

REPLACED SHEETS		SG
☒	Description : paged ...1... to paged ...68...	
☒	Claim(s) : paged ...69... to paged ...72...	
☒	Drawing(s) : paged ...42... to paged ...242...	
☒	Abstract : paged ...73... to paged	
DATE OF RECEIPT		

1 BACKGROUND OF THE INVENTION

This invention relates to a coating resin and an antifouling coating composition to be used for preventing attachment of marine organisms to the under-
5 water or submarine structures such as ships, fishing nets, drainage conduits, etc.

Numerous species of marine organisms, such as barnacle, ascidian, serpula, mussel, laver, etc., live in the sea water. When a structure such as a ship,
10 fishing net, drainage pipe, etc., is set or placed in comission in or on the sea, the marine organisms cling to the structure and grow to give various kinds of damage to the structure. For instance, if the ship's bottom is incrustated with marine organisms, the
15 frictional resistance of the sea water increases to cause a reduction of cruising performance of the ship, so that if it is tried to keep a constant cruising speed of the ship, its fuel consumption increases to pose a serious encomical problem. Also, if the marine
20 organisms cling to the fishing nets used for ocean culture, the meshes of the nets would be clogged up, which could prove fatal to the cultured fishes and shellfishes.

Hitherto, in order to prevent attachment of
25 the marine organisms to the underwater structures such



1 as mentioned above, the antifouling paints using single
polymers or copolymers of organotin-containing
unsaturated monomers as resinous component (see Japanese
Patent Application Kokoku (Post-Exam Publication) Nos.
5 40-21426, 44-9579, 46-13392, 49-20491, 51-11647,
51-12049, 52-48170, etc.) have been applied to said
structures. These polymers have their organotin portion
hydrolyzed with the sea water (pH: 8.0 - 8.3). As a
result, not only the organotin serves as an antifouling
10 agent, but also the polymer surface which has been made
soluble in sea water is gradually corroded by the moving
sea water to bare out the new coating surface, thus
producing a long-lasting stabilized antifouling effect.
However, the organotin released into the sea water from
15 the paints is hard to decompose and may be taken in by
and accumulated in the marine organisms and, through the
food chain, it may get into the human system. This
involves the possibility of causing serious physical
trouble such as deformity. So, use of organotin in the
20 antifouling paints has been banned.

Request is now voiced in the art for the
development of a resin for antifouling paints which are
capable of producing a long-lasting stabilized anti-
fouling effect, in place of the organotin-based resins
25 whose use has been banned. Ideally speaking, it is
desirable that the resins used for antifouling paints
are of a hydrolyzable type like the organotin-based
resins, but proposals involving use of hydrophilic or



1 water-repellent resins have also been made (Japanese
Patent Application Kokai (Laid-Open) Nos. 62-290768,
62-13471, 58-180566, 57-67672, etc.). However, it is
hardly possible to realize a long-lasting stabilized
5 antifouling effect by use of a resin having the
hydrophilic or water-repellent property alone.

In view of the above, various hydrolyzable
resins having a specific carboxylic acid ester in the
side chain have been proposed (WO 84/02915, Japanese
10 Patent Appln. Kokai Nos. H2-69576, 63-215780, 62-57464,
Japanese Patent Appln. Kokoku Nos. 55-39271, 61-3830,
etc.), but their effect has not been well satisfactory.

It is essential that the resin used for said
purpose is soluble in the aromatic solvents or the
15 mixtures of aromatic solvents (main solvent) and other
types of solvent such as alcohol type solvents, ketone
type solvents, halogen type solvents, ether type
solvents and ester type solvents so that the solvent
used won't affect the undercoat when coating is
20 performed.

SUMMARY OF THE INVENTION

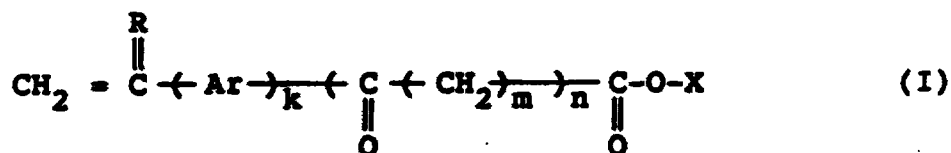
The present invention provides an excellent
coating resin and an antifouling coating composition
containing said resin which has no poisonous action like
25 the organotin copolymers, shows a hydrolytic property
well comparing with said organotin copolymers, and is
capable of forming a relatively long-lasting excellent



1 antifouling coat. This coating resin is also soluble in aromatic solvents.

The present inventors have pursued strenuous studies for solving said prior art problems and developing an antifouling coating composition which performs excellently for preventing attachment of the marine organisms to the underwater structures such as mentioned above and has no problem in safety and sanitation, and have consequently accomplished the present invention.

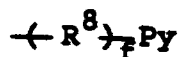
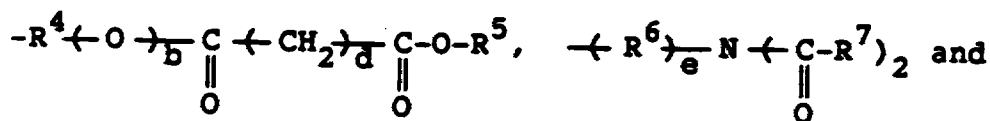
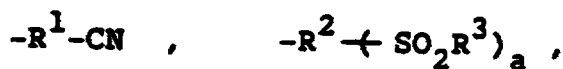
10 The present invention provides a coating resin comprising a polymer obtained by polymerizing an unsaturated monomer represented by the following formula (I) alone or together with at least one other unsaturated monomer copolymerizable therewith:



15 wherein R is a hydrogen atom or a straight or branched alkyl group having 1-4 carbon atoms; Ar is a benzene ring or a naphthalene ring; k, m and n represent independently a number of 0 or 1; and X is a substituent selected from those represented by the following

20 formulae:





- 1 wherein R^1 , R^4 , R^6 and R^8 each represents a straight,
 branched or alicyclic alkylene group having 1-6 carbon
 atoms; R^2 is a C_{1-6} straight, branched or cyclic hydro-
 carbon group connecting O and SO_2R^3 ; a is an integer of
 5 1 to 3 indicating the number of SO_2R^3 bonded to R^2 ;
 R^3 represents, independently when plural, a C_{1-22}
 straight, branched or cyclic alkyl group, a C_{6-10} aryl
 group or C_{7-18} aralkyl group which may have a sub-
 stituent; when a is 2 or 3, R^3 's may be the hydrocarbon
 10 groups forming a cyclic structure with each other; b, d,
 e and f represent independently a number of 0 or 1; R^5
 is a C_{1-4} straight or branched alkyl group; two R^7 's
 represent independently a C_{1-22} straight, branched or
 alicyclic alkyl group, a C_{6-10} aryl group or a C_{7-10}
 15 aralkyl group, or two R^7 's represent the groups forming
 a cyclic structure; and Py stands for a substituted or
 unsubstituted 2-, 3- or 4-pyridyl group.

The present invention also provides a coating
 resin of the type recited, using as other copolymeriz-
 20 able unsaturated monomer a monomer represented by the

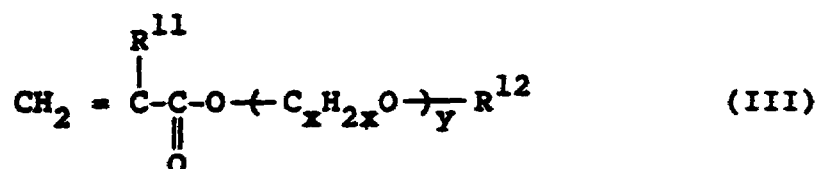


1 formula:



wherein R^9 is a hydrogen atom or CH_3 ; and R^{10} is a
 branched or alicyclic alkyl, aryl or aralkyl group
 having 3 or more carbon atoms, or an organic substituent
 5 having a similar structure but containing other atoms
 than carbon.

The present invention also provides a coating
 resin of the type recited, using as other copolymeriz-
 able unsaturated monomer an unsaturated monomer having a
 10 hydrophilic functional group, said monomer being either
 an unsaturated acid anhydride or an unsaturated monomer
 represented by the formula:



wherein R^{11} is a hydrogen atom or a CH_3 group; x is an
 integer of 1 to 6; y is an integer of 1 to 10; and R^{12}
 15 is a hydrogen atom or a straight, branched or cyclic
 alkyl, aryl or aralkyl group.



1 Fig. 11 is an IR spectrum of Compound No. 20
(R = CH₃).

 Fig. 12 is a ¹H-NMR spectrum of N-hydroxy-
methylsuccinimide.

5 Fig. 13 is an IR spectrum of N-hydroxymethyl-
succinimide.

 Fig. 14 is a ¹H-NMR spectrum of Compound No.
22 (R = CH₃).

 Fig. 15 is an IR spectrum of Compound No. 22
10 (R = CH₃).

 Fig. 16 is a ¹H-NMR spectrum of Compound No.
23 (R = CH₃).

 Fig. 17 is an IR spectrum of Compound No. 23
(R = CH₃).

15 Fig. 18 is a ¹H-NMR spectrum of Compound No.
26 (R = CH₃).

 Fig. 19 is an IR spectrum of Compound No. 26
(R = CH₃).

 Fig. 20 is a ¹H-NMR spectrum of Compound No.
20 9 (R = CH₃).

 Fig. 21 is an IR spectrum of Compound No. 9 (R
= CH₃).

