051	0	0	0	0	0	0
		Medetomidine	0	0	0	0	0	0
		Copper Omadine	2	2	0	0	2	2
		Cuprous oxide NC-803	41.5	45	0	0	45	45
	Thixotropic agent	Disparlon A603-20X	1	1	1	1	1	1
	Solvent	Xylene		7.2	9.7	9.7	11.7	11.7
(Subtotal)			87	92.7	90	90	93	93
	Polyether structure-containing amine	Jeffamine T-403			3	3	2	2
	Polyether structure-free amine	Ancamine 2074	13	7	7	7	5	5
(Subtotal)			13	7	10	10	7	7
[Total]			100	99.7	100	100	100	100

[Table 4-2] (continued)

			Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27
Property value	Specific gravity		2.022	2.022	1.634	1.637	1.891	1.887
	Heating residue (wt%)		100	100	85.7	85.8	85.2	85.2
	VOC (g/L)		0	0	229.7	229.9	279	278
Coating viscosity (coating temperature 23°C)	First component only		29ps	29ps	25ps	28ps	39ps	34ps
	Mixture of first component and second component		16 ps	17ps	10ps	11ps	15ps	15ps
Drying properties (drying recorder) 5°C drying	T2 (tack-free)		16 hrs	15 hrs	18 hrs	17 hrs	10 hrs	12 hrs
	T3 (curing)		22 hrs	21 hrs	23 hrs	23 hrs	12 hrs	14 hrs
Adhesion test (immersion in ordinary temperature seawater)	1 month		0	0	0	0	0	0
	2 months		0	0	0	0	0	0
Degree of coating film consumption (25°C/15 knots)		1 month	13.5	11.5	6.8	9.8	5.6	7.8
		2 months	21.7	16.7	13.4	14.4	9.8	13.4
		3 months	29.8	23.4	19.8	20.8	14.5	19.8
		4 months	36.7	29.8	24.5	27.8	20.3	24.5
		5 months	42.3	36.7	31.9	35.8	28.9	31.8
		6 months	51.3	42.3	39.8	44.3	35.4	37.8
Static antifouling properties		1 month	0	0	0	0	0	0
		2 months	0	0	0	0	0	0
		3 months	0	0	0	0	0	0
		4 months	0	0	0	0	0	0
		5 months	0	0	0	0.5	0.5	0
		6 months	0	0.5	0.5	0.5	0.5	0.5

[0122]

[Table 7]

Main raw materials used

Trade name	Manufacturer	Type	Solid content
SR295	Sartomer	pentaerythritol tetraacrylate (tetrafunctional)	100
SR351S	Sartomer	trimethylolpropane triacrylate (trifunctional)	100
SR502	Sartomer	ethoxylated (9) trimethylolpropane triacrylate (trifunctional)	100
SR494	Sartomer	ethoxylated (4) pentaerythritol tetraacrylate (tetrafunctional)	100
SR230	Sartomer	ethylene glycol diacrylate (bifunctional)	100
SR508	Sartomer	dipropylene glycol diacrylate (bifunctional)	100
Jeffamine D230	Huntsman	polyether-containing liquid polyether amine (diamine)	100
Jeffamine T403	Huntsman	polyether-containing liquid polyether amine (triamine)	100
Luckamide V6-221	DIC	MXDA (m-xylenediamine) Mannich modified polyamine	100
Luckamide TD-966	DIC	diethylenetriamine modified aliphatic polyamine	60
Ancamine 2074	Air Products	isophoronediamine modified alicyclic liquid polyamine	100
Cardolite NX4918	Cardolite	phenalkamine	80
Laropal A81	BASF	ketone resin	100
Epikote 828	Yuka Shell Epoxy	bisphenol A liquid epoxy resin	100
Epodil 759	Air Products	monofunctional liquid epoxy reactive diluent	100
Benzyl alcohol	Shell	liquid plasticizer	100
WW rosin		rosin	100