

REPLACED SHEETS		SG
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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

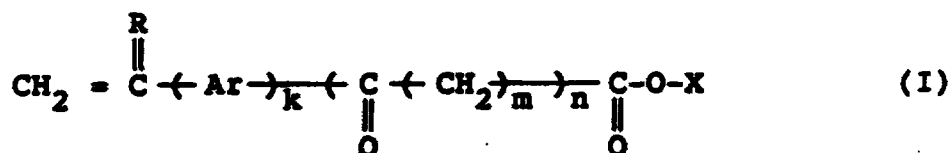
The present invention provides an excellent
coating resin and an antifouling coating composition
containing said resin which has no poisonous action like
25 the organotin copolymers, shows a hydrolytic property
well comparing with said organotin copolymers, and is
capable of forming a relatively long-lasting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

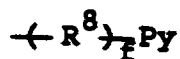
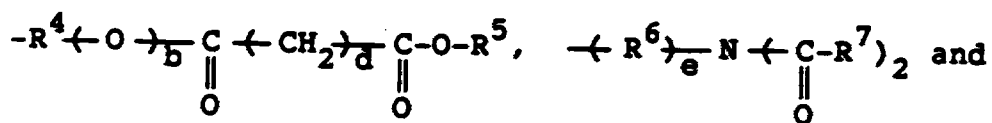
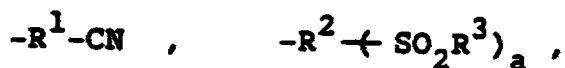
10 The present invention provides a coating resin comprising a polymer obtained by polymerizing an unsaturated monomer represented by the following formula (I) alone or together with at least one other unsaturated monomer copolymerizable therewith:



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 hydrocarbon 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 substituent; 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 copolymerizable unsaturated monomer a monomer represented by the

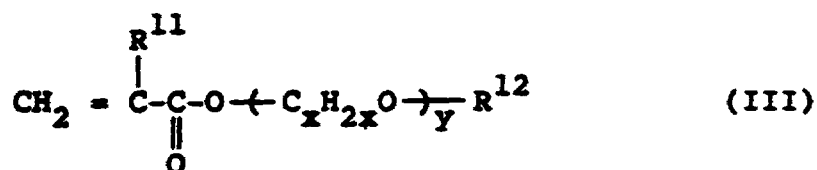


1 formula:



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 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 copolymerizable unsaturated monomer an unsaturated monomer having a 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} 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).

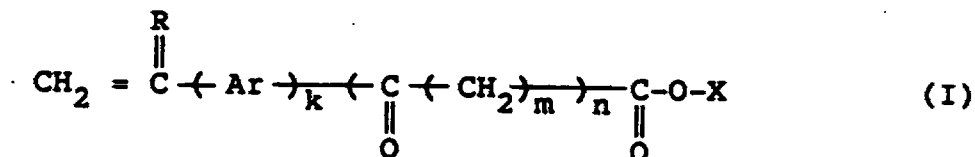
DESCRIPTION OF THE PREFERRED EMBODIMENTS

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

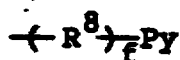
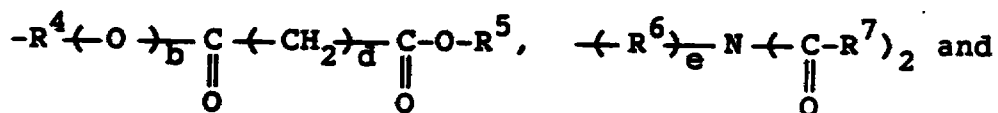
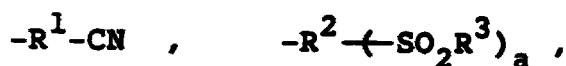
(1) A coating resin comprising a polymer obtained
by polymerizing an unsaturated monomer represented by



- 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
5 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



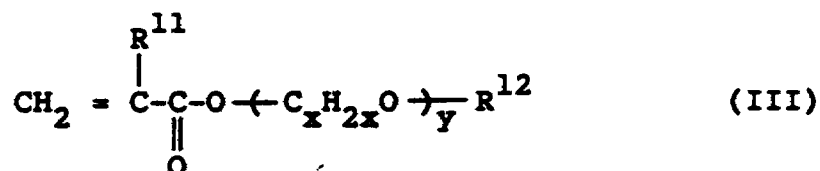
1 monomer copolymerizable with the unsaturated monomer of
the formula (I) is a monomer represented by the formula:



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,



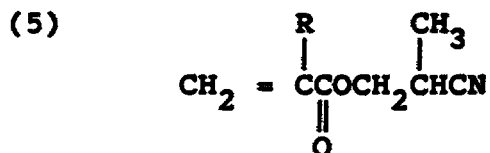
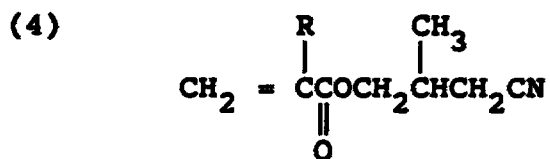
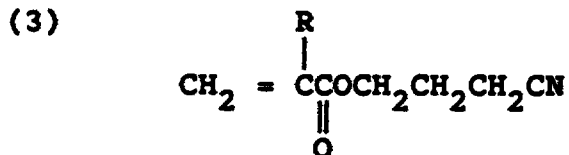
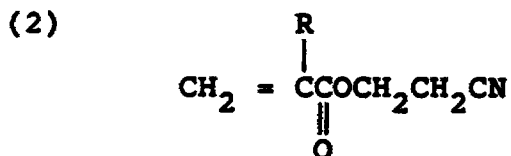
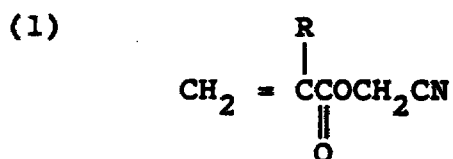
- 1 tert-tetradecyl, hexadecyl, tert-hexadecyl, octadecyl, tert-octadecyl, eicosyl, docodyl, etc. The C_{6-10} aryl groups or C_{7-18} aralkyl groups which may have a substituent include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, sulfonylphenyl, acylphenyl, naphthyl, benzyl, phenethyl, benzhydryl, 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, tetramethylene, etc.
- 10 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, 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.
- 20 The C_{6-10} aryl groups or C_{7-10} aralkyl groups represented by R^7 include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, naphthyl, benzyl, phenethyl, benzhydryl, etc. The groups forming a cyclic structure, represented by two R^7 , include methylene, ethylene, trimethylene, o-phenylene, 1,2-naphthylene, 2,3-naphthylene, etc.
- 25

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

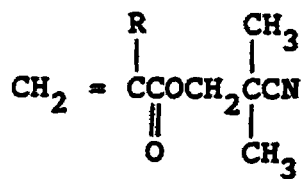


1 commercially available unsaturated monomers.

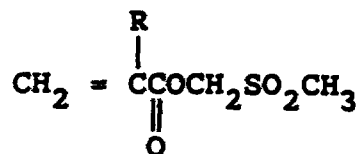
Listed below are the preferred examples of the unsaturated monomers represented by the formula (I) (R in the following formulae is hydrogen atom or methyl group):



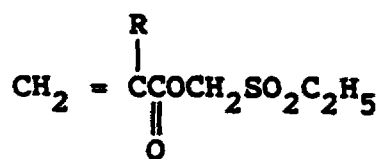
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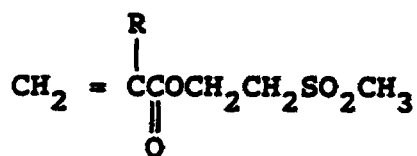
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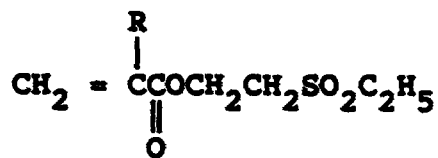
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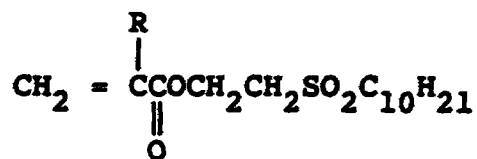
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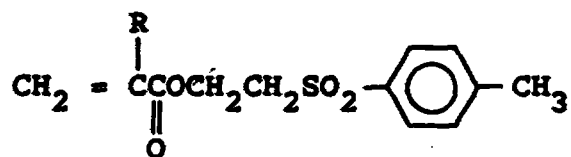
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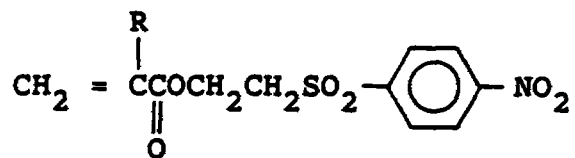
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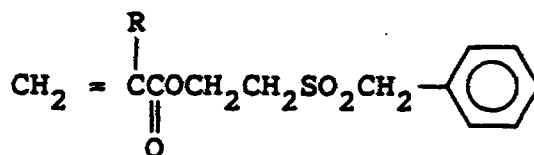
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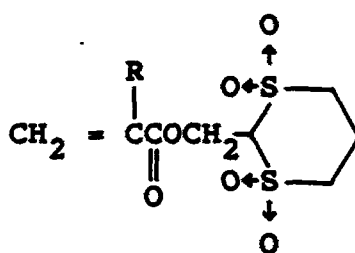
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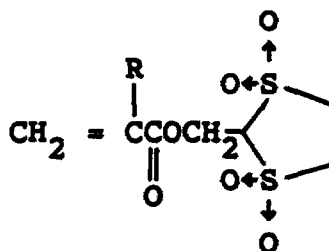
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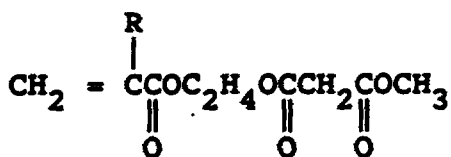
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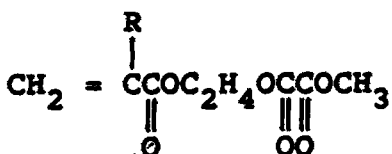
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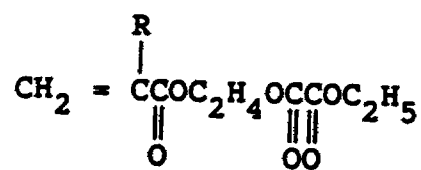
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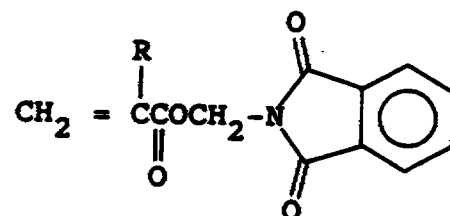
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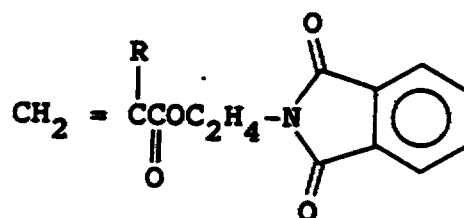
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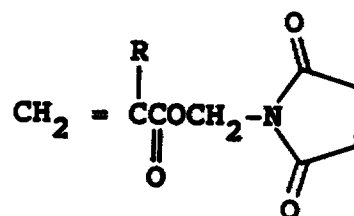
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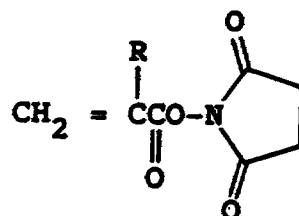
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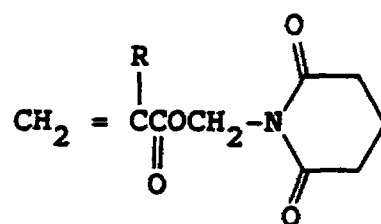
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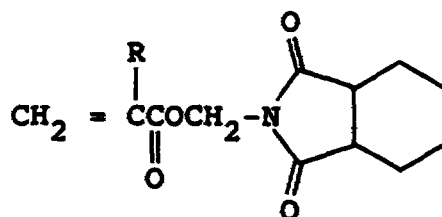
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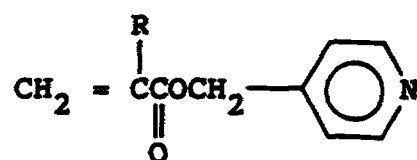
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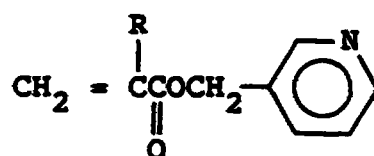
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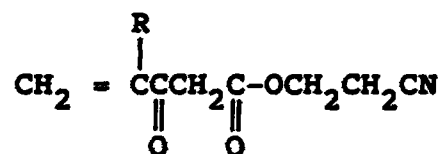
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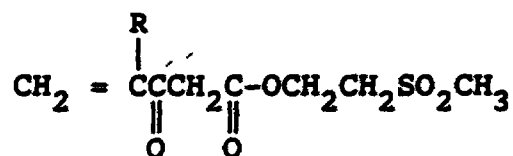
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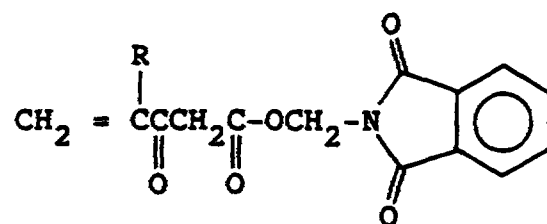
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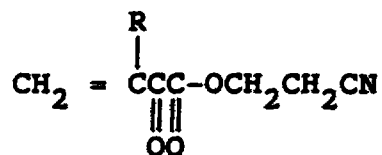
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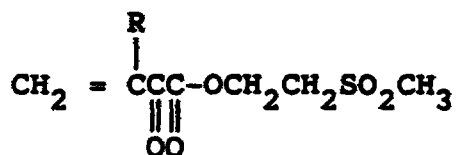
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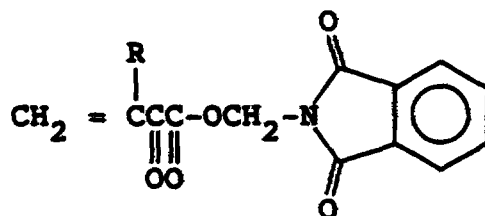
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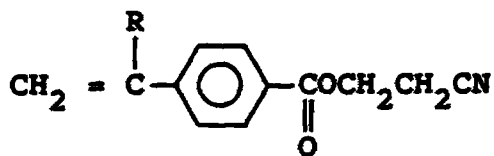
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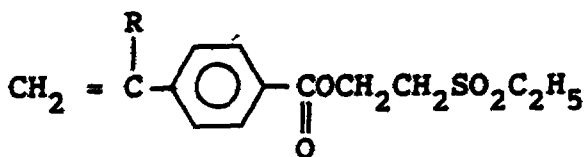
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(35)



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 pro-
20 vided that it is not less than 0.1 mol% based on the 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.