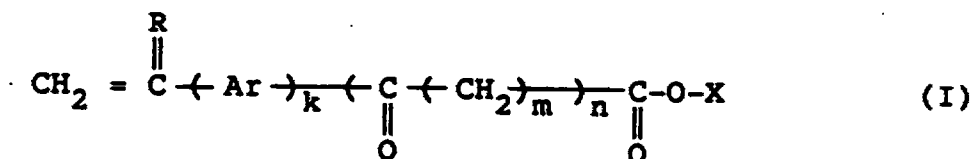
DESCRIPTION OF THE PREFERRED EMBODIMENTS

 The coating resins according to the present
25 invention are preferably those specified below (1) - (9):

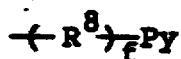
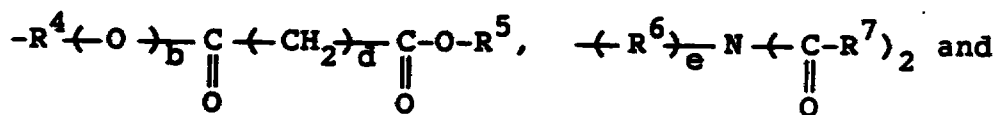
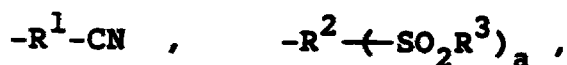
(1) A coating resin comprising a polymer obtained
by polymerizing an unsaturated monomer represented by



- 1 the following formula (I) alone or together with at least one other unsaturated monomer copolymerizable therewith:



- wherein R is a hydrogen atom or a straight or branched alkyl group having 1-4 carbon atoms; Ar is a benzene ring or a naphthalene ring; k, m and n represent independently a number of 0 or 1; and X is a substituent selected from those represented by the following formulae:



- 10 wherein R^1 , R^4 , R^6 and R^8 each represents a straight, branched or alicyclic alkylene group having 1-6 carbon atoms; R^2 is a C_{1-6} straight, branched or cyclic hydrocarbon group connecting O and SO_2R^3 ; a is an integer of 1 to 3 indicating the number of SO_2R^3 bonded to R^2 ;



- 1 R^3 represents, independently when plural, a C_{1-22} straight, branched or cyclic alkyl group, a C_{6-10} alkyl group which may have a substituent or a C_{7-18} aralkyl group which may have a substituent; when a is 2 or 3,
- 5 R^3 's may be the hydrocarbon groups forming a cyclic structure with each other; b, d, e and f represent independently a number of 0 or 1; R^5 is a straight or branched alkyl group having 1-4 carbon atoms; two R^7 's represent independently a straight, branched or
- 10 alicyclic alkyl group having 1-22 carbon atoms, an aryl group having 6-10 carbon atoms or an aralkyl group having 7-10 carbon atoms, or two R^7 's represent the groups forming a cyclic structure; and Py stands for a substituted or unsubstituted 2-, 3- or 4-pyridyl group.
- 15 (2) A coating resin specified in (1) above, using an unsaturated monomer of the formula (I) wherein k and n are both 0.
- (3) A coating resin specified in (1) or (2) above, using an unsaturated monomer of the formula (I) wherein
- 20 X is $-R^1-CH$.
- (4) A coating resin specified in (1) or (2) above, using an unsaturated monomer of the formula (I) wherein X is $-R^2-(SO_2R^3)_a$.
- (5) A coating resin specified in (1), (2), (3) or
- 25 (4) above, using an unsaturated monomer of the formula (I) wherein R is H or CH_3 .
- (6) A coating resin specified in (1), (2), (3), (4) or (5) above, wherein at least one other unsaturated



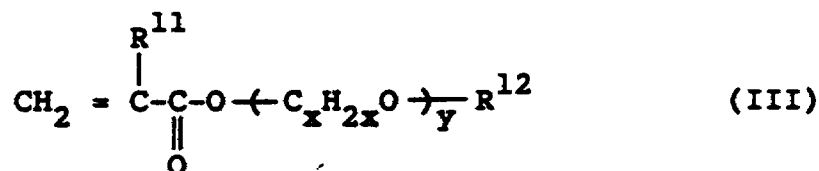
1 monomer copolymerizable with the unsaturated monomer of
the formula (I) is a monomer represented by the formula:



wherein R^9 is a hydrogen atom or CH_3 ; and R^{10} is a
branched or alicyclic alkyl, aryl or aralkyl group
5 having 3 or more carbon atoms, or an organic substituent
having a similar structure but containing other atoms
than carbon.

(7) A coating resin specified in (1), (2), (3),
(4), (5) or (6) above, wherein at least one other
10 unsaturated monomer copolymerizable with the unsaturated
monomer of the formula (I) is an unsaturated monomer
having a hydrophilic functional group.

(8) A coating resin specified in (7) above,
wherein the unsaturated monomer having a hydrophilic
15 functional group is an unsaturated acid anhydride or an
unsaturated monomer represented by the formula:



1 wherein R^{11} is a hydrogen atom or a CH_3 group; x is an integer of 1 to 6; y is an integer of 1 to 10; and R^{12} is a hydrogen atom or a straight, branched or cyclic alkyl, aryl or aralkyl group.

5 (9) A coating resin specified in any of (1) to (8) above, wherein the polymer is obtained by polymerizing a mixture of an unsaturated monomer represented by the formula (I), an unsaturated monomer represented by the formula (II) and one or more unsaturated monomers other
10 than those having a hydrophilic functional group.

In the unsaturated monomers represented by the formula (I), the C_{1-4} straight or branched alkyl groups represented by R include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, etc.

15 The C_{1-6} straight, branched or alicyclic alkylene groups represented by R^1 , R^4 , R^6 and R^8 in X include methylene, methine, ethylene, trimethylene, tetra-methylene, penta-methylene, neopentylene, hexamethylene, cyclopropylene, 1,2-cyclobutylene, 1,3-cyclobutylene, 1,2-cyclo-
20 pentylene, 1,3-cyclopentylene, 1,2-cyclohexylene, 1,3-cyclohexylene, 1,4-cyclohexylene, etc. The C_{1-22} straight, branched or cyclic alkyl groups represented by R^3 include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, cyclopropyl, cyclo-
25 butyl, pentyl, sec-pentyl, tert-pentyl, neo-pentyl, cyclopentyl, hexyl, tert-hexyl, cyclohexyl, heptyl, tert-heptyl, octyl, tert-octyl, nonyl, tert-nonyl, decyl, tert-decyl, dodecyl, tert-dodecyl, tetradecyl,



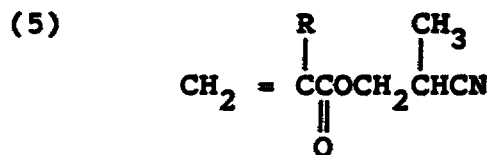
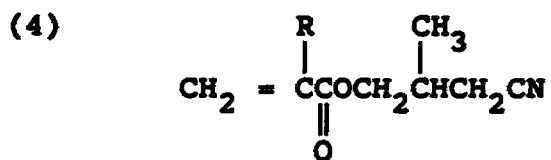
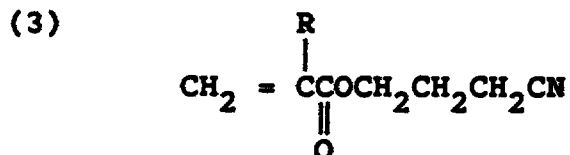
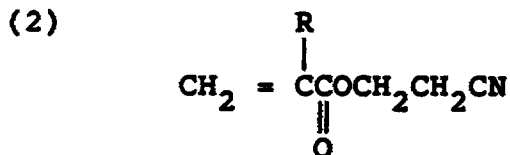
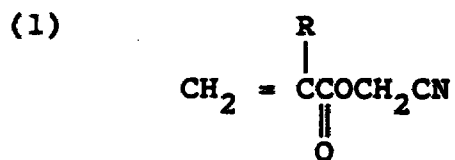
- 1 tert-tetradecyl, hexadecyl, tert-hexadecyl, octadecyl,
tert-octadecyl, eicosyl, docodyl, etc. The C_{6-10} aryl
groups or C_{7-18} aralkyl groups which may have a sub-
stituent include phenyl, tolyl, anisyl, cyanophenyl,
5 nitrophenyl, sulfonylphenyl, acylphenyl, naphthyl,
benzyl, phenethyl, benzhydryl, etc. As examples of the
hydrocarbon groups forming a cyclic structure with each
other, represented by R^3 or R^3 's (1-3), when n is 2,
there can be mentioned ethylene, trimethylene, tetra-
10 methylene, etc. The C_{1-4} straight or branched alkyl
groups represented by R^5 include methyl, ethyl,
propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-
butyl, etc. The C_{1-22} straight, branched or alicyclic
alkyl groups represented by R^7 include methyl, ethyl,
15 propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-
butyl, cyclopropyl, cyclobutyl, pentyl, sec-pentyl,
tert-pentyl, neo-pentyl, cyclopentyl, hexyl, cyclohexyl,
heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl,
hexadecyl, octadecyl, eicosyl, docosyl, etc. The
20 C_{6-10} aryl groups or C_{7-10} aralkyl groups represented by
 R^7 include phenyl, tolyl, anisyl, cyanophenyl, nitro-
phenyl, naphthyl, benzyl, phenethyl, benzhydryl, etc.
The groups forming a cyclic structure, represented by
two R^7 , include methylene, ethylene, trimethylene,
25 o-phenylene, 1,2-naphthylene, 2,3-naphthylene, etc.

The unsaturated monomers represented by the
formula (I) can be produced by various known processes
of synthesis. It is possible to use the pertinent

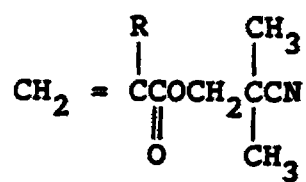


1 commercially available unsaturated monomers.

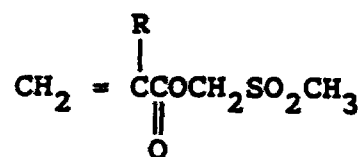
Listed below are the preferred examples of the unsaturated monomers represented by the formula (I) (R in the following formulae is hydrogen atom or methyl group):



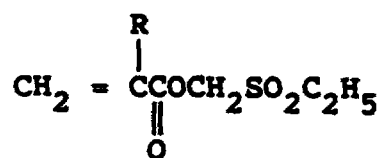
(6)



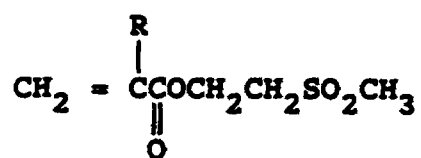
(7)



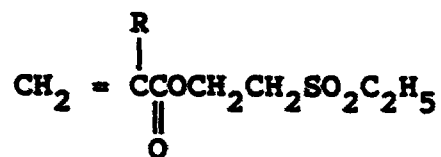
(8)



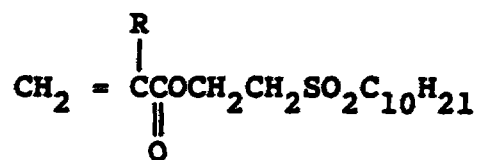
(9)



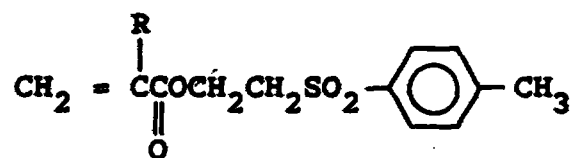
(10)



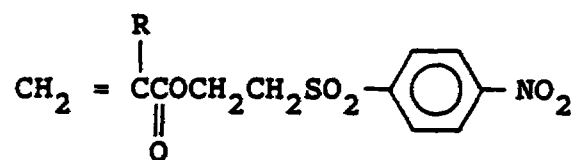
(11)



