[10] An anti-fouling coating composition containing the polymer-containing composition according to any one of [3], [4], or [7] to [9].

[11] The anti-fouling coating composition according to [10], further containing an anti-fouling agent.

[12] The anti-fouling coating composition according to [11], in which the anti-fouling agent contains at least one kind selected from the group consisting of cuprous oxide, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, pyridine-triphenylborane, and medetomidine.

[13] The anti-fouling coating composition according to any one of [10] to [12], in which a viscosity of the anti-fouling coating composition at 25°C is 5000 mPa·s or less.

[14] The anti-fouling coating composition according to any one of [10] to [13], in which a VOC content is 500 g/L or less.

[15] The anti-fouling coating composition according to any one of [10] to [14], further containing a thermoplastic resin other than the (meth)acrylic copolymer.

[16] A method for producing a (meth)acrylic copolymer, which includes a step of obtaining a (meth)acrylic copolymer by polymerizing a monomer mixture containing

at least one kind of monomer (a) selected from the group consisting of a monomer (a1) having at least one kind of structure (I) selected from the group consisting of structures represented by the following formula (1), formula (2), or formula (3), a monomer (a2) having triorganosilyloxycarbonyl group, and at least one kind of monomer (a3) selected from the group consisting of a monomer represented by the following formula (a3-1) and a monomer represented by the following formula (a3-2) and

a macromonomer (b):

The monomer (a3-1) is obtained, for example, by a method in which an inorganic metal compound containing a metal element corresponding to M in the formula (a3-1) is reacted with (meth)acrylic acid in a diluent such as an organic solvent or a reactive diluent having a polymerizable unsaturated group such as an ethylenically unsaturated monomer. The mixture which contains a metal-containing polymerizable monomer and is obtained by this method exhibits excellent compatibility with an organic solvent and other monomers and can be easily polymerized. The reaction is preferably conducted in the presence of water, and the content of water in the reaction product is preferably set to be in a range of from 0.01% to 30% by mass. Examples of the inorganic metal compound may include an oxide, a hydroxide, and a chloride of a metal selected from Zn, Cu, Mg, or Ca.

[0117] The monomer (a3-2) is obtained, for example, by a method in which an inorganic metal compound containing a metal element corresponding to M in the formula (a3-2) is reacted with (meth)acrylic acid and an organic acid corresponding to the organic acid residue R^{32} in the formula (a3-2) in a diluent such as an organic solvent or a reactive diluent having a polymerizable unsaturated group such as an ethylenically unsaturated monomer. Examples of the inorganic metal compound may include the same inorganic metal compounds as those for obtaining the monomer (a3-1).

[0118] The monomer mixture containing the monomer (a3-1) and the monomer (a3-2) is obtained, for example, by a method in which an inorganic metal compound containing the metal element corresponding to M in the formulas (a3-1) and (a3-2) is reacted with (meth)acrylic acid and an organic acid corresponding to the organic acid residue R^{32} in the formula (a 3-2) in a diluent such as an organic solvent or a reactive diluent such as an ethylenically unsaturated monomer.

At this time, the amount of the organic acid corresponding to R^{22} used is

contain components other than the copolymer (A-1), the copolymer (A-2), the organic solvent, and the anti-fouling agent. The other components may be those derived from the composition (B), those (those blended at the time of production of the anti-fouling coating composition) that are not derived from the composition (B), or a mixture thereof.

[0169] <Anti-fouling Agent>

Examples of the anti-fouling agent may include an inorganic anti-fouling agent and an organic anti-fouling agent, and one kind or two or more kinds of anti-fouling agents can be appropriately selected and used according to the performance required.

Examples of the anti-fouling agent may include copper-based anti-fouling agents such as cuprous oxide, cuprous thiocyanate, and copper powder, compounds of other metals (lead, zinc, nickel, and the like), amine derivatives such as diphenylamine, nitrile compounds, benzothiazole-based compounds, maleimide-based compounds, and pyridine-based compounds. One kind of these may be used singly or two or more kinds thereof may be used in combination.