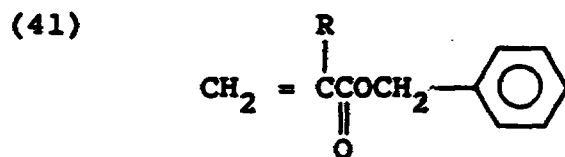
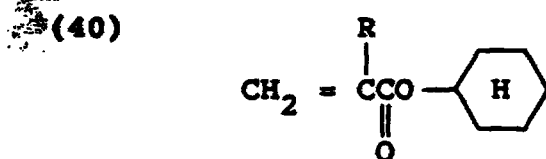
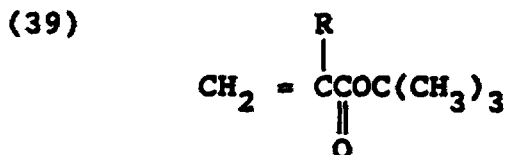
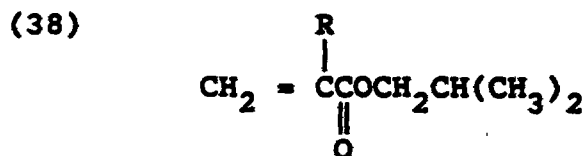
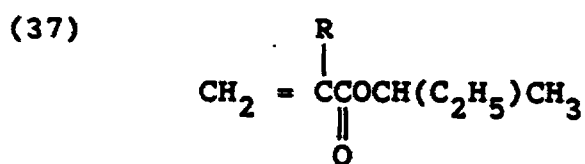
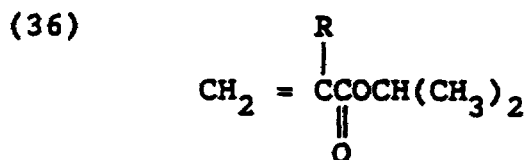
In the unsaturated monomers represented by the formula (II), the branched or alicyclic alkyl, aryl or
10 aralkyl groups having 3 or more carbon atoms, represented by R^{10} , include isopropyl, isobutyl, sec-butyl, tert-butyl, sec-pentyl, tert-pentyl, neopentyl, 2-ethylhexyl, cyclopropyl, cyclobutyl, 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.

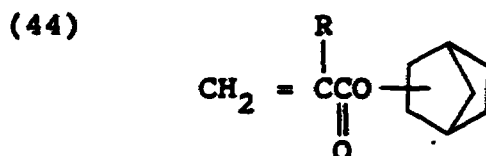
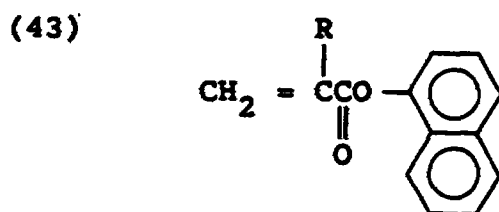
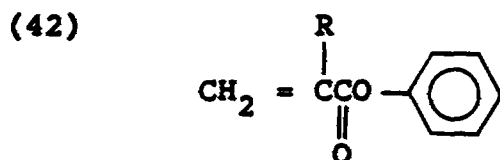
The unsaturated monomers represented by the
25 formula (II) can be produced by various known synthetic methods. The pertinent commercially available unsaturated monomers are also usable.

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):



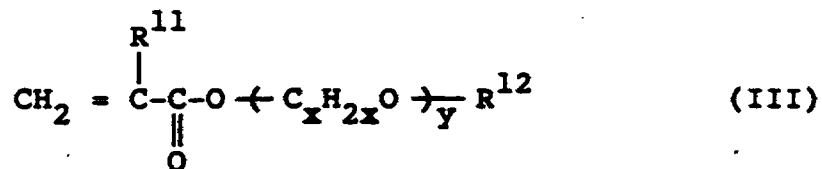


1 An unsaturated monomer of the formula (II) can
 be blended for the purpose of increasing solubility in
 the solvents, especially aromatic solvents. The
 blending ratio of this unsaturated monomer is preferably
 5 from 5 to 95 mol%. A too low blending ratio results in
 a poor solubility in the aromatic 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).

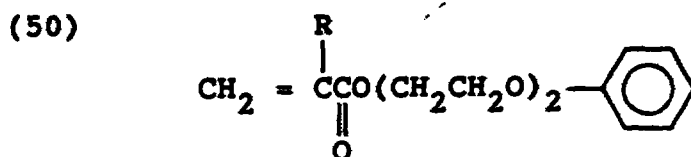
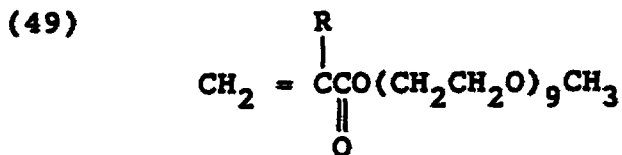
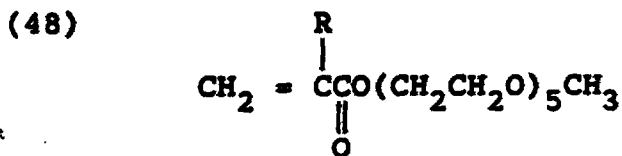
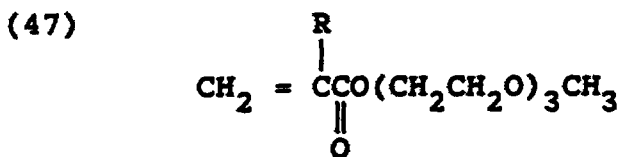
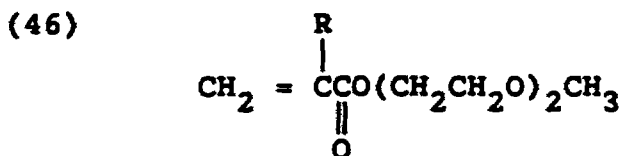
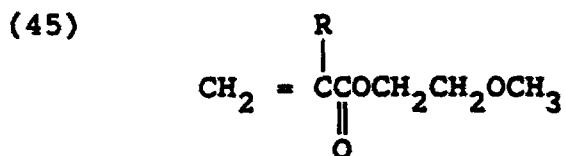
10 In the unsaturated monomers represented by the formula (III), the straight, branched or cyclic alkyl, aryl or aralkyl groups represented by R^{12} include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, sec-pentyl, tert-pentyl,
15 neopentyl, 2-ethylhexyl, cyclopropyl, 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.

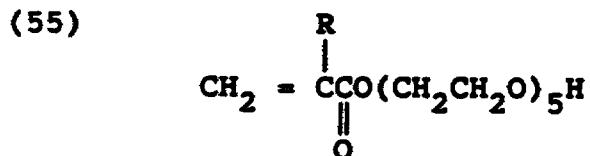
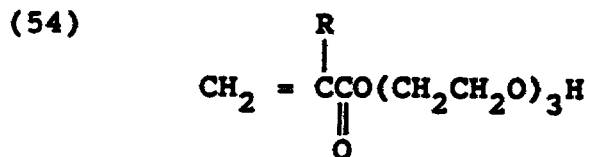
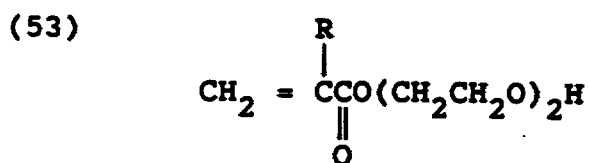
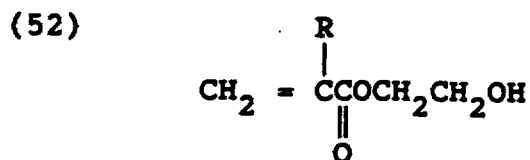
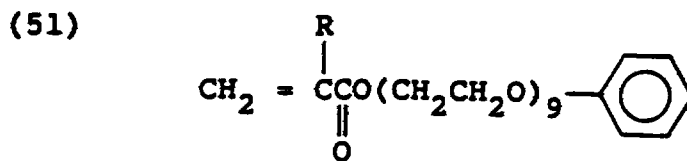
20 The unsaturated monomers of the formula (III) can be produced by various known synthetic methods. The commercially available unsaturated monomers are also



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 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 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 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 (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 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.

5 The antifouling coating composition of this
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 = CH₃)

 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-methoxallyloxyethyl 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-
allyloxyethyl 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 $0^\circ C$ 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: $134^\circ C$



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

5 $\delta(\text{CDCl}_3)$: 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).

- (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
15 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
20 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
25 crystals were confirmed to be N-hydroxymethylsuccinimide. These crystals were used for the following reaction without further purification.



- 1 (1) Melting point: 64°C
2 (2) ^1H -NMR spectral data (^1H -NMR spectrum as shown
3 in Fig. 12):

4 $\delta(\text{CDCl}_3)$: 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):

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



Table 1

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

- cont'd -



Table 1 (cont'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)		αMSD (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)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Table 2

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Table 2 (comp'd)

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

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Table 2 (comp'd)

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

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Table 3

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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.

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Table 4

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN α MSD (g)		NV (%)	Mn
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

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Table 4 (cont'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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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	-			

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Table 5 (cont'd)

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)		
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)

Exam- ple No.	Formulation in reactor: Monomer (g) and sol- vent (g)	Formulation in dropping funnel Monomers (g) or solvent (g)				NV (%)	Mn
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)	-	-			

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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 Monomers (g)			NV (%)	Mn
		AIBN (g)	αMSD (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

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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 Monomers (g)	AIBN α MSD (g)		NV (%)	Mn
			1.5	0.5		
3	Dioxane (117)	p-Nitrophenyl methacrylate (31.4) n-Butyl acrylate (9.8) Ethyl methacrylate (8.7)			30	12600

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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.

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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 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 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 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.



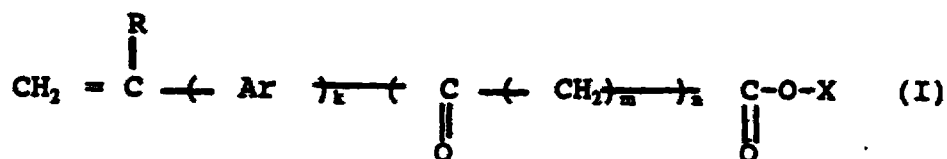
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CLAIMS

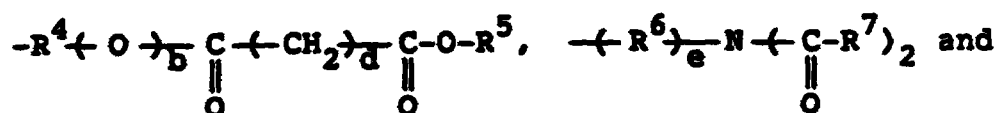
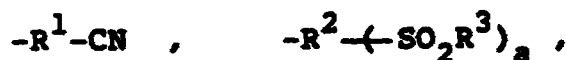


1. A coating resin comprising a polymer comprising, as repeating units, the residues of an unsaturated monomer of formula (I)

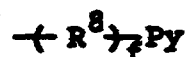


10

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:



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





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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 $-R^2-(SO_2R^3)_n$.

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

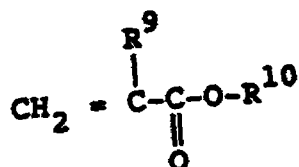


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1 to 5 further comprising as repeating units residues or one or more unsaturated monomer copolymerizable with the unsaturated monomer of the formula (I).

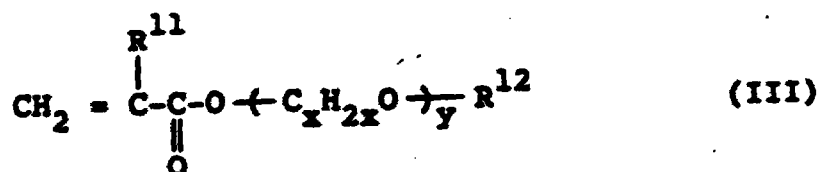
- 5 7. A coating resin according to claim 6 comprising as repeating units residues of a copolymerisable unsaturated monomer of formula (II)



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.

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

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)



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.

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

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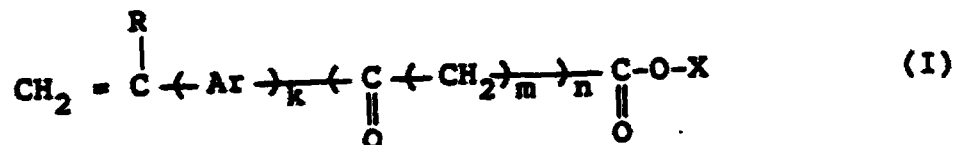


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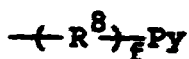
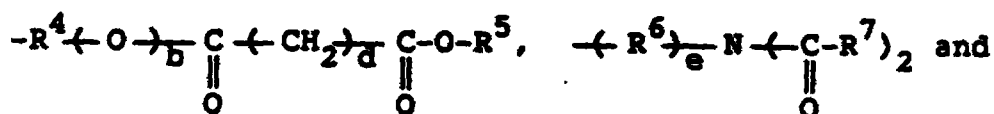
ABSTRACT

COATING RESIN AND ANTIFOULING COATING COMPOSITION

A coating resin comprising a polymer obtained by polymerising an unsaturated monomer represented by the formula (I):



wherein R is H or an alkyl group, and X is selected from:



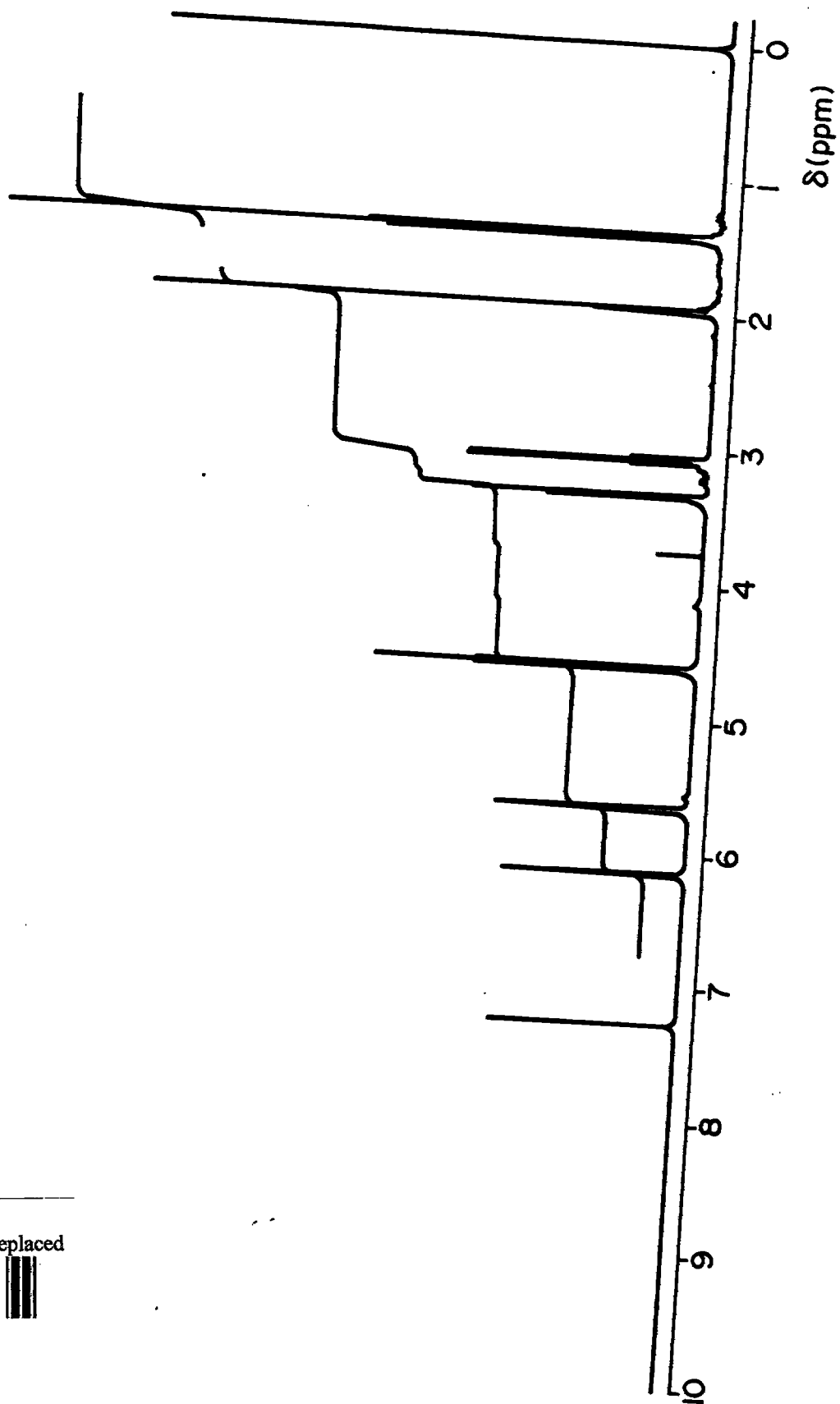
wherein R¹ to R⁸ represent independently a hydrocarbon group, etc., and Py is a pyridyl group, alone or together with one or more other unsaturated monomers may be used in antifouling coating compositions having no safety problems, good storage stability and excellent antifouling effect for a long period of time.

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FIG. 1

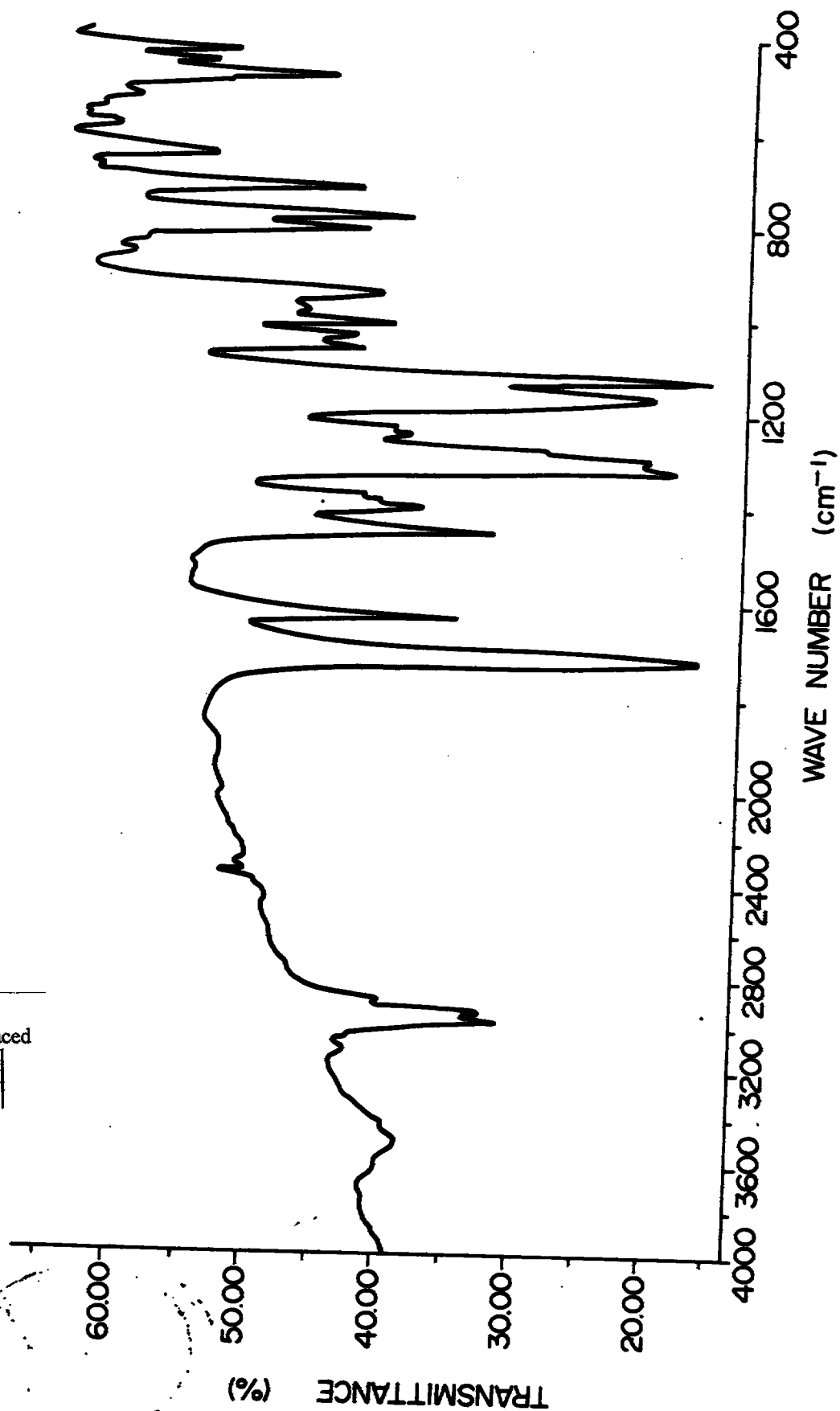


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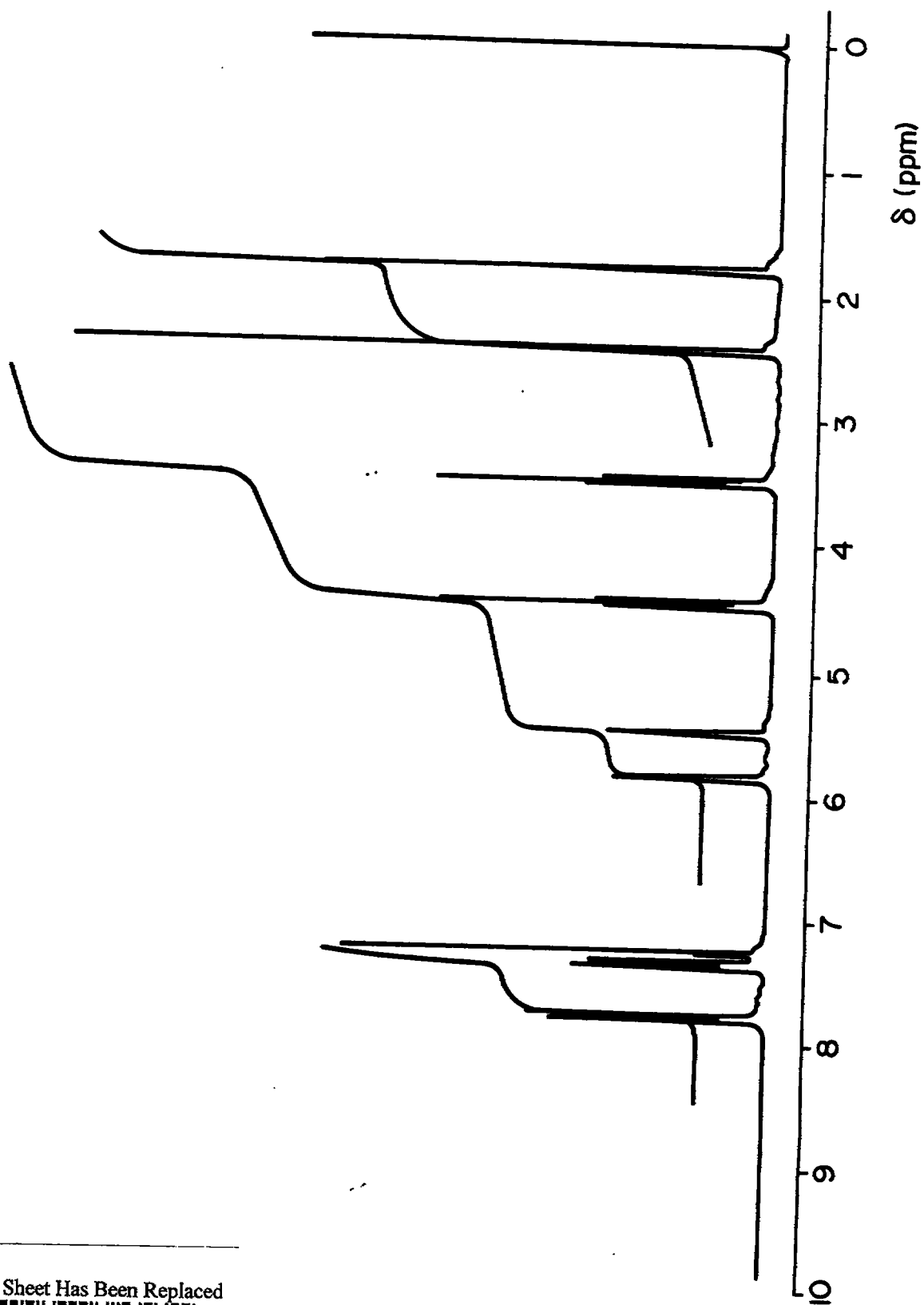
FIG. 2