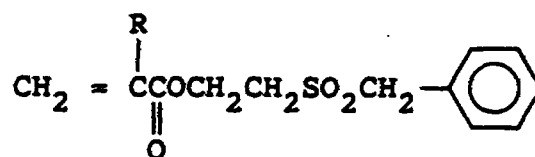
(12)



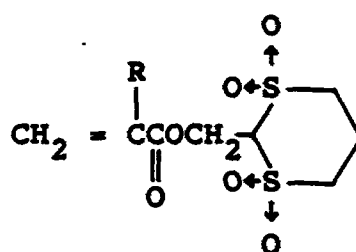
(13)



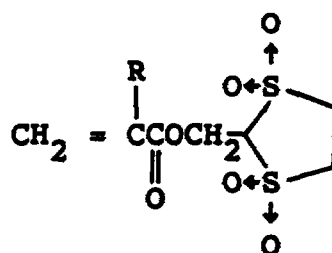
(14)



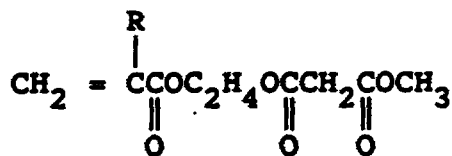
(15)



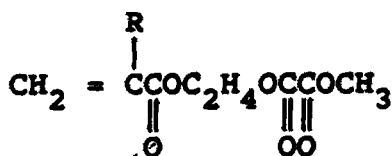
(16)



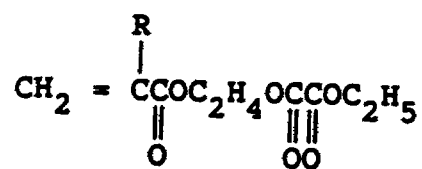
(17)



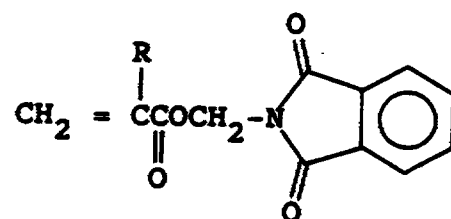
(18)



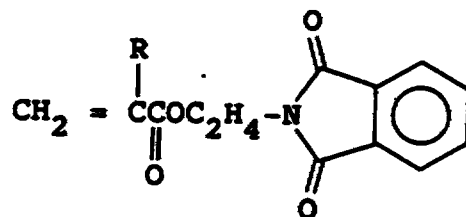
(19)



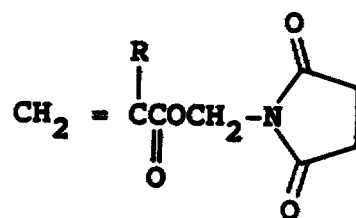
(20)



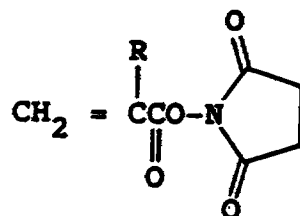
(21)



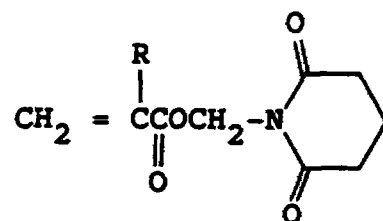
(22)



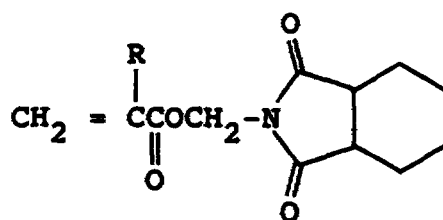
(23)



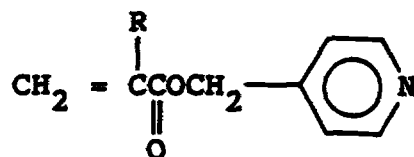
(24)



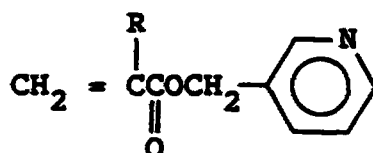
(25)



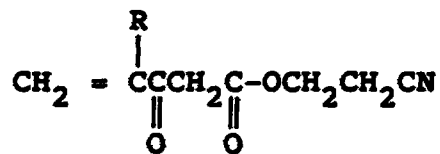
(26)



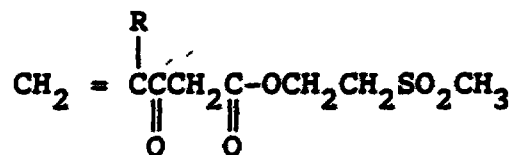
(27)



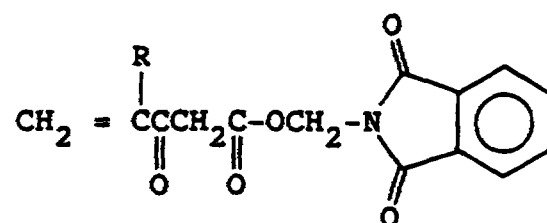
(28)



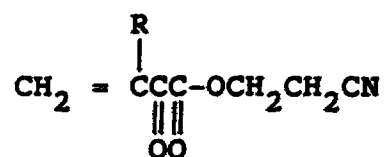
(29)



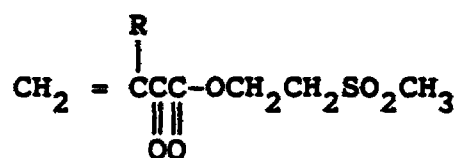
(30)



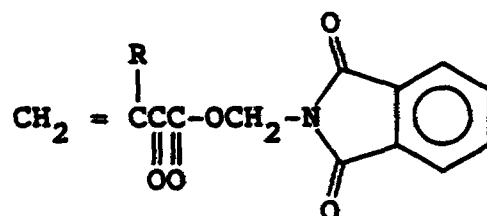
(31)



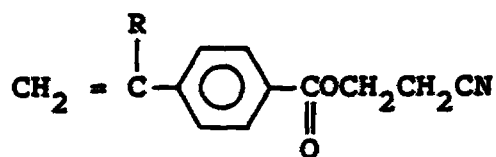
(32)



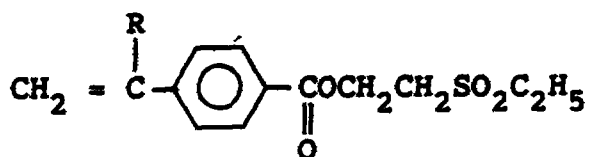
(33)



(34)



(35)



1 The compounds of the formula (I) wherein R^3 's represent the hydrocarbon groups forming a cyclic structure with each other are, for example, Compound No. 15 and Compound No. 16 shown in the above list.

5 The compounds of the formula (I) wherein two R^7 's represent the groups forming a cyclic structure are, for example, Compound Nos. 20, 21, 22, 23, 24, 25, 30 and 33 in the above list.

 These compounds are easily hydrolyzed in a
10 weakly alkaline atmosphere such as sea water.
Therefore, the resin obtained by polymerizing or copolymerizing these unsaturated monomers undergoes hydrolysis in the sea water and is gradually changed into a water-soluble type from its surface, and as this
15 portion is corroded by the moving sea water, the surface of a new coat is bared out successively, thus producing a lasting antifouling effect.

 The ratio of the unsaturated monomer of the formula (I) in the resin may be optionally selected provided that it is not less than 0.1 mol% based on the
20 whole amount of the monomers. Such unsaturated monomer may be used alone to form a homopolymer. But if its ratio is small, the proportion of the soluble portion in the resin created by the hydrolysis may prove too low to
25 produce a satisfactory antifouling performance. On the other hand, if its ratio is too high, the eluting rate tends to be increased, resulting in a poor long-time antifouling performance. Thus, the preferred ratio of



1 said unsaturated monomer is 1 to 95 mol%, more preferably 5 to 70 mol%.

As the other unsaturated monomer copolymerizable with the unsaturated monomer of the formula (I),
5 the unsaturated monomers represented by the formula (II) and the unsaturated monomers having a hydrophilic functional group are preferably used.

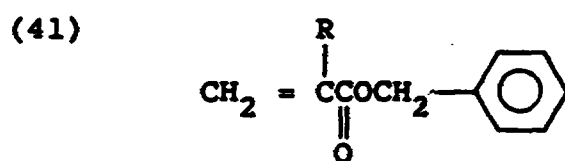
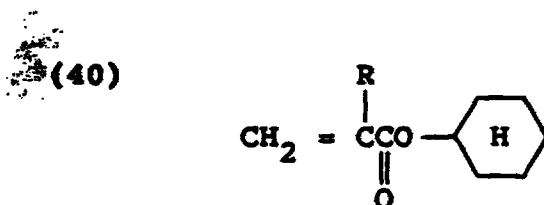
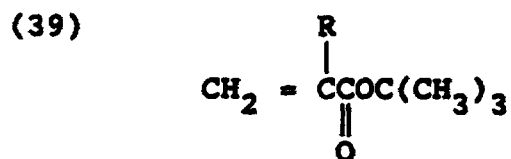
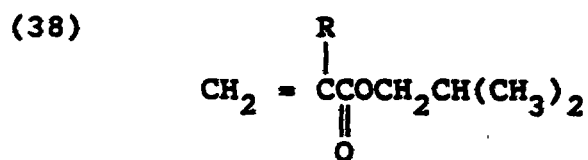
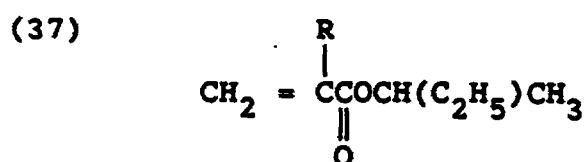
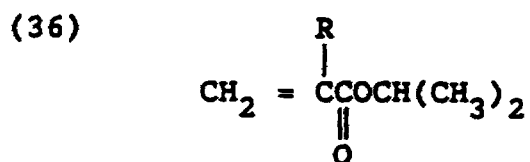
In the unsaturated monomers represented by the formula (II), the branched or alicyclic alkyl, aryl or
10 aralkyl groups having 3 or more carbon atoms, represented by R¹⁰, include isopropyl, isobutyl, sec-butyl, tert-butyl, sec-pentyl, tert-pentyl, neopentyl, 2-ethylhexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenyl, o-tolyl, m-tolyl, p-tolyl,
15 2,3-xylyl, 2,4-xylyl, o-cumenyl, m-cumenyl, p-cumenyl, mesityl, benzyl, phenethyl, trityl, naphthyl, norbornyl, adamantyl, etc. The organic substituents having a similar structure but containing other atoms than carbon include the compounds having silicon instead of carbon,
20 such as trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, triphenylsilyl, trimethoxysilyl, triethoxysilyl, tripropoxysilyl, tributoxysilyl, triphenoxysilyl, etc.