[0170] More specific examples of the anti-fouling agent may include 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, manganese ethylenebisdithiocarbamate, zinc dimethyldithiocarbamate, 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, 2,4,5,6-tetrachloroisophthalonitrile, N,N-dimethyldichlorophenyl urea, zinc ethylenebisdithiocarbamate, copper rhodanide, 4,5-dichloro-2-n-octyl-3(2H)isothiazolone, N-(fluorodichloromethylthio)phthalimide, N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)-sulfamide, 2-pyridinethiol-1-oxide zinc salt, tetramethylthiuram disulfide, Cu-10% Ni solid solution alloy, 2,4,6-trichlorophenylmaleimide-2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine, 3-iodo-2-propynyl butylcarbamate, diiodomethyl paratrisulfone, bisdimethyl dithiocarbamoyl zinc ethylenebisdithiocarbamate, phenyl-(bispyridyl)-bismuth dichloride, 2-(4-

thiazolyl)-benzimidazole, medetomidine, and pyridine-triphenylborane.

[0171] It is preferable that the anti-fouling agent contains at least one kind selected from the group consisting of cuprous oxide, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile (hereinafter also referred to as an "anti-fouling agent (1)", pyridine-triphenylborane, and medetomidine among those mentioned above.

In the case of combining cuprous oxide with the anti-fouling agent (1), the blending ratio (mass ratio) therebetween is that cuprous oxide/anti-fouling agent (1) is preferably 80/20 to 99/1 and more preferably 90/10 to 99/1.

Either or both of cuprous oxide and the anti-fouling agent (1) may be combined with anti-fouling agents other than these.

[0172] The content of the anti-fouling agent in the anti-fouling coating composition is not particularly limited, but it is preferably from 10 to 200 parts by mass and more preferably from 50 to 150 parts by mass with respect to 100 parts by mass of the copolymer (A-1) or (A-2). The anti-fouling effect of the coating film to be formed is superior when the content of the anti-fouling agent is equal to or higher than the lower limit value of the above range. The self-polishing properties are excellent when the content of the anti-fouling agent is equal to or lower than the upper limit value of the above range.

[0173] <Other Components>

Examples of other components may include polymers other than the copolymer (A-1) and the copolymer (A-2).

Examples of other polymers may include a thermoplastic resin (thermoplastic polymer) other than the copolymer (A-1) and the copolymer (A-2).

It is preferable that the anti-fouling coating composition of the present aspect contains a thermoplastic resin other than the copolymer (A-1) and the copolymer (A-2).

[0178] Examples of the dehydrating agent may include silicate-based, isocyanate-based, orthoester-based, and inorganic dehydrating agents. More specific examples thereof may include methyl orthoformate, ethyl orthoformate, methyl orthoacetate, an orthoboric acid ester, tetraethyl orthosilicate, anhydrous gypsum, calcined gypsum, and synthetic zeolite (molecular sieve). Particularly, molecular sieve is preferable. By adding a dehydrating agent to the anti-fouling coating composition, water is supplemented and the storage stability can be improved.

Examples of the anti-settling agent and anti-sagging agent other than the thermoplastic resin may include a bentonite-based agent, fine powder silica-based agent, a stearate salt, a lecithin salt, and an alkyl sulfonate salt.

[0179] Examples of the plasticizer other than the thermoplastic resin may include phthalic acid ester-based plasticizers such as dioctyl phthalate, dimethyl phthalate, dicyclohexyl phthalate, and diisodecyl phthalate; aliphatic dibasic acid ester-based plasticizers such as isobutyl adipate and dibutyl sebacate; glycol ester-based plasticizers such as diethylene glycol dibenzoate and pentaerythritol alkyl ester; phosphoric acid ester-based plasticizers such as tricresyl phosphate (TCP), triaryl phosphate, and trichloroethyl phosphate; epoxy-based plasticizers such as epoxy soybean oil and octyl epoxy stearate; organotin-based plasticizers such as dioctyltin laurate and dibutyltin laurylate; trioctyl trimellitate, and triacetylene. By containing a plasticizer in the anti-fouling coating composition, it is possible to enhance the crack resistance and peeling resistance of the coating film. As the plasticizer, TCP is preferable among those mentioned above.

[0180] The anti-fouling coating composition may or may not contain water.

The water content in the anti-fouling coating composition is preferably 15% by mass or less and more preferably 10% by mass or less. The lower limit is not

The viscosity of the measurement sample was measured at 25°C by using a B-type viscometer and the value was presented as the B-type viscosity.

[0198] (Weight Average Molecular Weight (Mw) and Number Average Molecular Weight (Mn))

· (Meth)acrylic copolymer containing constitutional unit (A-3):

The measurement was conducted by using a gel permeation chromatographic (GPC) instrument (HLC-8220 manufactured by Tosoh Corporation). A N,N-dimethylformamide (DMF) solution was prepared so as to contain the (meth)acrylic copolymer at 0.4% by mass, 100 μl of the solution was injected into a device equipped with a column manufactured by Tosoh Corporation (TSK gel α-M (manufactured by Tosoh Corporation, 7.8 mm × 30 cm), TSK guard column α (manufactured by Tosoh Corporation, 6.0 mm × 4 cm)), and the measurement was conducted at 40°C. The weight average molecular weight (Mw) or the number average molecular weight (Mn) was calculated in terms of standard polystyrene.