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FIG. 3

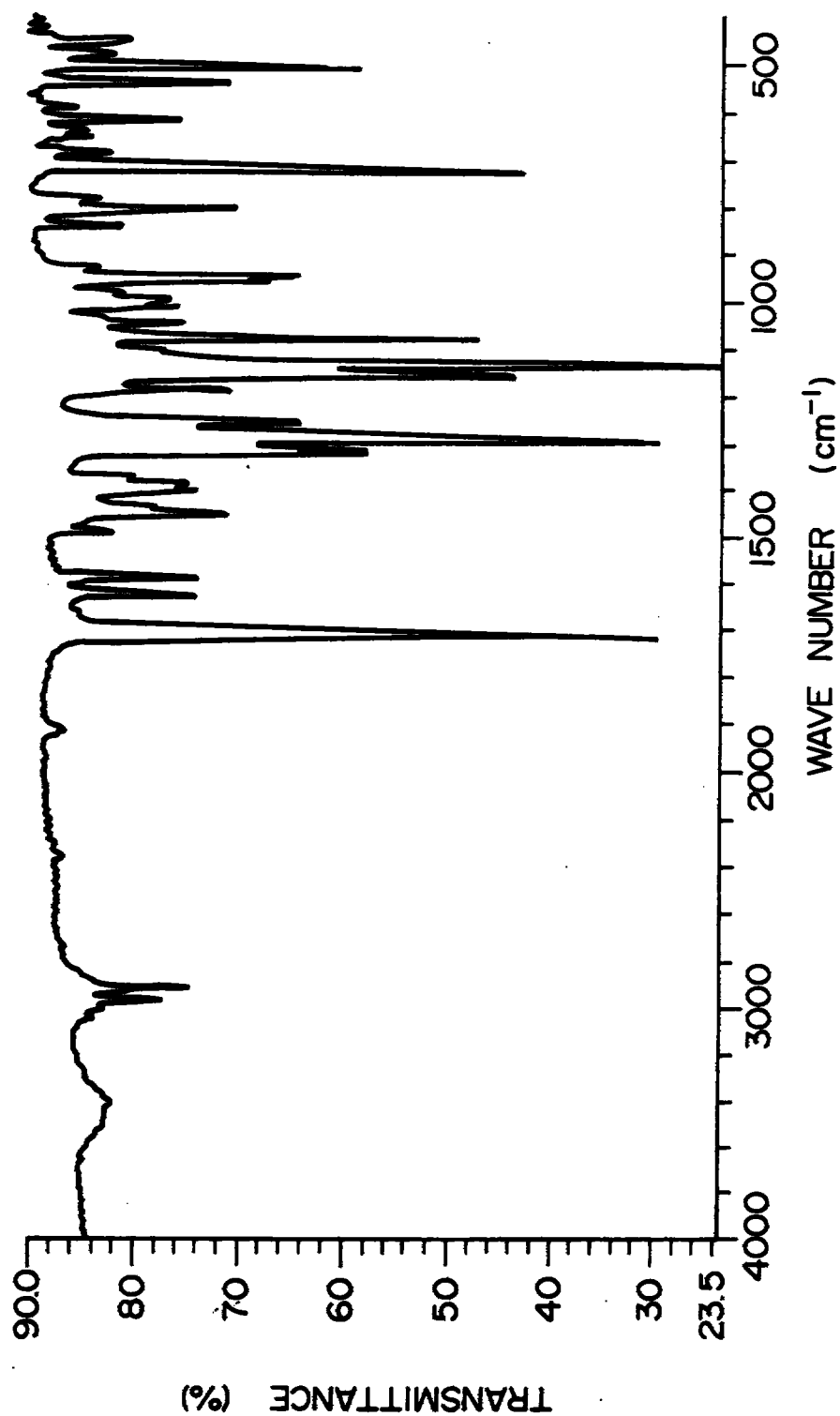


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FIG. 4

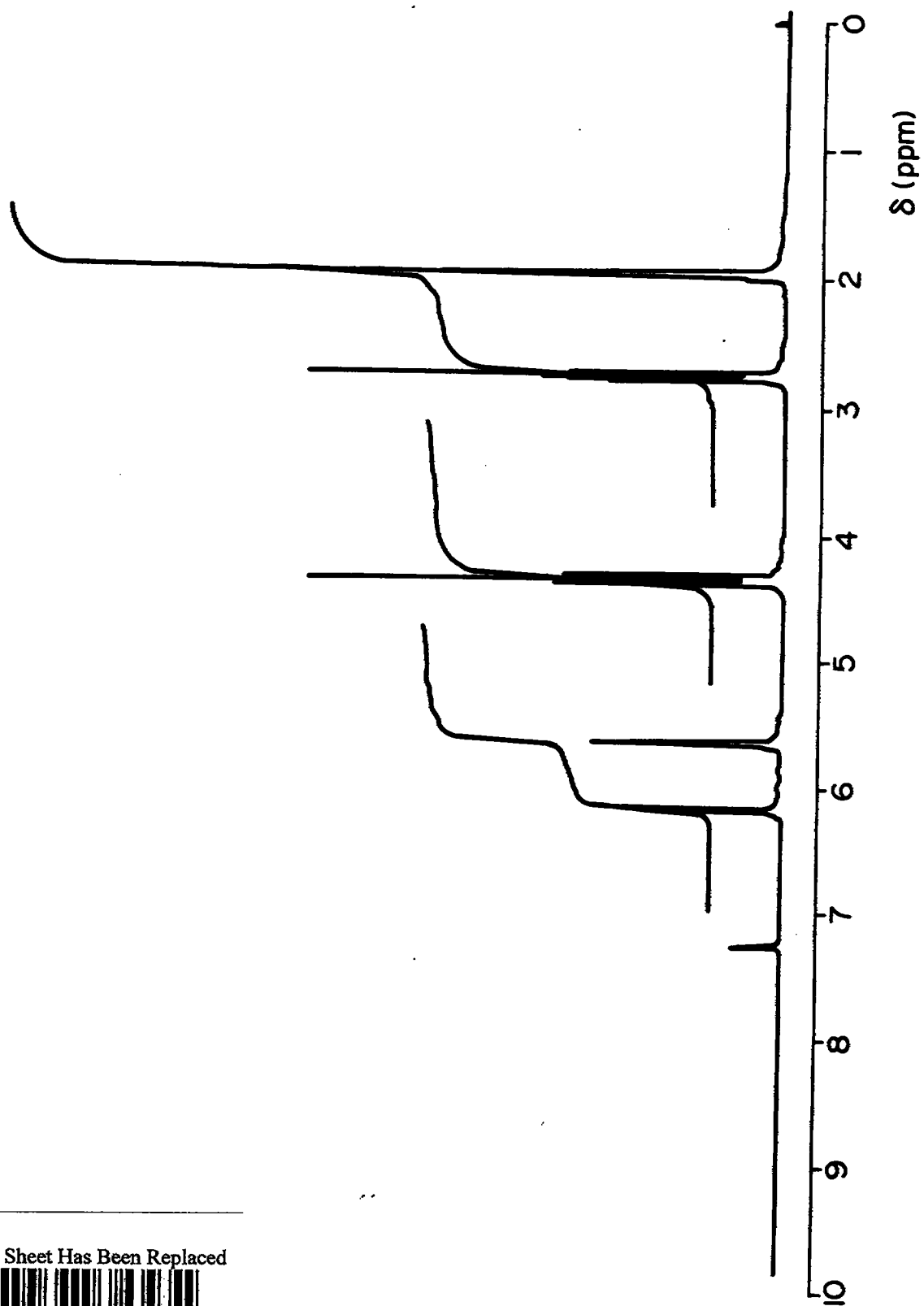


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FIG. 5

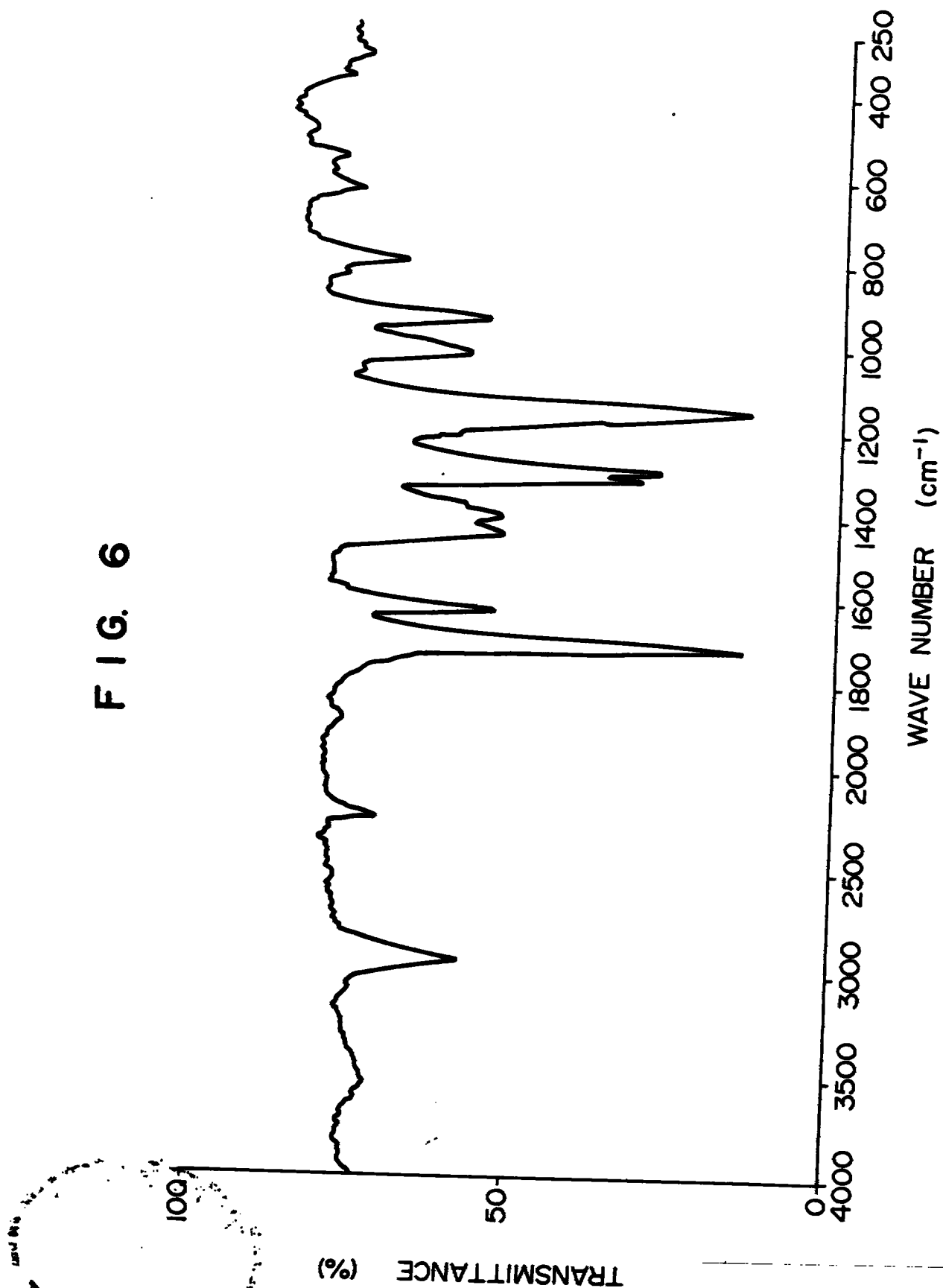


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FIG. 6

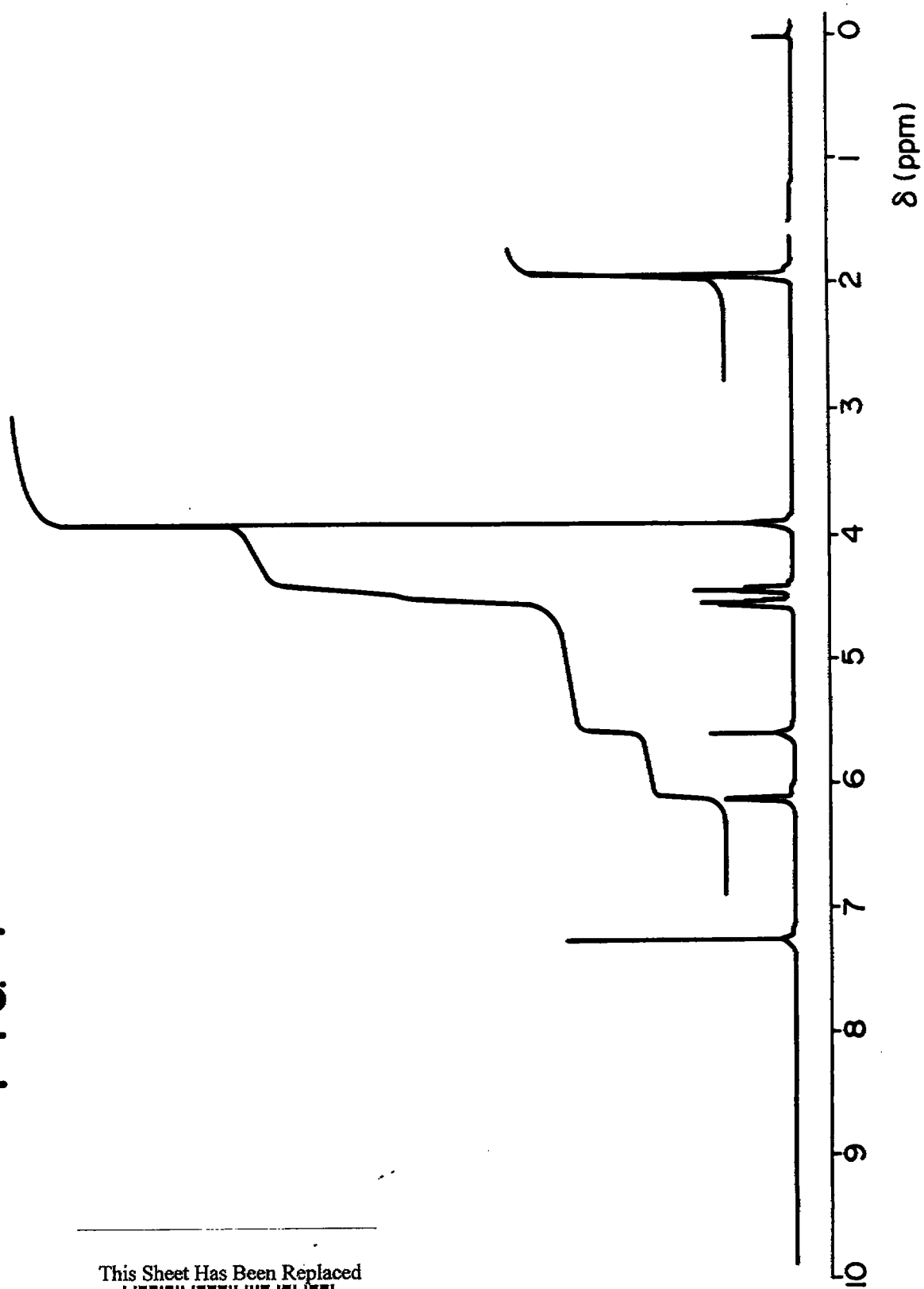


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FIG. 7