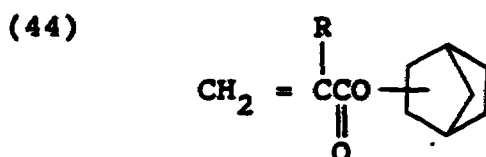
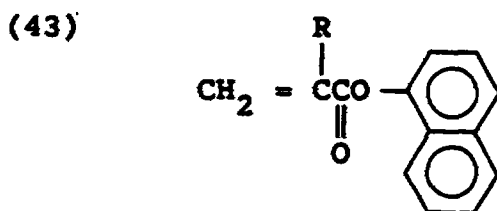
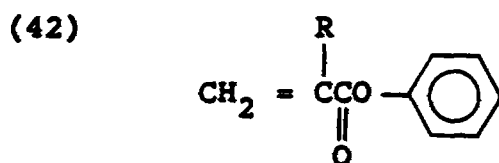
The unsaturated monomers represented by the
25 formula (II) can be produced by various known synthetic methods. The pertinent commercially available unsaturated monomers are also usable.

Listed below are the preferred examples of the



1 unsaturated monomers represented by the formula (II) (R in the following formulae is hydrogen atom or methyl group):



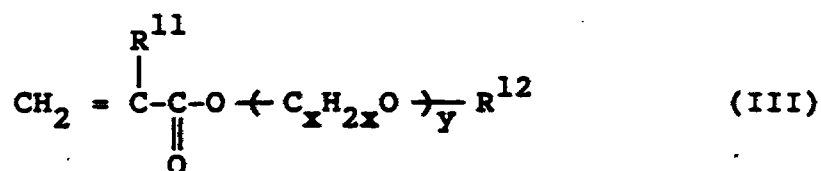


1 An unsaturated monomer of the formula (II) can
be blended for the purpose of increasing solubility in
the solvents, especially aromatic solvents. The
blending ratio of this unsaturated monomer is preferably
5 from 5 to 95 mol%. A too low blending ratio results in
a poor solubility in the aromatic solvents, while a too
high ratio leads to strengthened hydrophobic nature of
the resin, which impairs the hydrolytic characteristics
of the resin, resulting in poor antifouling performance
10 of the produced paint. Thus, the especially preferred
range of blending ratio of said unsaturated monomer is
from 5 to 50 mol%.

Examples of the unsaturated monomers having a
hydrophilic functional group, which are usable in this



1 invention, include unsaturated acid anhydrides or the unsaturated monomers represented by the formula:



wherein R^{11} is hydrogen atom or CH_3 group; x is an
 5 integer of 1 to 6; y is an integer of 1 to 100; and R^{12} is hydrogen atom or straight, branched or cyclic alkyl, aryl or aralkyl group. Use of these monomers can further enhance the hydrolytic nature provided by the unsaturated monomer of the formula (I).

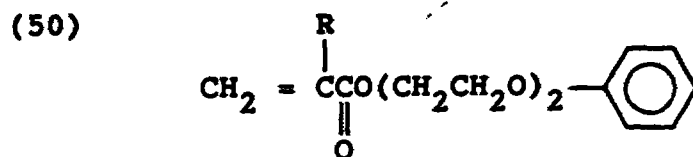
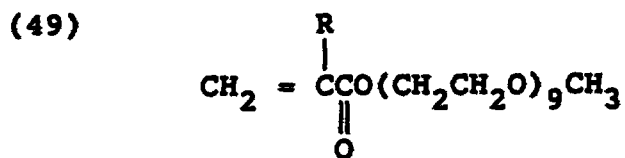
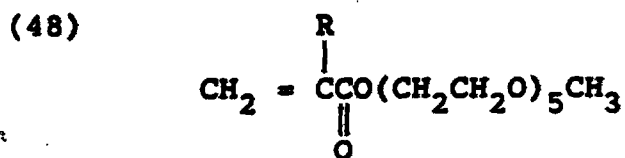
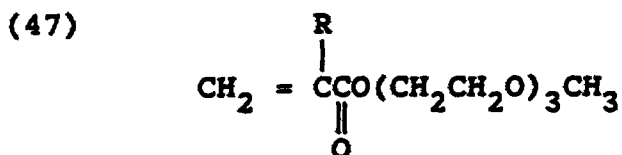
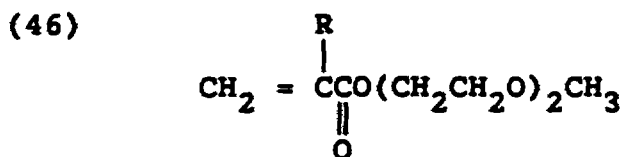
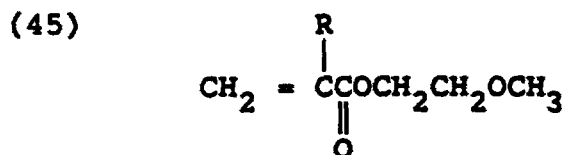
10 In the unsaturated monomers represented by the formula (III), the straight, branched or cyclic alkyl, aryl or aralkyl groups represented by R^{12} include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, sec-pentyl, tert-pentyl,
 15 neopentyl, 2-ethylhexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenyl, o-tolyl, m-tolyl, p-tolyl, 2,3-xylyl, 2,4-xylyl, o-cumenyl, m-cumenyl, p-cumenyl, mesityl, benzyl, phenetyl, trityl, naphthyl, norbonyl, etc.

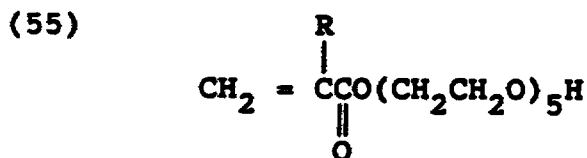
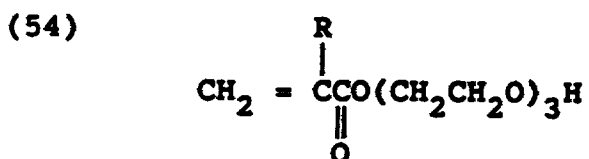
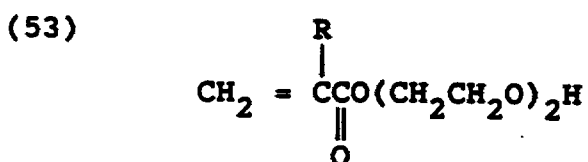
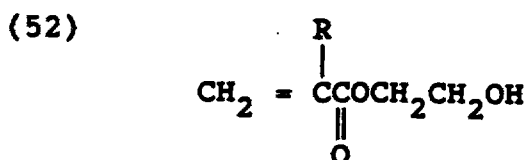
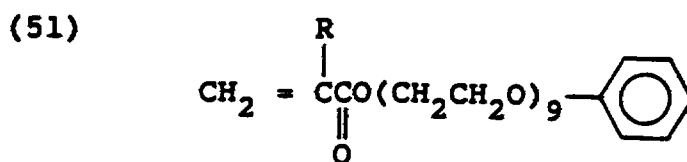
20 The unsaturated monomers of the formula (III) can be produced by various known synthetic methods. The commercially available unsaturated monomers are also



1 usable.

The following are the preferred examples of the compounds represented by the formula (III) (R in the following formulae is hydrogen atom or methyl group):





- 1 **Examples of the unsaturated acid anhydrides**
usable as an unsaturated monomer having a hydrophilic
functional group include maleic anhydride, methylmaleic
anhydride, dimethylmaleic anhydride, ethylmaleic
5 anhydride, phenylmaleic anhydride, chloromaleic
anhydride, itaconic anhydride, 1-methylitaconic
anhydride, 1,2-dimethylitaconic anhydride, 1-phenyl-



1 itaconic anhydride, 1-chloroitaconic anhydride,
endomethylenetetrahydrophthalic anhydride, chlorendic
anhydride, tetrahydrophthalic anhydride, etc.

The blending ratio of the unsaturated monomer
5 having a hydrophilic functional group is preferably from
1 to 70 mol%, more preferably from 5 to 50 mol%. When
the blending ratio is less than 1 mol%, the effect of
addition of this unsaturated monomer is almost nil. On
the other hand, when the blending ratio exceeds 70 mol%,
10 there not only tend to arise the adverse effects such as
reduction of coating hardness, but there also takes
place elution by the action derived from the hydrophilic
nature alone, making it impossible to obtain the desired
coating film properties to be provided by a good resin
15 for antifouling paints.

These unsaturated monomers having a hydro-
philic functional group may be used either singly or in
combination.

As examples of the unsaturated monomers other
20 than those of the formulae (I) and (II) and those having
a hydrophilic functional group, there can be cited
acrylic or methacrylic ester monomers such as acrylic or
methacrylic methyl ester, ethyl ester, n-propyl ester,
n-butyl ester, etc., styrene monomers such as styrene,
25 α -methylstyrene, p-t-butylstyrene, etc., polyolefin
monomers such as butadiene, isoprene, chloroprene, etc.,
vinyl monomers such as vinyl chloride, vinyl acetate,
etc., acrylonitrile, methacrylonitrile, and the like.



1 These monomers may be used either singly or as a mixture
of two or more of them.

The unsaturated monomers other than those of
the formulae (I) and (II) and those having a hydrophilic
5 functional group are used for the purpose of adjusting
hardness of the coating film, glass transition
temperature (T_g) of the resin, pigment dispersibility of
the paint, rate of hydrolysis and elution by the sea
water, etc. The blending ratio of this monomer is
10 selected within the range of 1 to 95 mol%, preferably 10
to 90 mol%.

In order to afford additional qualities such
as reactivity to the polymer, a monomer such as acrylic
acid, methacrylic acid, glycidyl acrylate, glycidyl
15 methacrylate, N-vinylpyrrolidone or a derivative thereof
may be copolymerized depending on purposes.

Said unsaturated monomers may be used either
singly or in combination.

Preparation of the polymer or copolymer
20 (hereinafter simply refer to as "polymer") can be
accomplished by treating said substances according to a
per se known method, for example, by carrying out a
reaction of said unsaturated monomers (mixture) in an
appropriate solvent in the presence of a radical
25 polymerization catalyst at a temperature of about 0 to
180°C, preferably about 40 to 170°C, for a period of
about one to 20 hours, preferably about 4 to 10 hours.