·(Meth)acrylic copolymer containing at least one kind of constitutional unit selected from the group consisting of constitutional units (A1) and (A2) and macromonomer (b):

The measurement was conducted by using a gel permeation chromatographic (GPC) instrument (HLC-8320 manufactured by Tosoh Corporation). A tetrahydrofuran solution was prepared so as to contain the copolymer and the macromonomer at 0.2% by mass, 10 μl of the solution was injected into a device equipped with a column manufactured by Tosoh Corporation (TSK gel Super HZM-M × HZM-M × HZ 2000, TSK guard column Super HZ-L), the measurement was conducted under the conditions of a flow rate: 0.35 ml/min, an eluent: tetrahydrofuran (stabilizer: BHT), and a column temperature: 40°C, and the weight average molecular weight (Mw) or the number

A sample (polymer-containing composition or anti-fouling coating composition) was coated on a glass substrate by using a 500 μm applicator and dried at room temperature for 1 week to form a coating film, thereby obtaining a test plate. This test plate was immersed in the sterilized and filtered sea water for 1 month and then dried at room temperature of 20°C for 1 week. The haze of the test plate after drying was measured by using a haze meter (manufactured by MURAKAMI COLOR RESEARCH LABORATORY CO., LTD., trade name: HM-150). It indicates that the degree of whitening of the surface of coating film is lower and the water resistance of coating film is superior as the haze value is smaller.

[0206] (Degree of Consumption of Coating Film)

The anti-fouling coating composition was coated on a hard vinyl chloride plate of 50 mm × 50 mm × 2 mm (thickness) by using an applicator so as to have a dry film thickness of 120 μm and dried to form a coating film, thereby obtaining a test plate. This test plate was attached to a rotating drum installed in the sea water and rotated at a peripheral speed of 7.7 m/s (15 knots), and the film thickness of the coating film after 3 months was measured. The film thickness consumed per month ((120 μm - measured film thickness (μm))/3) was calculated from the measured film thicknesses, and the value was taken as the degree of consumption. The degree of consumption is preferably from 1 to 30 μm/M.

[0207] (Static Anti-fouling Properties)

The anti-fouling coating composition was coated on a sandblasted steel plate of 150 mm × 70 mm × 1.6 mm (thickness) coated with a rust proof coating in advance by using a brush so as to have a dry film thickness of 120 μm and dried to form a coating film, thereby obtaining a test plate. This test plate was immersed in the sea and allowed to stand still for 3 months, then the proportion (the area occupied by marine

minutes after the dropwise addition was competed, 1.0 part of t-butylperoxy 2-ethylhexanoate and 10 parts of xylene were added dropwise to the resultant mixture over 1.5 hours, and the mixture was further stirred for 1 hour, thereby obtaining a polymer-containing composition (polymer solution) A-12 in the form of a solution having a solid content of 61.1% by mass and a B-type viscosity of 760 mPa·s.

[0235] <Examples 22 to 23 and Comparative Example 5>

Polymer-containing compositions A-13, A-14, and A -16 were produced in the same manner as in Example 21 except that the amounts (parts) of the monomer and the initiator AMBN charged were changed as presented in Table 3.

[0236] <Example 24>

In a reaction vessel equipped with a stirrer, a temperature controller, and a dropping funnel, 40 parts of xylene was charged, and the temperature of the xylene was raised to 90°C while stirring it. Subsequently, a mixture composed of 50 parts of TIPX, 10 parts of macromonomer (MM2), 25 parts of MMA, 10 parts of EA, 5 parts of MTA, and 1.0 part of AMBN was added dropwise thereto from the dropping funnel at a constant rate over 4 hours funnel in a nitrogen atmosphere. In 30 minutes after the dropwise addition was competed, 1.0 part of t-butylperoxy 2-ethylhexanoate and 26 parts of xylene were added dropwise to the resultant mixture over 1.5 hours, and the mixture was further stirred for 1 hour, thereby obtaining a polymer-containing composition (polymer solution) A-15 in the form of a solution having a solid content of 61.1% by mass and a B-type viscosity of 690 mPa·s.