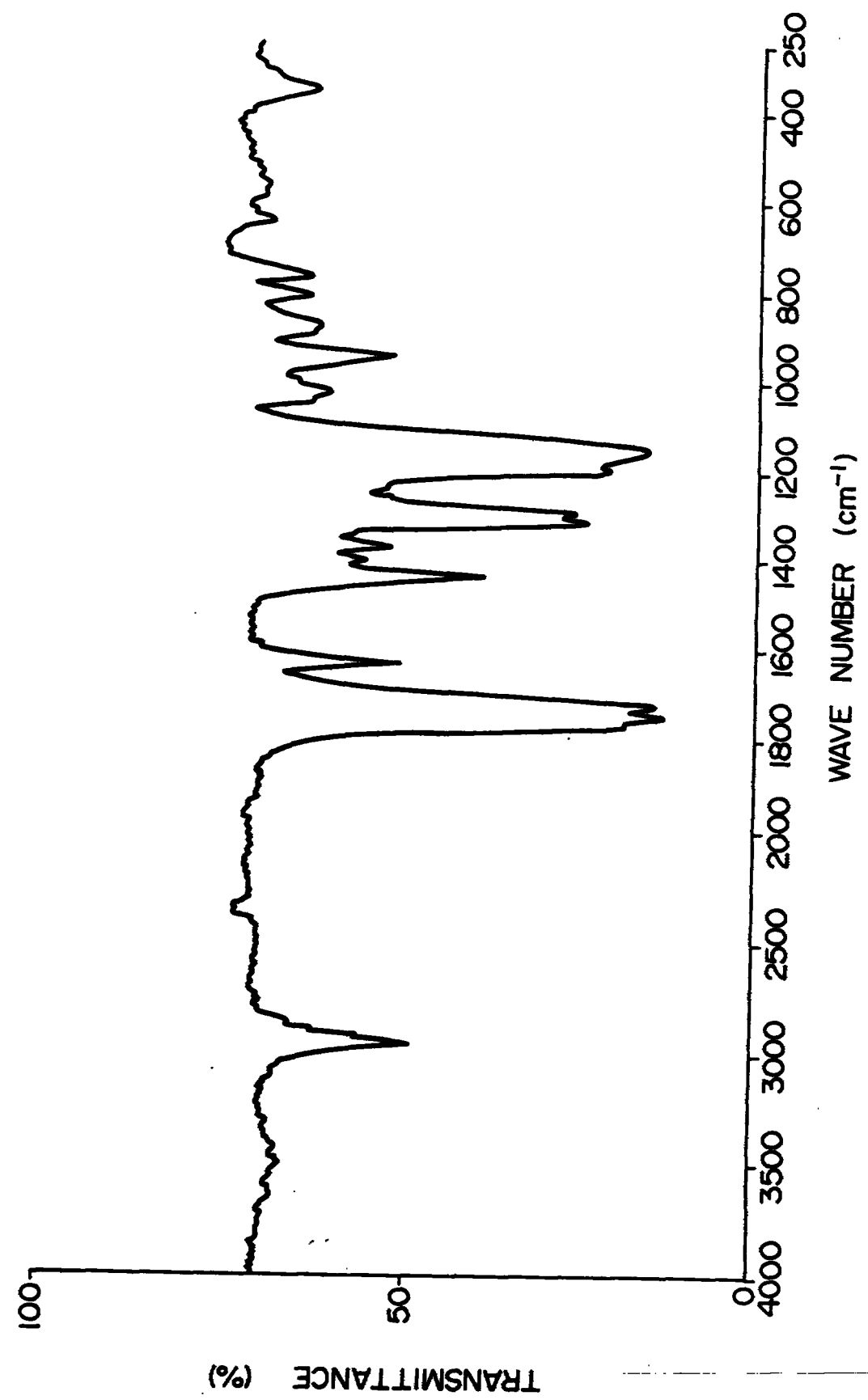


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FIG. 8

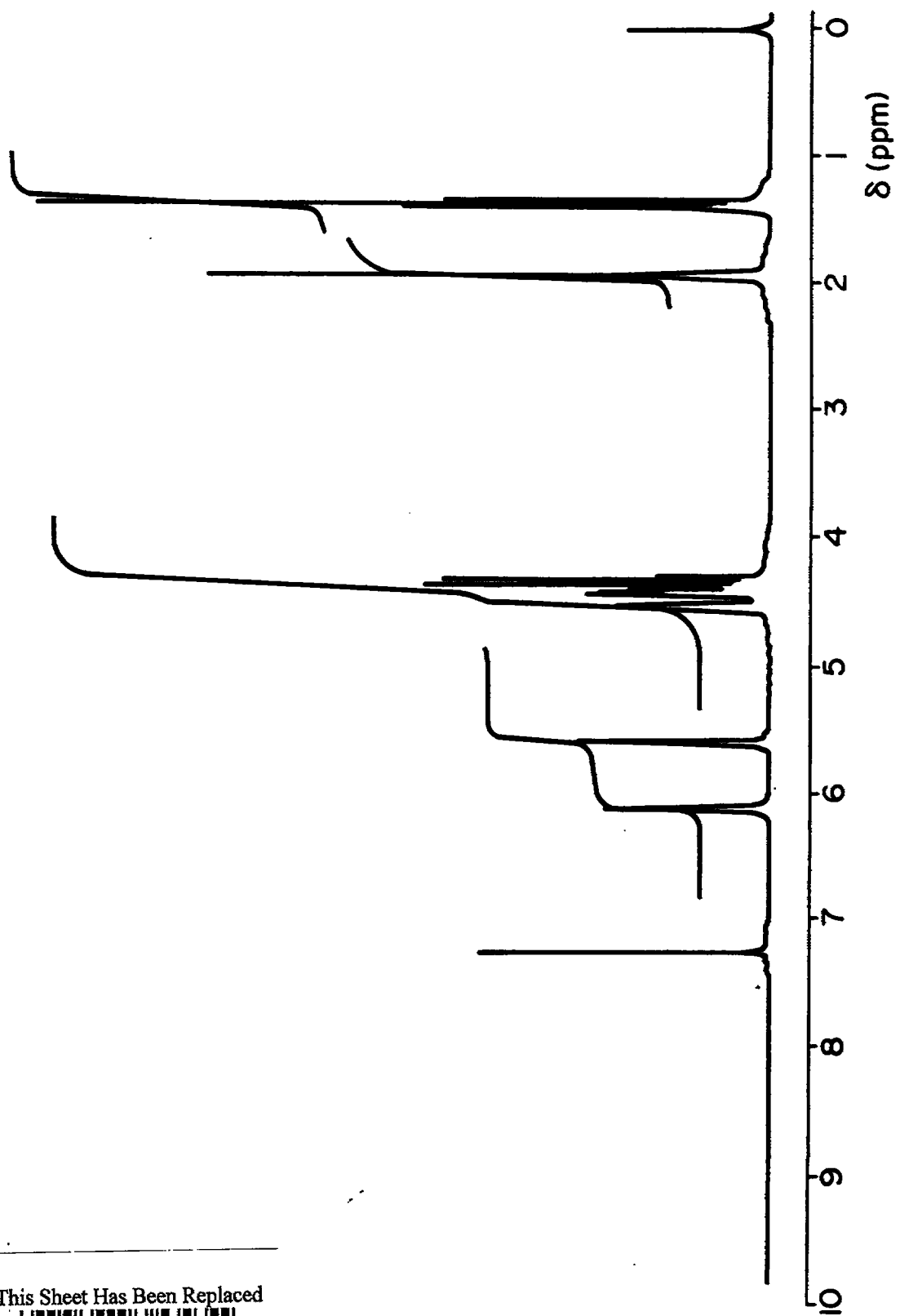


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FIG. 9



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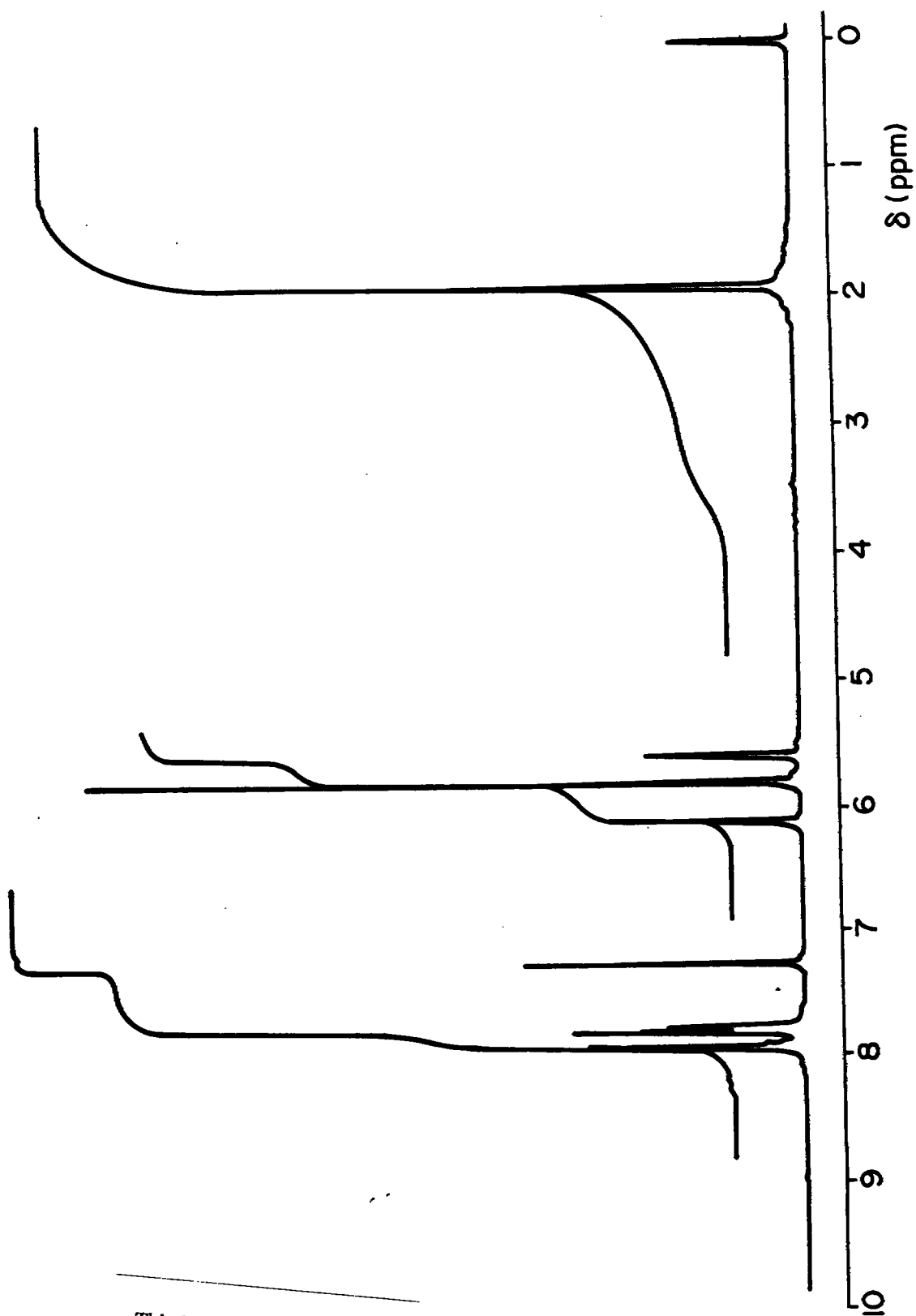
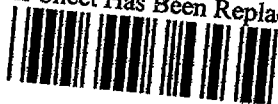


FIG. 10

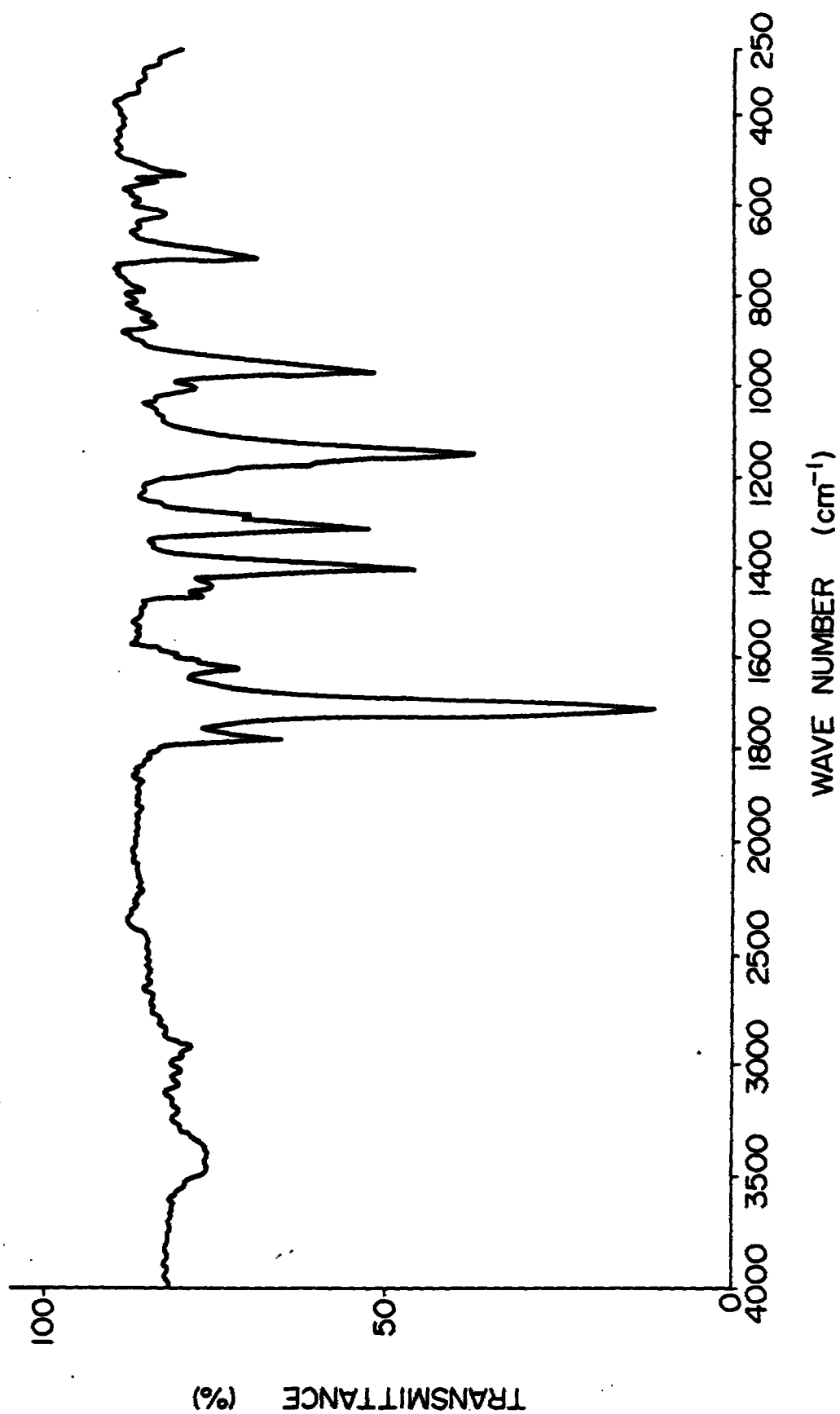
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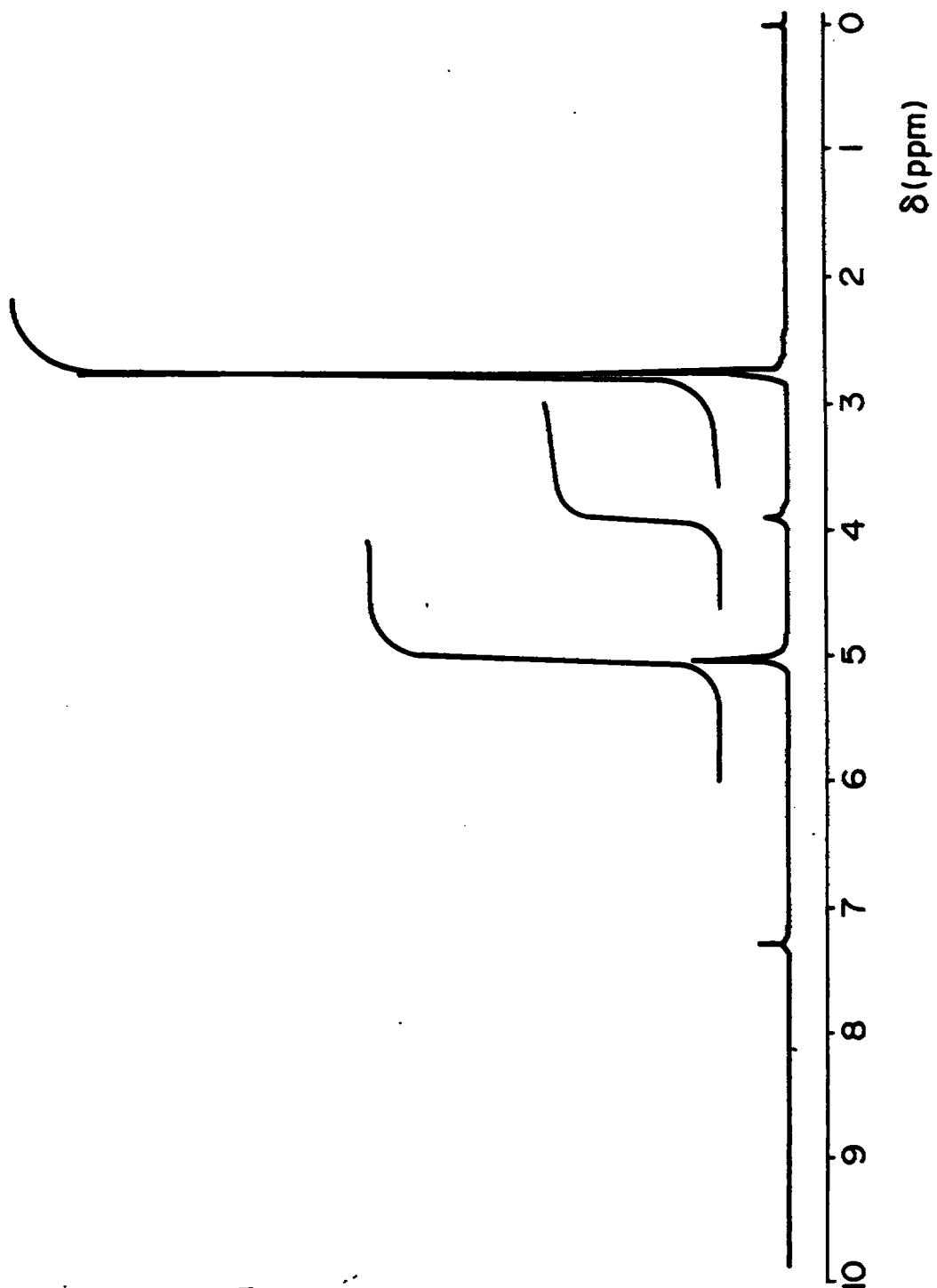
FIG. II