As for the organic solvent used for the



1 polymerization, any type of organic solvent can be used
as far as it is capable of dissolving the produced
polymer so that no gelation will occur in the course of
polymerization reaction. Examples of such organic
5. solvents include the alcohol type solvents such as
ethanol, propanol, butanol, isobutanol and benzyl
alcohol; ether type solvents such as methyl Cellosolve,
ethyl Cellosolve, ethylene glycol dimethyl ether,
ethylene glycol monoacetate and 1,4-dioxane; aromatic
10 hydrocarbon type solvents such as toluene and xylene;
ester type solvents such as ethyl acetate and butyl
acetate; ketone type solvents such as cyclohexanone and
methyl isobutyl ketone; and halogen type solvents such
as carbon tetrachloride and trichloroethane. However,
15 when the product is intended to be used as an antifoul-
ing paint, it is preferable to use an aromatic solvent
or a mixture of an aromatic solvent with other type(s)
of solvent (in a smaller amount) so that the solvent
won't act on the undercoat in the coating operation.

20 As regards the radical polymerization catalyst
used in the preparation of said polymer, it is possible
to employ the radical polymerization initiators used for
ordinary radical polymerization, such as azo-compounds,
peroxide compounds and the like. The number-average
25 molecular weight of the obtained polymer is not critical
in this invention, but in view of the properties of
coating resin, said number-average molecular weight is
preferably in the range from 3,000 to 200,000, more



1 preferably from 5,000 to 50,000. The number-average
molecular weight shown herein is the value determined by
measuring the molecular weight according to gel
permeation chromatography and reducing it according to a
5 standard polystyrene calibration curve.

An appropriate chain transfer agent may be
blended at the time of polymerization for the purpose of
adjusting the molecular weight. Examples of the chain
transfer agents usable for said purpose include
10 methanethiol, ethanthiol, n-propanethiol, isopropane-
thiol, n-butanethiol, 2-methylpropanethiol,
3-methylpropanethiol, 1,1-dimethylethanethiol,
1-hexanethiol, 1-octanethiol, 1-decanethiol,
benzenethiol, 2-methylbenzenethiol, 3-methylbenzene-
15 thiol, 4-methylbenzenethiol, 2-ethylbenzenethiol,
3-ethylbenzenethiol, 4-ethylbenzenethiol, bis(4-hydroxy-
dimethylphenyl)disulfide, bis(2-chloromethylphenyl)
disulfide, bis(2-bromophenyl) disulfide, dinaphthyl
disulfide, di-2-benzothia disulfide, α -methylstyrene
20 dimer, carbon tetrachloride, carbon tetrabromide and
chloroform. The amount of the chain transfer agent to
be blended may be properly selected according to the
molecular weight of the polymer to be produced.

The thus obtained polymer shows an appro-
25 priate hydrolysis-elution property and can be applied
as a coating resin suited for antifouling coating
compositions. The coating resin according to



1 the present invention may further comprises other
polymer(s) within limits not prejudicial to the effect
of the present invention. Such polymers include, for
example, vinyl copolymers such as acrylic copolymers,
5 styrene-acrylic copolymers, polyvinyl chloride, etc.;
polyesters; polysiloxanes; etc.

The coating resin of this invention, if
necessary, may be blended with a known coloring matter,
a known antifouling agent and various other additives in
10 the course of preparation of an antifouling coating
composition.

Typical examples of the antifouling agents
usable in this invention are zinc suboxide, zinc
chromate, strontium chromate, cupric chromate, cupric
15 ferrocyanate, cupric quinone, cupric δ -hydroquinone,
cupric oleate, cupric nitrate, cupric phosphate, cupric
tartrate, cuprous oxide, cuprous iodide and cuprous
sulfite.

Typical examples of the pigments usable in
20 this invention include inorganic pigments such as
titanium oxide (titanium white), iron oxide and carbon
black, and organic pigments such as azo type, cyanine
type and quinacridone type. Usually, however, an
inorganic pigment is used.

25 Joint use of an organotin compound, triazine
compound, organosulfur compound or the like with the
above-mentioned compounds as antifouling agent is
embraced within the concept of this invention.



1 It is also possible to use rosin, gum rosin,
wood rosin, tall oil rosin or the like as elution
assistant.

 The antifouling coating composition of this
5 invention obtained in the manner described above is
useful as bottom paint, paint for fishing nets, etc.

 The present invention is further described
below with reference to the Examples of the invention,
which Examples however do not limit the present
10 invention in any way.

Synthesis Example 1

Synthesis of 2-ethylsulfonylethyl methacrylate (Compound No. 10, $R = CH_3$)

 A mixture of 315 g (3.15 mol) of methyl meth-
15 acrylate, 145 g (1.05 mol) of 2-ethylsulfonylethanol,
8.7 g (30.6 mmol) of titanium tetraisopropoxide and 0.16
g of hydroquinone was reacted at 100°C for 4.5 hours
under air-bubbling with removal of methanol produced.
After cooling, 11 ml of water was added to the reaction
20 mixture and the resulting mixture was stirred well.
After removal of the aqueous phase, 200 ml of water was
added to the organic layer and the resulting mixture was
extracted with chloroform. The chloroform solution was
dried over anhydrous sodium sulfate and then chloroform
25 and excess methyl methacrylate were distilled off under
reduced pressure to obtain 164 g of a colorless
transparent oily substance in a yield of 75%. From its



1 physical properties shown below, this oily substance was confirmed to be 2-ethylsulfonylethyl methacrylate (Compound No. 10, R = CH₃).

(1) ¹H-NMR spectral data (¹H-NMR spectrum as shown in Fig. 1):

5 δ(solvent: CDCl₃) unit: ppm, in all Examples)
6.14 (1H, t-like m), 5.65 (1H, quintet-like m),
4.60 (2H, t, J=5.80 Hz), 3.34 (2H, t, J=5.8 Hz),
3.07 (2H, q, J=7.60 Hz), 1.96 (3H, t-like m),
10 1.42 (3H, t, J=7.60 Hz).

(2) IR spectral (neat) values (IR spectrum as shown in Fig. 2):

1721 cm⁻¹ (C=O), 1321, 1126 cm⁻¹ (SO₂).

Synthesis Example 2

15 Synthesis of 2-(p-toluenesulfonyl)ethyl methacrylate (Compound No. 12, R = CH₃)

To a 15 ml acetone solution of 4.8 g (24 mmol) of 2-(p-toluenesulfonyl)ethanol and 2.4 g (24 mmol) of triethylamine, 0.5 mg of hydroquinone was added, followed
20 by dropwise addition of 2.5 g (24 mmol) of methacryloyl chloride while maintaining the mixture temperature below 10°C by cooling with an ice bath. After the dropwise addition was completed, the mixture was stirred for 30 minutes while maintaining the mixture temperature at 0°C
25 and then further stirred for additional 30 minutes at room temperature. The white precipitate of triethylammonium chloride was filtered off and the filtrate was poured into



1 ice water. The precipitated colorless solid was
filtered, dried and recrystallized from hexane to give
4.3 g of colorless crystals (yield: 68%). From the
analytical results shown below, the obtained crystals
5 were confirmed to be those of 2-(p-toluenesulfonyl)ethyl
methacrylate (Compound No. 12, R = CH₃).

(1) Melting point: 72°C

(2) ¹H-NMR spectral values (¹H-NMR spectrum as shown in
Fig. 3):

10 δ(CDCl₃): 7.80 (2H, d, J=8.09 Hz), 7.36 (2H,
d, J=8.09 Hz), 5.84 (1H, t-like m), 5.49 (1H,
quintet-like m); 4.47 (2H, t, J=6.11 Hz),
3.49 (2H, t, J=6.11 Hz), 2.44 (3H, s), 1.80
(3H, t-like m).

15 (3) IR spectral values (KBr method) (IR spectrum as
shown in Fig. 4):

1705 cm⁻¹ (C=O), 1300, 1140 cm⁻¹ (SO₂).

Synthesis Example 3

20 Synthesis of 2-cyanoethyl methacrylate (Compound
No. 2, R = CH₃)

A mixture of 120 g (1.20 mol) of methyl
methacrylate, 28.4 g (0.4 mol) of 2-cyanoethanol, 1.46 g
(5.14 mmol) of titanium tetraisopropoxide and 42 mg of
hydroquinonemonomethyl ether was treated as in Synthesis
25 Example 1, and the resulting oily substance was
distilled under reduced pressure to obtain 21 g of a
colorless liquid having a boiling point of 70°C/0.5 mmHg



1 (yield: 75%). From its physical properties shown below,
this liquid was confirmed to be 2-cyanoethyl meth-
acrylate (Compound No. 2, $R = CH_3$).

(1) 1H -NMR spectral data (1H -NMR spectrum as shown
5. in Fig. 5):

$\delta(CDCl_3)$: 6.19 (1H, t-like m), 5.66 (1H,
quintet-like m), 4.36 (2H, t, $J=6.41$ Hz), 2.76
(2H, t, $J=6.4$ Hz), 1.97 (3H, t-like m).

(2) IR spectral (neat) data (IR spectrum as shown in
10 Fig. 6):

2250 cm^{-1} (C N), 1721 (C=O).

Synthesis Example 4

Synthesis of 2-methoxalyloxyethyl methacrylate
(Compound No. 18, $R = CH_3$)

15 A mixture of 45.4 g (384 mmol) of dimethyl
oxalate, 10 g (77 mmol) of 2-hydroxyethyl methacrylate,
0.2 g (0.7 mmol) of titanium tetraisopropoxide and 5 mg
of hydroquinone was reacted at 100°C for 6 hours under
air-bubbling with removal of methanol produced. Excess
20 dimethyl oxalate was removed by sublimation. The result-
ing material containing the white precipitate was filtered
to remove the white precipitate, and the mother liquor was
purified by silica gel column chromatography (eluent:
hexane/ethyl acetate = 8/2) to obtain 10.7 g of a color-
25 less liquid (yield: 64%). From its analytical results
shown below, this liquid was confirmed to be 2-methox-
alyloxyethyl methacrylate (Compound No. 18, $R = CH_3$).



- 1 (1) ^1H -NMR spectral data (^1H -NMR spectrum as shown in Fig. 7):

$\delta(\text{CDCl}_3)$: 6.14 (1H, t-like m), 5.61 (1H, quintet-like m), 4.56 (2H, m), 4.44 (2H, m),
5 3.92 (3H, s), 1.95 (3H, t-like m).

- (2) IR spectral (neat) data (IR spectrum as shown in Fig. 8):

1750, 1725 cm^{-1} (C=O).