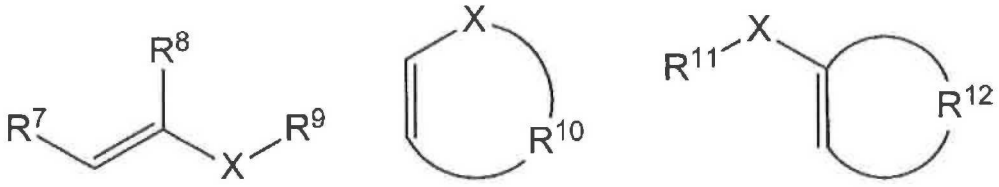
[0237] The values of properties (solid content (% by mass), amount of organic solvent (% by mass), B-type viscosity, and the number average molecular weight (Mn), weight average molecular weight (Mw), and acid value of the copolymer contained in each of the polymer-containing compositions) of the polymer-containing compositions A-12 to

[0260] [Table 8]

			Example 60	Example 61	Example 62	Example 63	Example 64	Comparative Example 9	Comparative Example 10	Example 65	Example 66	Example 67	Example 68
Composition	Polymer-containing composition	A-17	-	-	-	-	100	-	-	-	-	-	100
		A-29	100	-	-	-	-	-	-	-	-	-	-
		A-30	-	100	-	-	-	-	-	-	-	-	-
		A-31	-	-	100	-	-	-	-	-	-	-	-
		A-32	-	-	-	100	-	-	-	-	-	-	-
		A-33	-	-	-	-	-	100	-	-	-	-	-
		A-34	-	-	-	-	-	-	100	-	-	-	-
		A-35	-	-	-	-	-	-	-	100	-	-	-
		A-36	-	-	-	-	-	-	-	-	100	-	-
		A-37	-	-	-	-	-	-	-	-	-	100	-
	Pigment	Talc	30	30	30	30	-	30	30	30	30	30	30
		Zinc oxide	60	60	60	60	-	60	60	60	60	60	60
	Anti-fouling agent	Cuprous oxide	-	-	-	-	120	-	-	-	-	-	-
		Copper pyrithione	-	-	-	-	1.5	-	-	-	-	-	-
		Zinc pyrithione	5	5	5	5	-	5	5	5	5	5	5
		Medetomidine	0.1	0.1	0.1	0.1	-	0.1	0.1	0.1	0.1	0.1	0.1
		Anti-fouling agent (1)	8	8	8	8	-	8	8	8	8	8	-
		Pyridine-triphenylborane	-	-	-	-	-	-	-	-	-	-	8
	Additive	Additive (1)	1	1	1	1	2	1	1	1	1	1	1
		Additive (2)	2	2	2	2	5	2	2	2	2	2	2
		Additive (4)	-	-	-	-	-	-	-	-	-	-	1
	Organic solvent	BuOH	5	5	5	5	5	5	-	5	5	5	5
	Water		-	-	-	-	-	-	5	-	-	-	-
Properties of coating		Heating residue (% by mass)	71.3	70.9	75.1	72.4	73.5	70.7	65.1	73.5	70.8	70.7	70.7
		B-type viscosity (mPa·s)	1600	4400	2300	2300	4400	4400	4000	2000	3100	1900	1500
		VOC (g/L)	395	395	375	395	420	395	270	395	395	395	395
Performance of coating film		Degree of consumption (3 months) (μm/M)	2.4	20.0	2.4	2.1	1.7	4.9	1.4	3.2	10.1	3.1	2.0

formula (12), and a compound represented by the following formula (13), wherein the (meth)acrylic copolymer has the constitutional unit (A1):

[Chem. 5]



(11) (12) (13)

(where, X represents -O-, -S-, or -NR^{14}-, R^{14} represents a hydrogen atom or an alkyl group, R^7 represents a hydrogen atom or an alkyl group having from 1 to 9 carbon atoms, R^8 represents a hydrogen atom or an alkyl group having from 1 to 10 carbon atoms, R^9 and R^{11} each represent an alkyl group having from 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, R^{10} represents a single bond or an alkylene group having from 1 to 9 carbon atoms, and R^{12} represents an alkylene group having from 1 to 9 carbon atoms).

10. An anti-fouling coating composition comprising the polymer-containing composition according to any one of claims 3, 4, and 7 to 9.

11. The anti-fouling coating composition according to claim 10, further comprising an anti-fouling agent.

12. The anti-fouling coating composition according to claim 11, wherein the anti-fouling agent contains at least one kind selected from the group consisting of cuprous oxide, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, pyridine-triphenylborane, and medetomidine.