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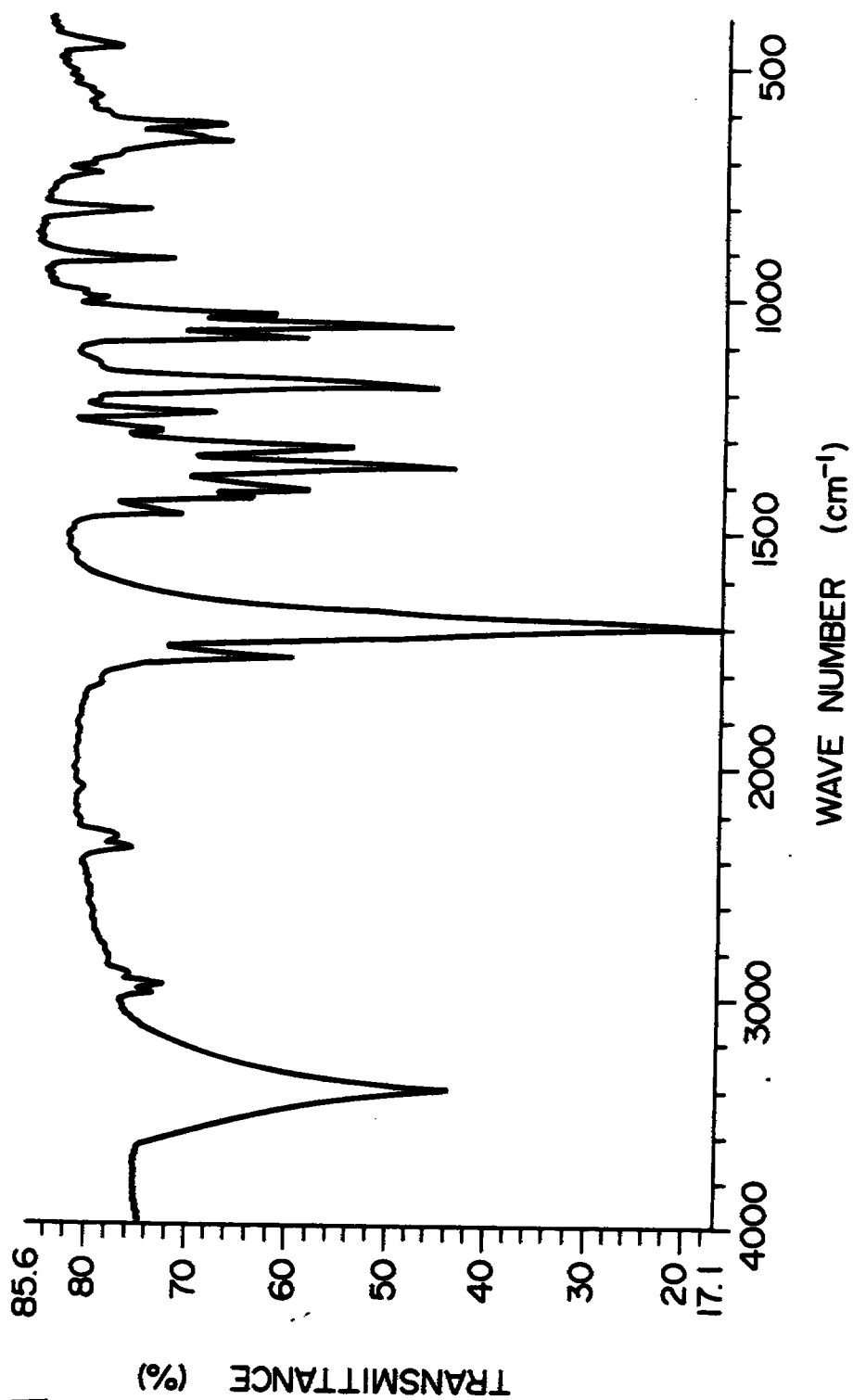
FIG. 12



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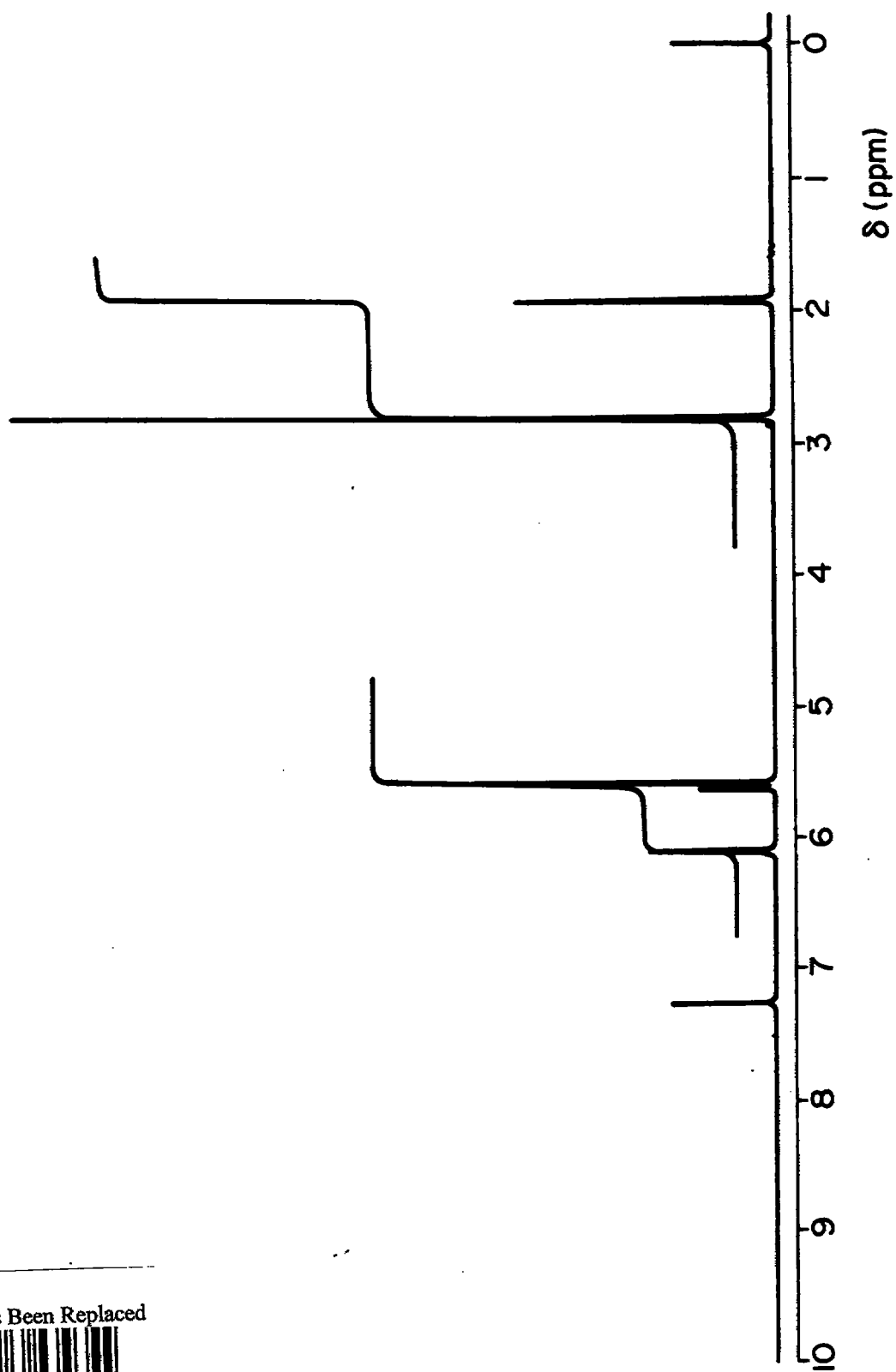
FIG. 13



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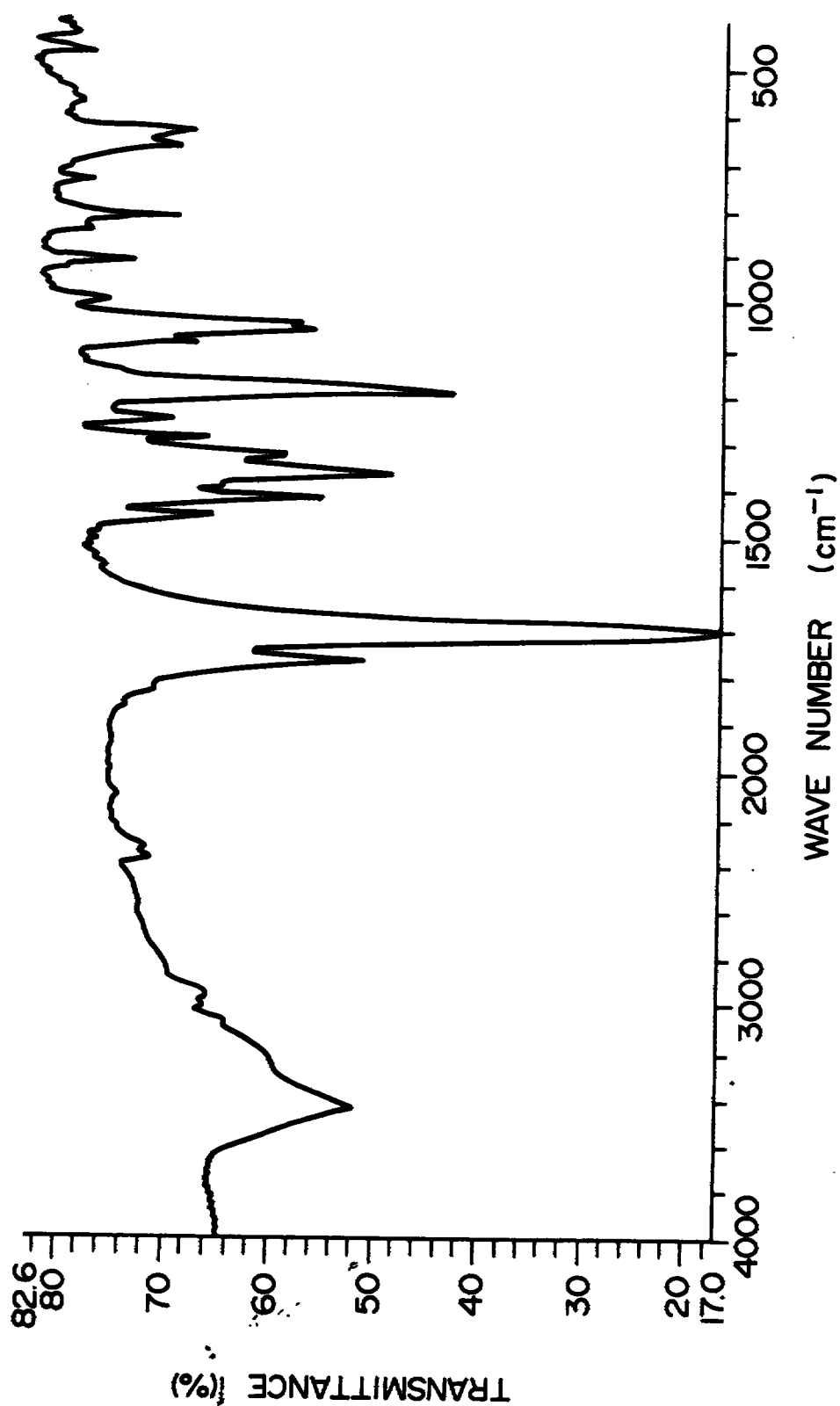
FIG. 14



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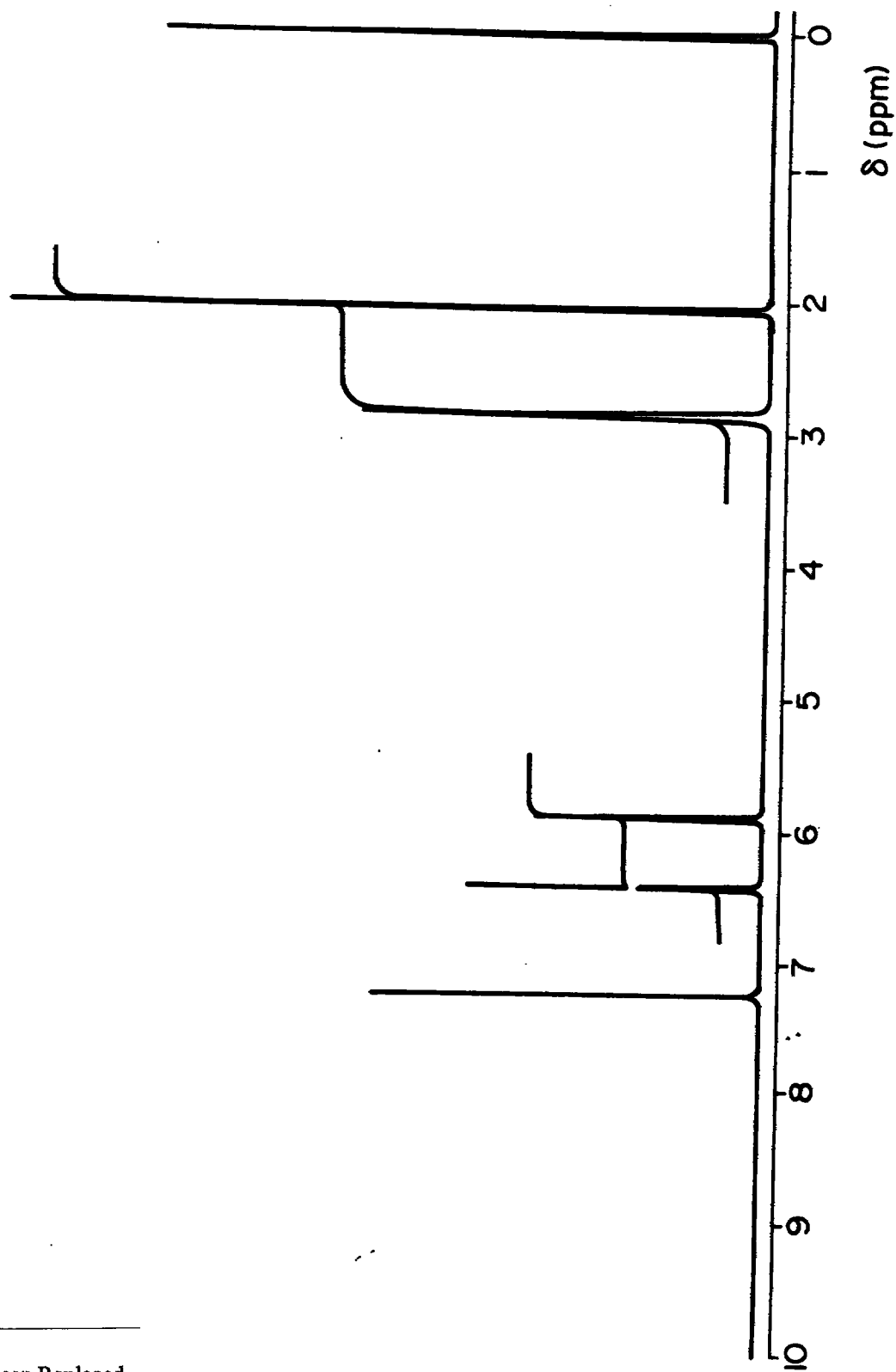
FIG. 15