Synthesis Example 5

- 10 Synthesis of 2-ethoxalyloxyethyl methacrylate
(Compound No. 19, R = CH_3)

A 20 ml acetone solution of 4.8 g (36.6 mmol) of 2-hydroxyethyl methacrylate, 3.7 g (36.6 mmol) of triethylamine and 1 mg of hydroquinone was cooled to
15 0°C . Then 5 g (36.6 mmol) of ethyl chloroglyoxalate was added dropwise to the solution with stirring while maintaining the mixture temperature substantially at 0°C . After the dropwise addition was completed, the reaction mixture was stirred at 0°C for 30 minutes and
20 then further stirred at room temperature for additional 30 minutes. The produced white precipitate was filtered off and the filtrate was concentrated to obtain an oily substance. This oily substance was purified by silica gel column chromatography (eluent: hexane/ethyl acetate
25 = 8/2) to obtain 5.9 g of a colorless liquid (yield: 70%). From its analytical results shown below, this liquid was confirmed to be 2-ethoxalyloxyethyl



1 methacrylate (Compound No. 19, $R = CH_3$).

(1) 1H -NMR spectral data (1H -NMR spectrum as shown
in Fig. 9):

5 $\delta(CDCl_3)$: 6.12 (1H, t-like m), 5.59 (1H,
quintet-like m), 4.53 (2H, m), 4.43 (2H, m),
4.35 (2H, q, $J=6.02$ Hz), 1.94 (3H, t-like m),
1.37 (3H, t, $J=6.02$ Hz).

Synthesis Example 6

Synthesis of N-methacryloyloxymethylphthalimide

10 (Compound No. 20, $R = CH_3$)

A 20 ml pyridine solution of 9 g (50.8 mmol)
of N-hydroxymethylphthalimide and 1 mg of hydroquinone
was kept at about 0°C in an ice bath, and 5.3 g (50.8
mmol) of methacryloyl chloride was added dropwise to the
15 solution while stirring it well. After the dropwise
addition was completed, the solution was stirred at this
temperature for 30 minutes and then at room temperature
for additional 30 minutes. The resulting reaction mix-
ture was poured into icy water and stirred for a while.
20 The precipitated solid was filtered and recrystallized
from methanol to obtain 7.2 g of colorless crystals
(yield: 58%). From their physical properties shown
below, these crystals were confirmed to be N-methacry-
loyloxymethylphthalimide (Compound No. 20, $R = CH_3$).
25 (1) Melting point: 134°C



- 1 (2) ^1H -NMR spectral data (^1H -NMR spectrum as shown in Fig. 10):

$\delta(\text{CDCl}_3)$: 7.94 (2H, m), 7.80 (2H, m), 6.12 (1H, t-like m), 5.80 (2H, s), 5.60 (1H, quintet-like m), 1.93 (3H, t-like m).

- 5 (3) IR spectral (KBr) data (IR spectrum as shown in Fig. 11):

1785, 1715 cm^{-1} (C=O).

Synthesis Example 7

- 10 Synthesis of N-methacryloyloxymethylsuccinimide
(Compound No. 22, R = CH_3)

To a suspension, heated to 30°C, of 99.1 g (1.0 mol) of succinimide and 81 ml of formalin (37% formaldehyde solution), 3 ml of a 5 wt% aqueous solution of sodium hydroxide was added dropwise while well stirring the suspension. After the dropwise addition was completed, the mixture was further stirred at room temperature for 2.5 hours. After the reaction, water was distilled off under reduced pressure and the residual mixture was extracted with methylene chloride. The resulting methylene chloride solution was concentrated and the residual solid was recrystallized from ether to obtain 109 g of colorless crystals (yield: 63%). From their physical properties shown below, these crystals were confirmed to be N-hydroxymethylsuccinimide. These crystals were used for the following reaction without further purification.

15
20
25



1 (1) Melting point: 64°C

(2) ^1H -NMR spectral data (^1H -NMR spectrum as shown in Fig. 12):

$\delta(\text{CDCl}_3)$: 5.03 (2H, br-s), 3.90 (1H, br-s),

5 2.75 (4H, s).

(3) IR spectral data (KBr) (IR spectrum as shown in Fig. 13):

1770, 1700 cm^{-1} (C=O).

To a 236 ml methylene chloride solution of 30
10 g (232 mmol) of N-hydroxymethylsuccinimide synthesized in the manner described above, 20 g (232 mmol) of methacrylic acid and 10 mg of hydroquinonemonomethyl ether, 48 g (232 mmol) of dicyclohexylcarbodiimide (DCC) was added while cooling the solution in an ice bath.
15 Then 2.84 g (23.2 mmol) of N,N-dimethylaminopyridine (DMAP) was further added to the solution with stirring. The mixture was further stirred at room temperature for 3 hours. The produced white precipitate was filtered off, the filtrate was concentrated and the residue was
20 purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 1/1) to give 39.7 g of colorless crystals (yield: 87%). From their physical properties these crystals were identified to be N-methacryloyloxy-methylsuccinimide (Compound No. 22, R = CH_3).

25 (1) Melting point: 76°C



1 (2) ^1H -NMR spectral data (^1H -NMR spectrum as shown
in Fig. 14):

$\delta(\text{CDCl}_3)$: 6.11 (1H, t-like m), 5.62 (1H,
quintet-like m), 5.59 (2H, s), 2.80 (4H, s),
5 1.93 (3H, t-like m).

(3) IR spectral data (KBr) (IR spectrum as shown in
Fig. 15):

1780, 1705 cm^{-1} (C=O)

Synthesis Example 8

10 Synthesis of N-methacryloyloxysuccinimide (Compound
No. 23, R = CH_3)

To a 250 ml methylene chloride suspension of 30
g (261 mmol) of N-hydroxysuccinimide, 22.4 g (261 mmol)
of methacrylic acid and 10 mg of hydroquinonemonomethyl
15 ether under cooling in an ice bath, 53.8 g (251 mmol) of
DDC was added, followed by further addition of 3.2 g
(26.1 mmol) of DMAP while well stirring the suspension.
The mixture was further stirred at room temperature for
3 hours. The produced white precipitate was filtered
20 off, the filtrate was concentrated and the residue was
purified by silica gel column chromatography (eluent:
hexane/ethyl acetate = 3/2) to obtain 14.7 g of color-
less crystals (yield: 31%). From the following physical
properties, these crystals were confirmed to be N-meth-
25 acryloyloxysuccinimide (Compound No. 23, R = CH_3).



- 1 (1) Melting point: 102°C
- (2) $^1\text{H-NMR}$ spectral data ($^1\text{H-NMR}$ spectrum as shown in Fig. 16):
- $\delta(\text{CDCl}_3)$: 6.42 (1H, t-like m), 5.89 (1H, m), 2.86 (4H, s), 2.06 (3H, t-like m).
- 5 (3) IR spectral data (KBr) (IR spectrum as shown in Fig. 17):
- 1763, 1737 cm^{-1} (C=O).

Synthesis Example 9

- 10 Synthesis of 4-pyridylmethyl methacrylate (Compound No. 26, R = CH_3)

A mixture of 25 g (82.5 mmol) of 4-pyridyl-methanol, 91.7 g (330 mmol) of methyl methacrylate, 5 mg of hydroquinone and 0.5 g (1.38 mmol) of dioctyltin

15 oxide was reacted at 100°C for 24 hours under air bubbling with removal of methanol produced. After the reaction, excess methyl methacrylate was distilled off under reduced pressure and the precipitated solid was filtered off. The filtrate was purified by silica gel

20 column chromatography (eluent: ethyl acetate) to obtain 39.2 g of a light-red liquid (yield: 97%). From its physical properties shown below, this liquid was confirmed to be 4-pyridylmethyl methacrylate (Compound No. 26, R = CH_3).



- 1 (1) ^1H -NMR spectral data (^1H -NMR spectrum as shown in Fig. 18):

5 $\delta(\text{CDCl}_3)$: 8.61 (2H, d, $J=6.10$ Hz), 7.27 (2H, d, $J=6.10$ Hz), 6.22 (1H, t-like m), 5.66 (1H, quintet-like m), 5.22 (2H, s), 2.01 (3H, t-like m).

- (2) IR spectral (neat) data (IR spectrum as shown in Fig. 19):

1720 cm^{-1} (C=O).

10 Synthesis Example 10

Synthesis of 2-methylsulfonylethyl methacryalte
(Compound No. 9, $\text{R} = \text{CH}_3$)

A mixture of 315 g (3.15 mol) of methyl methacryalte, 130 g (1.05 mol) of 2-methylsulfonyl-
15 ethanol, 7.8 g (27.4 mmol) of titanium tetraisopropoxide and 0.15 g of hydroquinone was reacted at 100°C for 3 hours under air bubbling with removal of methanol produced. After cooling, 20 ml of water was added, to the reaction mixture and the resulting mixture was
20 stirred at 80°C for 20 minutes. After removal of the aqueous layer, 200 ml of water was further added to the organic layer and the resulting mixture was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate and was concentrated under
25 reduced pressure to obtain 130 g of colorless crystals (yield: 64%). From their physical properties, these crystals were confirmed to be 2-methylsulfonylethyl



1 methacrylate (Compound No. 9, $R = CH_3$).

(1) Melting point: $48^\circ C$

(2) 1H -NMR spectral data (1H -NMR spectrum as shown in Fig. 20):

5 $\delta(CDCl_3)$: 6.14 (1H, t-like m), 5.66 (1H, quintet-like m), 4.62 (2H, t, $J=5.90$ Hz), 3.38 (2H, t, $J=5.90$ Hz), 2.99 (3H, s), 1.96 (3H, t-like m).

(3) IR spectral data (KBr) (IR spectrum as shown in Fig. 21):

10 1710 cm^{-1} (C=O), $1300, 1140\text{ cm}^{-1}$ (SO_2).

Examples 1 - 20

Into a four-necked flask equipped with a stirrer, a condenser, an N_2 gas feed pipe, a dropping
15 funnel and a thermometer, a measured amount of a solvent or solvents was supplied and stirred at $95^\circ C$. Then a mixed solution comprising monomers, azobisisobutyronitrile (AIBN) and α -methylstyrene dimer (α MSD) was charged into the dropping funnel and added dropwise into
20 the flask in an N_2 gas stream while maintaining the temperature of the reaction mixture at about $95^\circ C$ and stirring the mixture. After the dropwise addition was completed, the mixture was further stirred at $95^\circ C$ for 6 hours to obtain a viscous liquid with a specified solid
25 content. The detailed experimental conditions and the properties of the obtained resins are shown in Tables 1 to 3.