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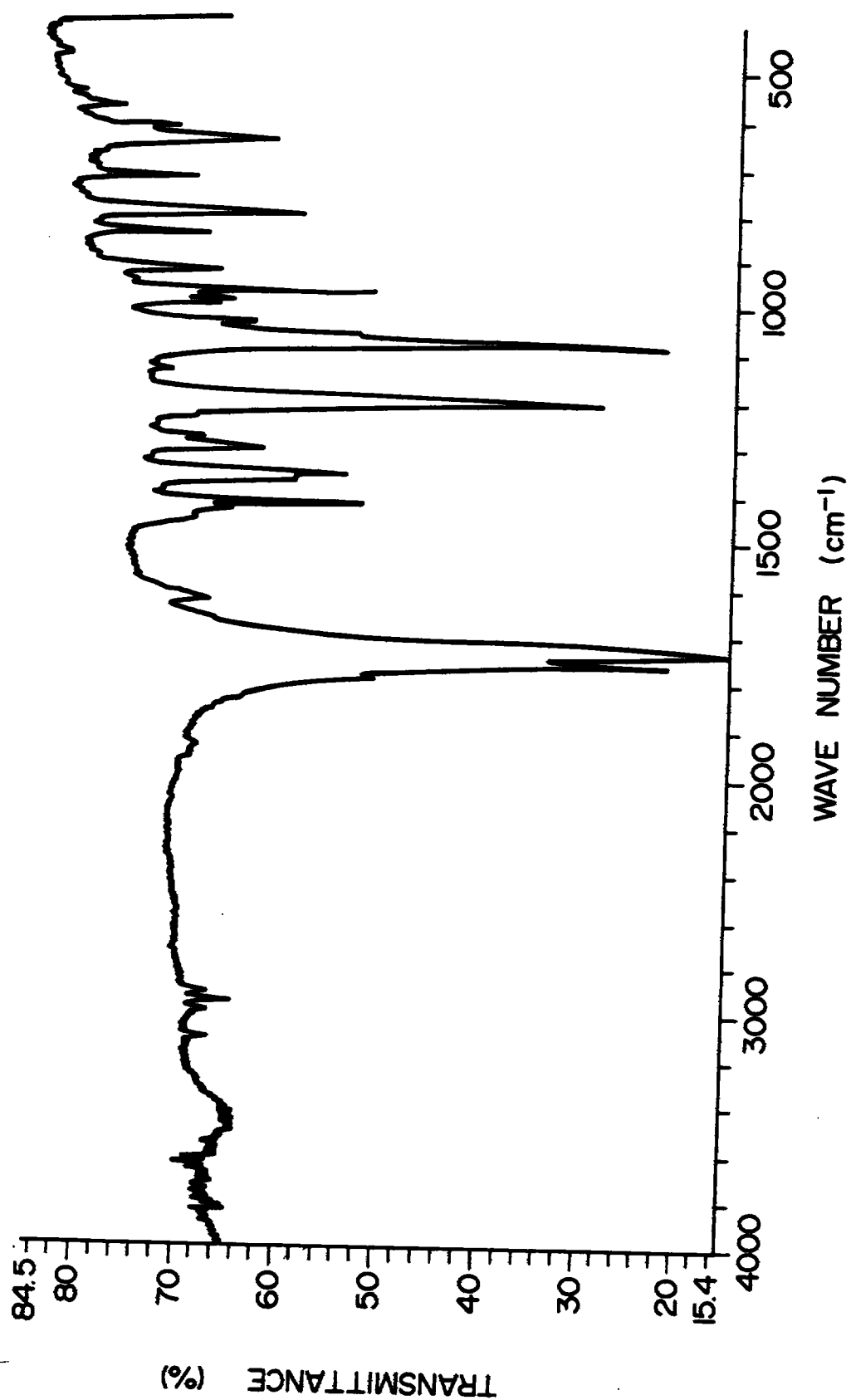
FIG. 16



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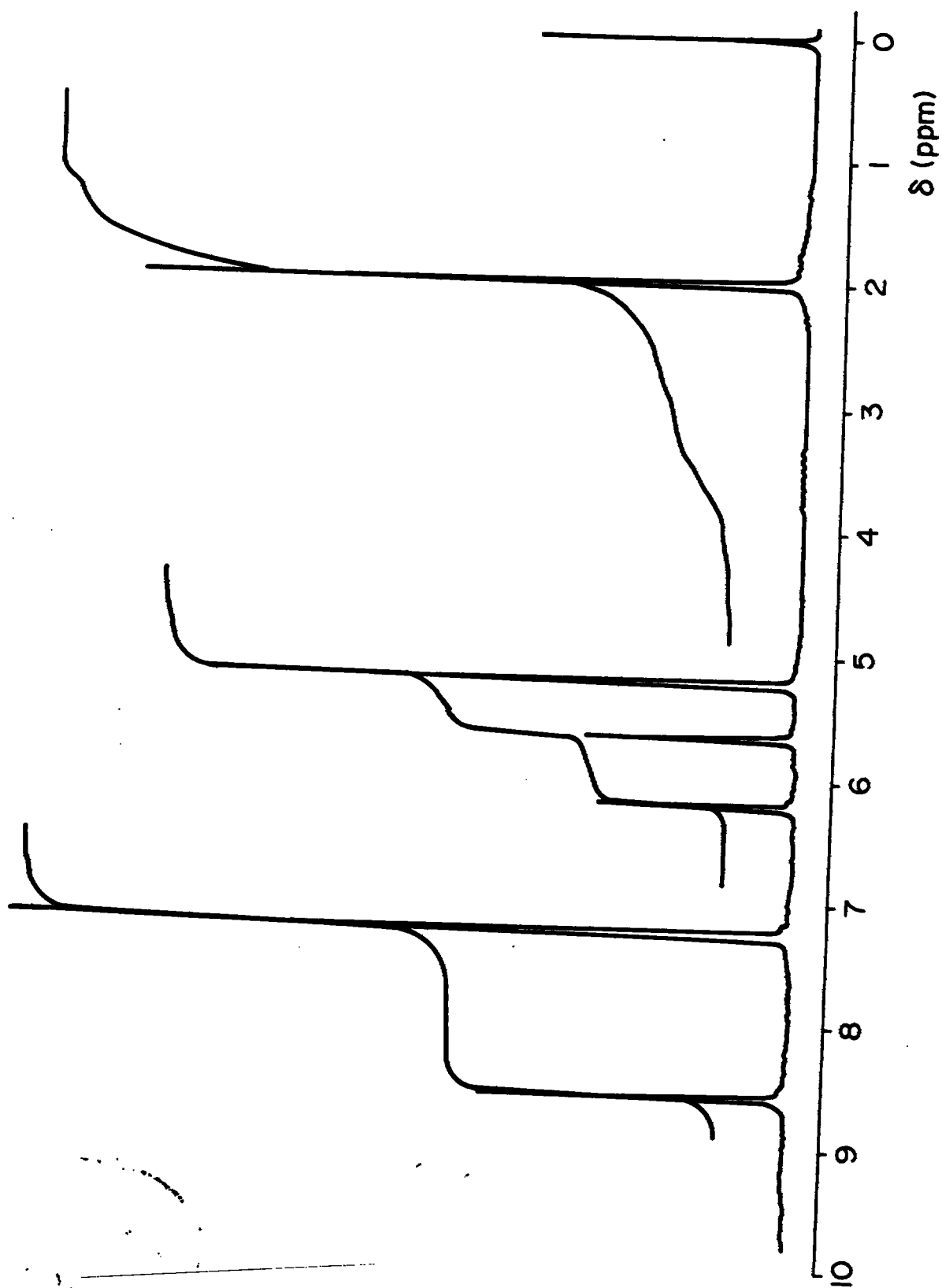
FIG. 17



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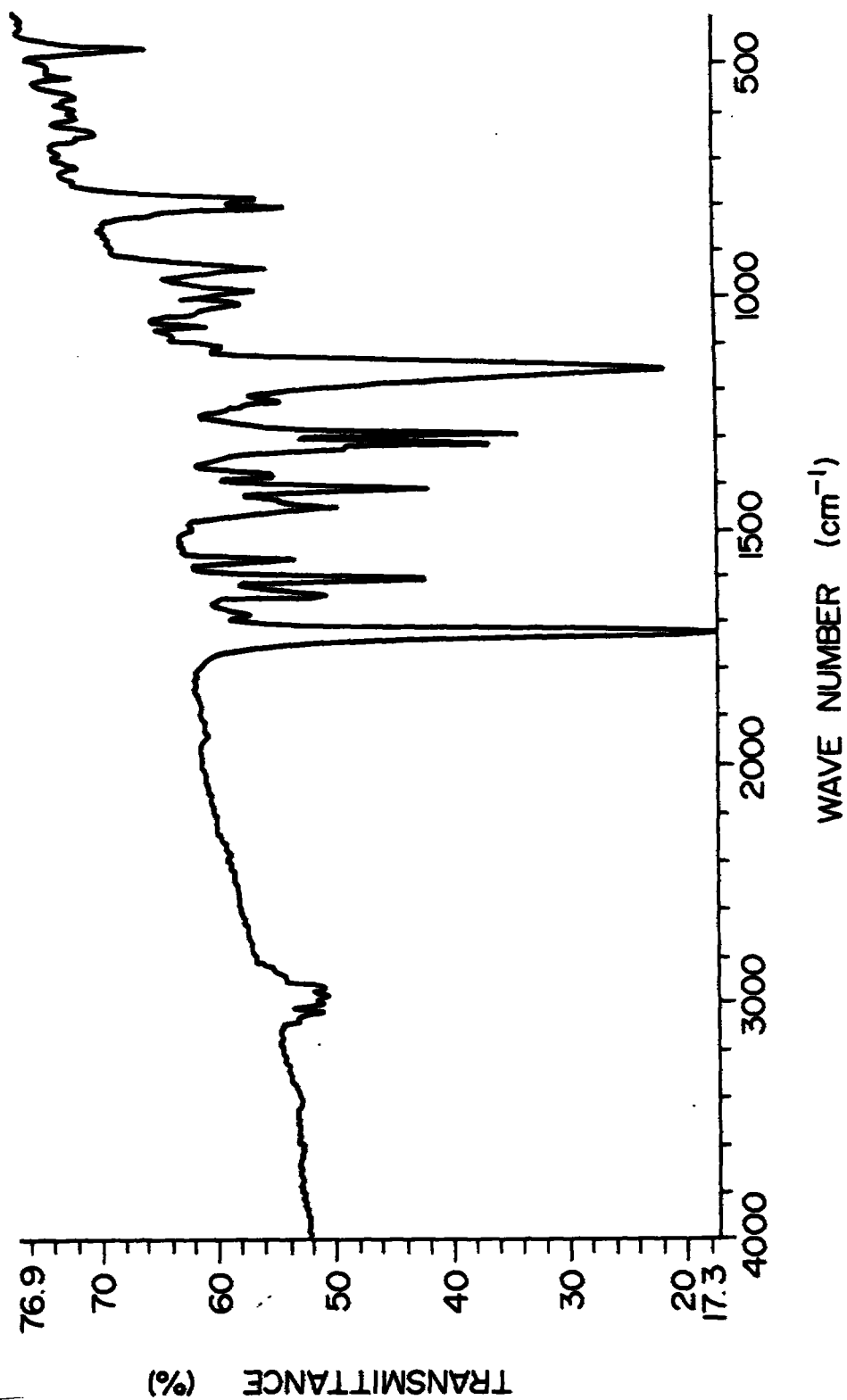
FIG. 18



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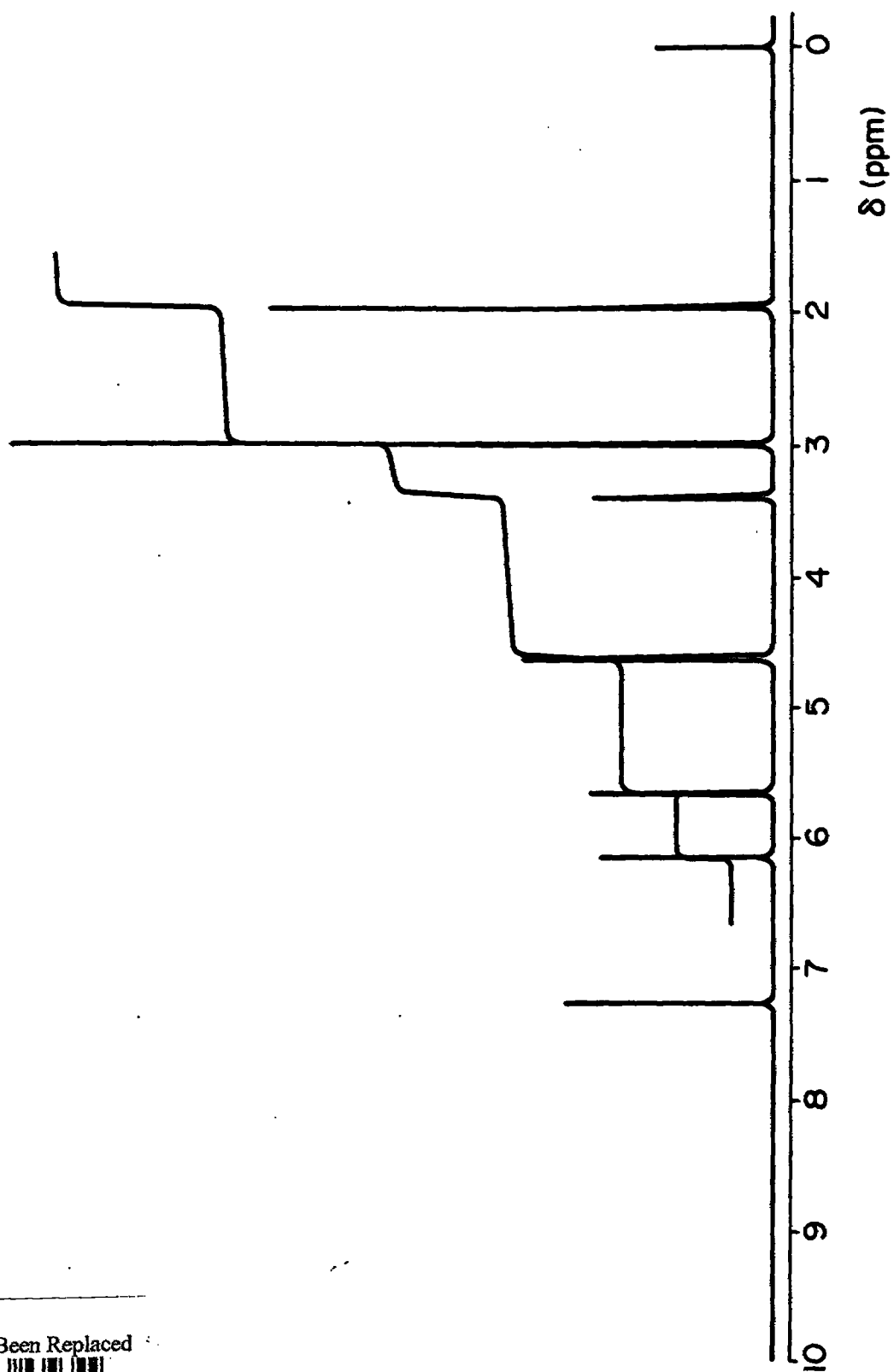
FIG. 19