This Sheet Has Been Replaced

Table 1

Exam- ple No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
1	Dioxane (60)	2-Cyanoethyl methacrylate (69.6) (Compound No. 2, R=CH ₃) n-Butyl acrylate (32) Ethyl methacrylate (28.5)	1.5	0.5	50	9400
2	Methyl isobutyl ketone (MIBK) (36)	2-Cyanoethyl acrylate (20) (Compound No. 2, R=H) Methyl methacrylate (16)	1.1	0.36	60	8100
3	Xylene (40) n-Butanol (10)	2-Cyanoethyl acrylate (26) (Compound No. 2, R=H) tert-Butyl methacrylate (11.8) (Compound No. 39, R=CH ₃) Methyl methacrylate (12.4)	1.66	0.55	50	7000

Table 1 (cont'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)	α MSD (g)	NV (%)	Mn
4	Xylene (40) n-Butanol (10)	2-Cyanoethyl acrylate (24.5) (Compound No. 2, R=H) tert-Butyl methacrylate (8.4) (Compound No. 39, R=CH ₃) : Compound No. 46, R=CH ₃ (7.4) Methyl methacrylate (9.8)	1.57	0.55	50	7000
5	Dioxane (165)	Compound No. 10, R=CH ₃ (103) n-Butyl acrylate (32) Ethyl methacrylate (28.5)	1.5	0.5	50	9100
6	Xylene (40) n-Butanol (10)	Compound No. 10, R=CH ₃ (30) tert-Butyl methacrylate (12) (Compound No. 39, R=CH ₃) Methyl methacrylate (3) Compound No. 46, R=CH ₃ (5)	1.6	0.55	50	7600

- cont'd -

Table 1 (cont'd)

Example No.	Solvent (g)	Formulation Monomers (g)			NV (%)	Mn
			AIBN (g)	α MSD (g)		
7	Dioxane (60)	Compound No. 19, R=CH ₃ (29.4) n-Butyl acrylate (12.4) Ethyl methacrylate (18.6)	1.5	0.55	50	9200

Table 2

Example No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
8	Dioxane (58.6)	Compound No. 18, R=CH ₃ (22.1) n-Butyl acrylate (13.1) Ethyl methacrylate (23.4)	1.5	0.55	50	9400
9	Xylene (40)	Compound No. 2, R=H (8.0) Compound No. 40, R=CH ₃ (32.1)	1.2	0.4	50	7200
10	Xylene (40)	Compound No. 2, R=H (9.1) Compound No. 39, R=CH ₃ (30.9)	1.2	0.4	50	7300
11	Xylene (40)	Compound No. 2, R=H (7.7) Compound No. 41, R=CH ₃ (32.3)	1.2	0.4	50	7100
12	Xylene (40)	Compound No. 2, R=H (9.1) Compound No. 38, R=CH ₃ (30.9)	1.2	0.4	50	7200

- cont'd -

Table 2 (comp'd)

Example No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
13	Xylene (40)	Compound No. 2, R=H (18.7) Compound No. 39, R=CH ₃ (21.3)	1.2	0.4	50	7400
14	Xylene (40)	Compound No. 2, R=H (19.3) Compound No. 39, R=CH ₃ (17.6) Methyl methacrylate (3.1)	1.2	0.4	50	7400
15	Xylene (32) n-Butanol (8)	Compound No. 2, R=H (20.0) Compound No. 39, R=CH ₃ (13.6) Methyl methacrylate (6.4)	1.3	0.4	50	7300
16	Xylene (32) n-Butanol (8)	Compound No. 2, R=H (20.3) Compound No. 39, R=CH ₃ (11.5) Methyl methacrylate (8.1)	1.2	0.4	50	7300

- cont'd -

This Sheet Has Been Replaced



Table 2 (comp'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)	α MSD (g)	NV (%)	Mn
17	Xylene (40) n-Butanol (10)	Compound No. 2, R=H (25.9) Compound No. 39, R=CH ₃ (11.8) Methyl methacrylate (12.4)	1.66	1.2	50	6400
18	Xylene (40) n-Butanol (10)	Compound No. 2, R=H (25.9) Compound No. 39, R=CH ₃ (11.8) Methyl methacrylate (12.4)	1.66	1.66	50	5800

This Sheet Has Been Replaced

Table 3

Example No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
19	Dioxane (53.7)	Compound No. 26, R=CH ₃ (22.7) n-Butyl acrylate (12.4) Ethyl methacrylate (18.6)	1.5	0.55	50	8400
20	Dioxane (54.6)	Compound No. 27, R=CH ₃ (18.1) n-Butyl acrylate (13.1) Ethyl methacrylate (23.4)	1.5	0.55	50	8200

1 Examples 21 - 26

A solvent, monomers, AIBN and α MSD were put into a four-necked flask equipped with a stirrer, a condenser, an N_2 gas feed pipe, and a thermometer, and
5 the mixture was stirred while bubbling with N_2 gas with keeping the reaction temperature about 95°C . After the initial vigorous exothermic reaction abated, the reaction mixture was further stirred under the above conditions for 6 hours. There was consequently obtained
10 a viscous liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 4.



Table 4

Example No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
21	Dioxane (150)	Compound No. 7, R=CH ₃ (89) n-Butyl acrylate (32) Ethyl methacrylate (28.5)	1.5	0.5	50	9400
22	Dioxane (155)	Compound No. 9, R=CH ₃ (96) n-Butyl acrylate (32) Ethyl methacrylate (28.5)	1.5	0.5	50	8500
23	Dioxane (196)	Compound No. 12, R=CH ₃ (134) n-Butyl acrylate (32) Ethyl methacrylate (28.5)	1.5	0.5	50	9700
24	Dioxane (200)	Compound No. 15, R=CH ₃ (141) n-Butyl acrylate (32) Ethyl methacrylate ((28.5)	1.5	0.5	50	8800

- cont'd -

Table 4 (cont'd)

Exam- ple No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
25	Dioxane (62.4)	Compound No. 20, R=CH ₃ (31.4) n-Butyl acrylate (12.4) Ethyl methacrylate (18.6)	1.5	0.55	50	8500
26	Dioxane (56.6)	Compound No. 22, R=CH ₃ (20.1) n-Butyl acrylate (13.1) Ethyl methacrylate (23.4)	1.5	0.55	50	8100

This Sheet Has Been Replaced


1 Examples 27 - 30

Measured amounts of a solvent and a lowly reactive monomer were placed in a four-necked flask equipped with a stirrer, a condenser, an N₂ gas feed
5 pipe, a dropping funnel and a thermometer, and the mixture was kept therein with stirring. Then, a mixed solution of other monomers, AIBN and αMSD was supplied into the flask from the dropping funnel in an N₂ gas stream with stirring the mixture and maintaining its
10 temperature at about 95°C. After completion of the dropwise addition, the reaction mixture was stirred at 95°C for 1 hour. A mixture of AIBN and xylene or xylene alone was added dropwise to the mixture one to three times every 30 minutes. The reaction mixture was
15 further stirred at 95°C for 6 hours to obtain a viscous liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 5.



Table 5

Exam- ple No.	Formulation in reactor: Monomer (g) and sol- vent (g)	Formulation in dropping funnel			NV (%)	Mn
		Monomers (g) or solvent (g)	AIBN (g)	α MSD (g)		
27	Xylene (40) Maleic anhydride (12)	1st: Compound No. 2, R=H (10) Compound No. 39, R=CH ₃ (11) n-Butyl methacrylate (17)	0.5	0.55	50	11300
		2nd: Xylene (10)	0.2	-		
28	Xylene (40) Maleic anhydride (13.6)	1st: Compound No. 2, R=CH ₃ (5.5) Compound No. 39, R=CH ₃ (14) n-Butyl methacrylate (16.9)	0.5	0.55	50	10100
		2nd: Xylene	0.2	-		

- cont'd -

This Sheet Has Been Replaced



Table 5 (cont'd)

Example No.	Formulation in reactor: Monomer (g) and solvent (g)	Formulation in dropping funnel			NV (%)	Mn
		Monomers (g) or solvent (g)	AIBN (g)	α MSD (g)		
29	Xylene (40) Maleic anhydride (15)	1st: Compound No. 10, R=CH ₃ (7.8) Compound No. 38, R=CH ₃ (16.3) n-Butyl methacrylate (10.9)	1.4	0.55	50	7100
		2nd: Xylene (10)	0.2	-		

- cont'd -



Table 5 (cont'd)

Example No.	Formulation in reactor: Monomer (g) and solvent (g)	Formulation in dropping funnel			NV (%)	Mn
		Monomers (g) or solvent (g)	AIBN (g)	α MSD (g)		
30	Xylene (63) Maleic anhydride (29.4)	1st: Compound No. 2, R=H (25) n-Butyl methacrylate (71)	1.25	0.5	50	22000
		2nd: Xylene (12.5)	0.25	-		
		3rd: Xylene (12.5)	0.25	-		
		4th: Xylene (37.5)	-	-		

1 As seen from Examples 3, 4, 6, 9 - 18 and 27 -
30, the copolymers obtained by using the unsaturated
monomers represented by the formula (II) are soluble in
solvents, especially aromatic solvents such as xylene
5 and xylene/n-butyl (4/1), and suited for use as a resin
for antifouling paints.

Comparative Preparation Example 1

A determined amount of a solvent was put into
a four-necked flask equipped with a stirrer, a
10 condenser, an N_2 gas feed pipe, a dropping funnel and
a thermometer, and the solvent was kept at 95°C with
stirring. Then a mixed solution of the monomers, AIBN
and α MSD was supplied into the dropping funnel and
added dropwise into the flask under N_2 gas stream with
15 stirring the mixture and maintaining its temperature at
about 95°C. After completion of the dropwise addition,
the reaction mixture was further stirred at 95°C for 6
hours to obtain a viscous liquid with a specified solid
content. The detailed experimental conditions and the
20 properties of the obtained resins are shown in Table 6.



Table 6

Comp. Prep. Ex. No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
1	Xylene (50)	Tributyltin methacrylate (25.6) n-Butyl acrylate (8.8) Ethyl methacrylate (15.6)	0.75	0.5	50	7500
2	Xylene (50)	2,2,2-Trifluoroethyl meth- acrylate (29.1) n-Butyl acrylate (11.1) Ethyl methacrylate (9.9)	1.5	0.5	50	7200



This Sheet Has Been Replaced

1 Comparative Preparation Example 3

A solvent, monomers, AIBN and α MSD were supplied into a four-necked flask equipped with a stirrer, a condenser, an N_2 gas feed pipe, and a
5 thermometer, and the mixture was stirred while bubbling with N_2 gas with keeping the reaction temperature about 95°C. After the initial vigorous exothermic reaction abated, the mixture was further stirred under the above conditions for 6 hours to obtain a viscous
10 liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 7.



Table 7

Comp. Prep. Ex. No.	Solvent (g)	Formulation			NV (%)	Mn
		Monomers (g)	AIBN (g)	α MSD (g)		
3	Dioxane (117)	p-Nitrophenyl methacrylate (31.4) n-Butyl acrylate (9.8) Ethyl methacrylate (8.7)	1.5	0.5	30	12600

This Sheet Has Been Replaced



1 Test Example

Each of the varnish formulations obtained in the Examples and the Comparative Preparation Examples described above was coated on a 150 mm x 100 mm polypropylene plate. The coating thickness was about 50 μ m. The coated polypropylene plate was heated at 80°C for 3 hours to perfectly remove the solvent in the coat and the initial weight of the plate was measured. Then the coated polypropylene plate was immersed in 1,750 ml of an alkaline buffer solution with a pH of 10.2. After left in said buffer solution at 45°C for 24 hours, the polypropylene plate was taken out, washed with water and dried, followed by measurement of the final weight of the plate. The rate of decrease of the coating after said immersion was determined from the difference between the initial weight (weight before immersion) and the final weight (weight after immersion) of the plate.

For the sake of comparison, the above test was also conducted on the organotin-containing resin obtained in Comparative Preparation Example 1 and the resin disclosed in Japanese Patent Application Publication No. 60-500452 (Comparative Preparation Examples 2 and 3) proposed as a substitute for said organotin-containing resin. The test results are shown in Table 8.



Table 8

Varnish	Loss in weight of the coat (mg/100 cm ²)
Example 1	21
Example 2	32
Example 3	27
Example 4	30
Example 5	53
Example 6	42
Example 7	7
Example 8	7
Example 15	20
Example 20	7
Example 21	76
Example 22	63
Example 23	60
Example 24	97
Example 25	14
Example 26	8
Example 27	67
Example 28	51
Example 29	59
Example 30	92
Comp. Prep. Example 1	17
Comp. Prep. Example 2	5
Comp. Prep. Example 3	6

As noted from the foregoing results, the
coating resin compositions according to the present



1 invention are equal to or higher than the organotin-
containing resin in rate of decrease of coating, and
needless to say, they are free of toxicity possessed by
organotin. It was also found that the resin composi-
5 tions of this invention are superior to the resins
disclosed in Japanese Patent Application Publication No.
60-500452, which were proposed as a substitute material
for the organotin-based resin, in rate of decrease of
coating and useful as a resin for antifouling paints.

10 Antifouling Performance Test

Paints were prepared by blending 40 parts by
weight of cuprous oxide and 3 parts by weight of ZnO
with 15 parts by weight (as solid) of the resin
varnishes synthesized in the Examples described above.

15 Each of these paints was spray coated on both sides of a
coated steel plate (100 x 200 x 1 mm) which had been
applied with an anticorrosive coating. Said spray
coating was conducted twice so that the dry coating
thickness on each side would become 100 μ m, thereby
20 preparing the test plates.

Each of the test plates was subjected to a sea
water immersion test at Nakaminato Port of Nakaminato
City, Ibaragi Pref., and the number of the shellfishes
(barnacles) attached to the test plate was counted
25 periodically. The results are shown in Table 9.



Table 9

Antifouling performance test Run No.	Resin varnish (Example No.)	Number of barnacles attached to test plate			
		Period of immersion			
		0	2 months	4 months	6 months
1	3	0	0	0	1
2	4	0	0	0	0
3	5	0	0	0	0
4	6	0	0	0	0
5	17	0	0	0	1
6	21	0	0	0	0
7	23	0	0	0	0
8	24	0	0	0	1
9	27	0	0	0	1
10	28	0	0	0	0
11	29	0	0	0	0
12	30	0	0	0	0

1 Comparative Antifouling Performance Test

The same antifouling performance test as described above was conducted on the resin varnishes synthesized in Comparative Preparation Examples 2 and 3. The results are shown in Table 10.

This Sheet Has Been Replaced



Table 10

Comparative antifouling Performance test Run No.	Resin varnish (Comp. Prep. Example No.)	Number of barnacles attached to test plate			
		Period of immersion			
		0	2	4	6
			months	months	months
1	2	0	9	17	24
2	3	0	10	19	31

1 As noted from the results of the antifouling performance tests shown above, any of the paints prepared by using the resin compositions according to the present invention showed excellent antifouling
5 performance, substantially precluding attachment of barnacles to the plate applied with the paint.

Viscosity Stability Test

A mixture of 100 parts by weight of cuprous oxide and 100 parts by weight of resin solid of each of
10 the resin varnishes selected from those synthesized in the above Examples was kneaded into a paste, and the paste was transferred into a 150 ml sample bottle and its viscosity was measured by a Brookfield viscometer. Further, after sealing the sample bottle, it was stored
15 in a thermostatic chamber of 40°C for 20 days and then the viscosity of the paste was measured in the same way. The rate of change of viscosity after storage was



- 1 determined from the following equation (1). The test results are shown in Table 11.

$$\text{Rate of change of viscosity} = \frac{\text{Viscosity after storage}}{\text{Viscosity before storage}} \quad (1)$$

Table 11

Viscosity stability test Run No.	Resin varnish (Example No.)	Rate of change of Viscosity (after left at 40°C for 20 days)
1	3	1.04
2	4	1.03
3	5	1.07
4	23	1.05
5	27	1.10
6	28	1.12

It is seen from the above results that the rate of change of viscosity of the coating resin composition according to the present invention, when mixed with cuprous oxide, is slight, indicating excellent storage stability of the coating resin of this invention.

The coating resin according to the present invention has no poisoning problem noted in use of the organotin copolymers, possesses excellent keeping quality and also shows a hydrolytic property comparable



1 with the organotin-containing resins, so that the
coating resin of this invention is capable of forming a
coat which can maintain an excellent antifouling effect
for a long period of time. Further, since the coating
5 resin of this invention is soluble in the aromatic
solvents, it is very useful for preparing an excellent
antifouling paint.

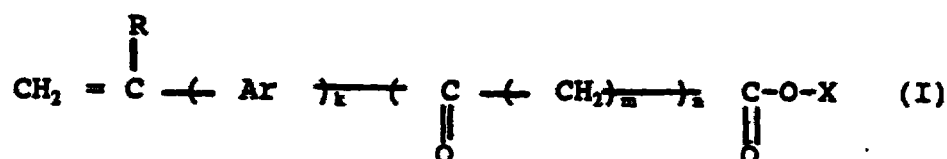


This Sheet Has Been Replaced



CLAIMS

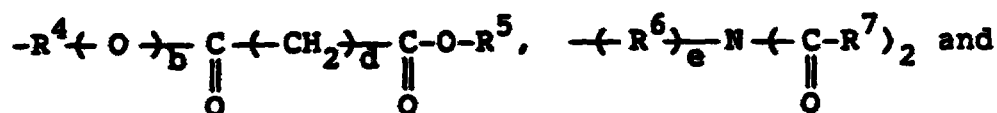
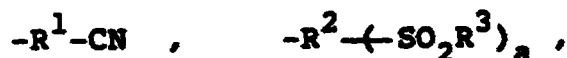
1. A coating resin comprising a polymer comprising, as repeating units, the residues of an unsaturated monomer of formula (I)



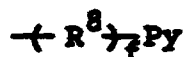
10

wherein R is hydrogen or a straight or branched alkyl group having 1 to 4 carbon atoms; Ar is a benzene ring or naphthalene ring; k, m and n represent independently a number of 0 or 1; and X is a substituent selected from the groups:

15

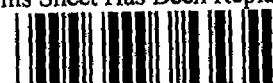


20



- 25 wherein R¹, R⁴, R⁶ and R⁸ are each a straight, branched or alicyclic alkylene group having 1 to 6 carbon atoms; R² is a straight, branched or cyclic hydrocarbon group having 1 to 6 carbon atoms and connecting O and SO₂R³; a is an integer of 1 to 3 indicating the number of SO₂R³ groups bonded to R²; the





- 70 -

groups R^3 are the same or different and each is a straight, branched or cyclic alkyl group, having 1-22 carbon atoms, an aryl group having 6-10 carbon atoms, which may have a substituent, or an aralkyl group having 7-18 carbon atoms, which may have a substituent provided that when a is 2 or 3, at least two of the groups R^3 may together form a hydrocarbon cyclic structure with each other and R^2 , b , d , e and f are each a number of 0 or 1; R^5 is a straight or branched alkyl group having 1-4 carbon atoms, the groups R^7 are the same or different and each is a straight, branched or alicyclic alkyl group, having 1-22 carbon atoms, an aryl group having 6-10 carbon atoms or an aralkyl group having 7-10 carbon atoms, or the groups R^7 together with the carbonyl carbon form a cyclic structure; and Py is a substituted or unsubstituted 2-, 3- or 4-pyridyl group.

2. A coating resin according to claim 1 wherein k and n are zero.

20 3. A coating resin according to claim 1 or claim 2 wherein X is $-R^1-CN$.

4. A coating resin according to claim 1 or claim 2 wherein X is $-R^2-(SO_2R^3)_6$.

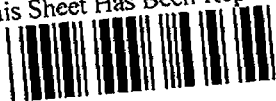
25

5. A coating resin according to any one of claims 1 to 4 wherein R is hydrogen or methyl.

6. A coating resin according to any one of claims



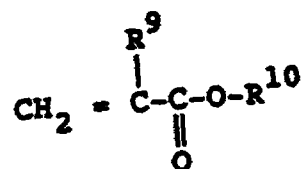
* C L M S *



1 to 5 further comprising as repeating units residues or one or more unsaturated monomer copolymerizable with the unsaturated monomer of the formula (I).

- 5 7. A coating resin according to claim 6 comprising as repeating units residues of a copolymerisable unsaturated monomer of formula (II)

10



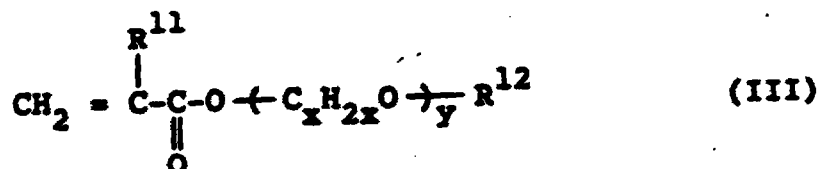
wherein R⁹ is hydrogen or methyl and R¹⁰ is branched or alicyclic alkyl, aryl or aralkyl optionally containing one or more hetero atoms and having 3 or more carbon atoms.

15

8. A coating resin according to claim 6 comprising, as repeating units the residues of a copolymerizable unsaturated monomer having a hydrophilic functional group.
- 20

9. A coating resin according to any one of claims 6 to 8 wherein the unsaturated monomer having a hydrophilic functional group is a monomer of formula (III)

25



wherein R^{11} is hydrogen or methyl; x is an integer of 1 to 6;
 y is an integer of 1 to 10; and R^{12} is hydrogen or a
straight, branched or cyclic alkyl, aryl or aralkyl group.

5

10. A antifouling coating composition comprising
the coating resin of Claim 1.

This Sheet Has Been Replaced



* C L M S *