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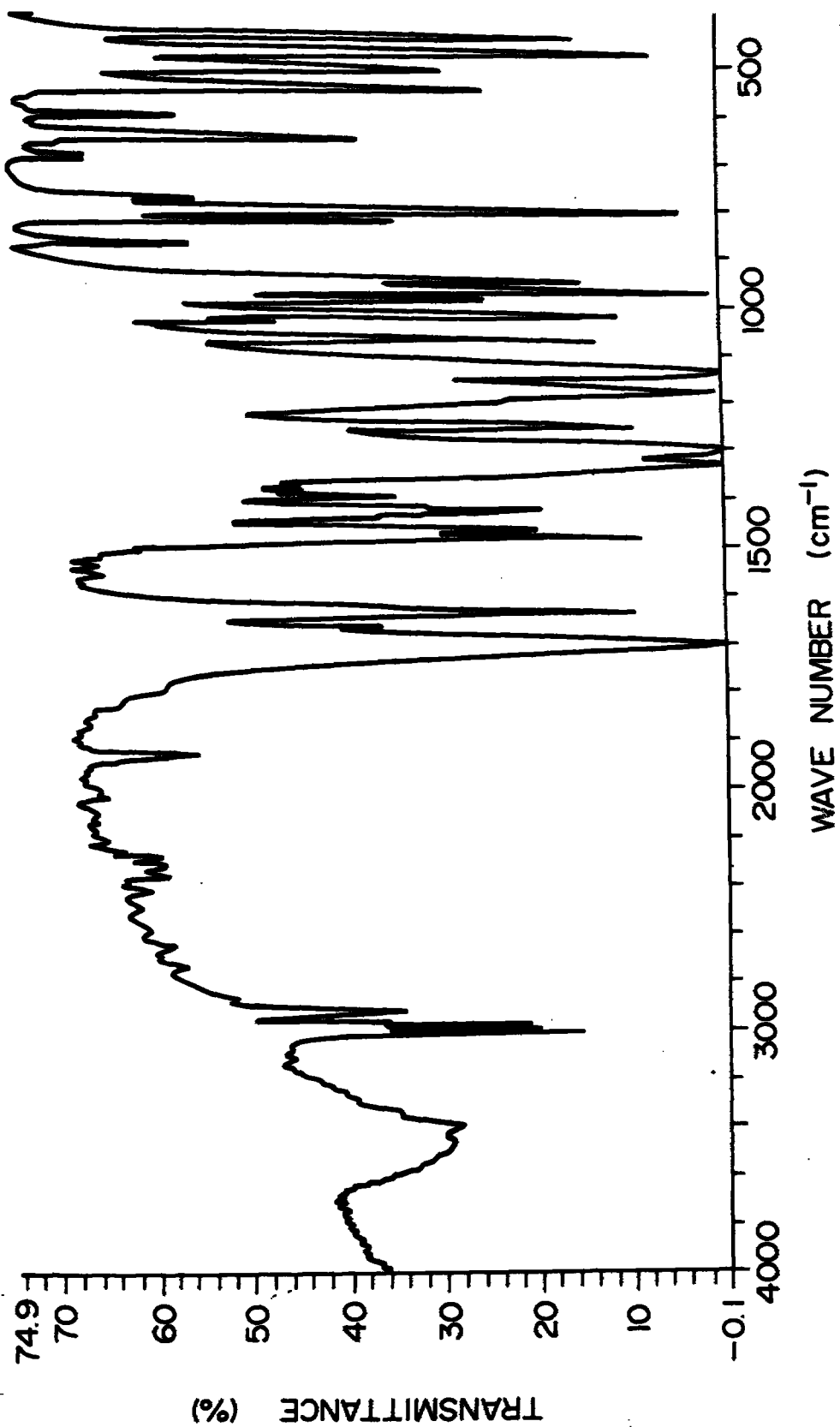
FIG. 20



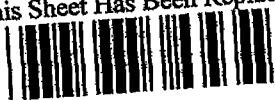
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FIG. 21



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☒ Claim(s)	: paged 1... to paged 22.....	
☒ Drawing(s)	: paged 1/2... to paged 24.....	
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☒ Description	: paged 1... to paged 18.....
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COATING RESIN AND ANTIFOULING COATING COMPOSITION

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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 underwater 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, fishing net, drainage pipe, etc., is set or placed in commission 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 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 economical problem. Also, if the marine 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 the marine organisms to the underwater structures such

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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. 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 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 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 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 antifouling effect, in place of the organotin-based resins 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



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 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 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 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 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 the organotin copolymers, shows a hydrolytic property well comparing with said organotin copolymers, and is capable of forming a relatively long-lasting excellent

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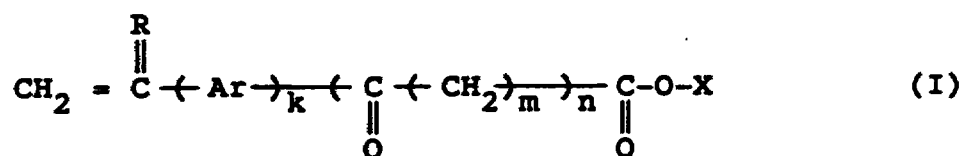
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antifouling coat. This coating resin is also soluble in aromatic solvents.

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.

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:



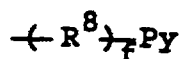
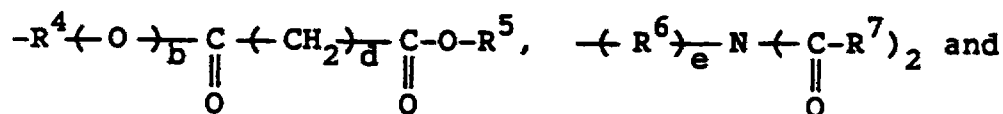
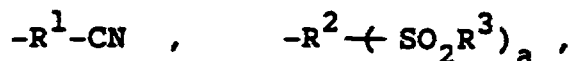
wherein R is a hydrogen atom or a straight or branched alkyl group having 1-4 carbon atoms; Ar is a benzene ring or a naphthalene ring; k, m and n represent independently a number of 0 or 1; and X is a substituent selected from those represented by the following formulae:

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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 ; 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 substituent; when a is 2 or 3, 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 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} 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 copolymerizable unsaturated monomer a monomer represented by the

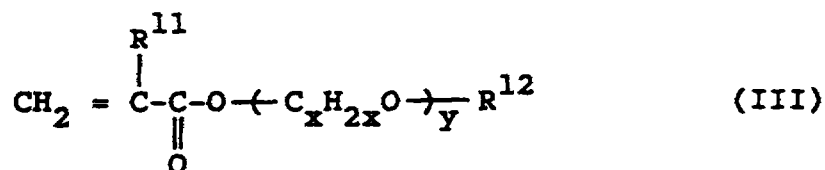


formula:



wherein R^9 is a hydrogen atom or CH_3 ; and R^{10} is a branched or alicyclic alkyl, aryl or aralkyl group having 3 or more carbon atoms, or an organic substituent 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 copolymerizable unsaturated monomer an unsaturated monomer having a 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} is a hydrogen atom or a straight, branched or cyclic alkyl, aryl or aralkyl group.

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The present invention further provides an antifouling coating composition comprising said coating resin.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ^1H -NMR spectrum of Compound No. 10 ($\text{R} = \text{CH}_3$) in the list, given below, of the preferred examples of the unsaturated monomers represented by the formula (I).

Fig. 2 is an IR spectrum of Compound No. 10 ($\text{R} = \text{CH}_3$).

Fig. 3 is a ^1H -NMR spectrum of Compound No. 12 ($\text{R} = \text{CH}_3$).

Fig. 4 is an IR spectrum of Compound No. 12 ($\text{R} = \text{CH}_3$).

Fig. 5 is a ^1H -NMR spectrum of Compound No. 2 ($\text{R} = \text{CH}_3$).

Fig. 6 is an IR spectrum of Compound No. 2 ($\text{R} = \text{CH}_3$).

Fig. 7 is a ^1H -NMR spectrum of Compound No. 18 ($\text{R} = \text{CH}_3$).

Fig. 8 is an IR spectrum of Compound No. 18 ($\text{R} = \text{CH}_3$).

Fig. 9 is a ^1H -NMR spectrum of Compound No. 19 ($\text{R} = \text{CH}_3$).

Fig. 10 is a ^1H -NMR spectrum of Compound No. 20 ($\text{R} = \text{CH}_3$).

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

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

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 (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).

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. 9 (R = CH₃).

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

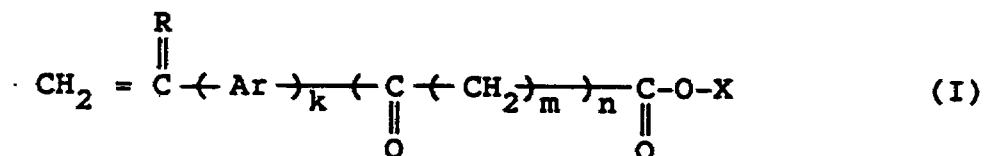
DESCRIPTION OF THE PREFERRED EMBODIMENTS

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

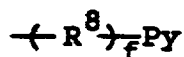
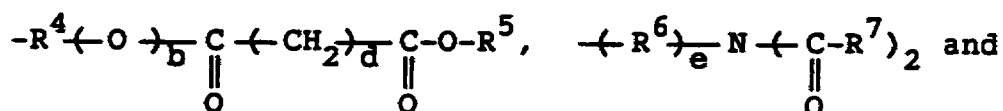
(1) A coating resin comprising a polymer obtained by polymerizing an unsaturated monomer represented by



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



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:



wherein R¹, R⁴, R⁶ and R⁸ each represents a straight, branched or alicyclic alkylene group having 1-6 carbon atoms; R² is a C₁₋₆ straight, branched or cyclic hydrocarbon group connecting O and SO₂R³; a is an integer of 1 to 3 indicating the number of SO₂R³ bonded to R²;

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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, 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 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.

(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 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 (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



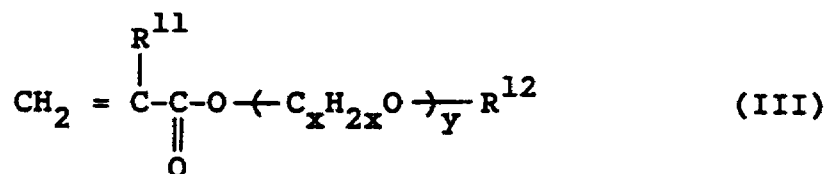
monomer copolymerizable with the unsaturated monomer of the formula (I) is a monomer represented by the formula:



wherein R^9 is a hydrogen atom or CH_3 ; and R^{10} is a branched or alicyclic alkyl, aryl or aralkyl group 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 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 functional group is an unsaturated acid anhydride or an unsaturated monomer represented by the formula:



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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.

(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 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. 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-cyclopentylene, 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, cyclobutyl, 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,

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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 substituent include phenyl, tolyl, anisyl, cyanophenyl, 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, tetramethylene, 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, 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 C_{6-10} aryl groups or C_{7-10} aralkyl groups represented by R^7 include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, naphthyl, benzyl, phenethyl, benzhydryl, etc. The groups forming a cyclic structure, represented by two R^7 , include methylene, ethylene, trimethylene, 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

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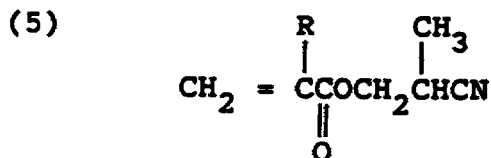
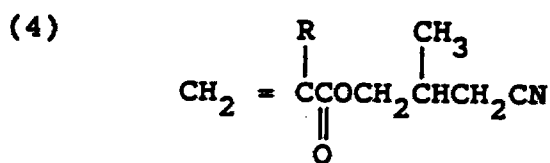
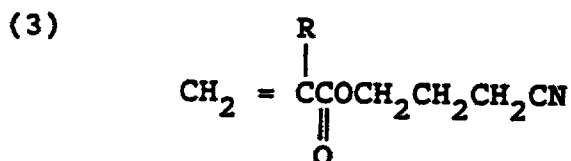
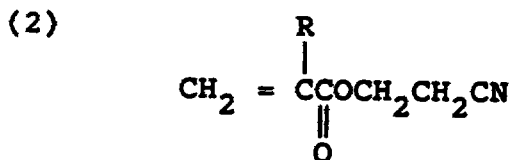
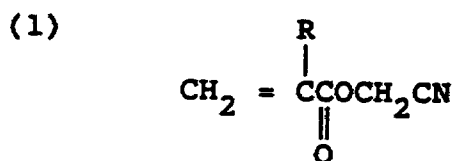


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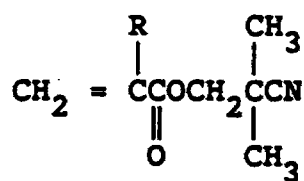
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commercially available unsaturated monomers.

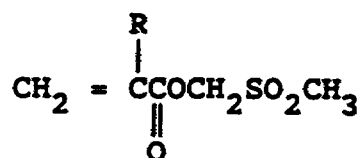
Listed below are the preferred examples of the unsaturated monomers represented by the formula (I) (R in the following formulae is hydrogen atom or methyl group):



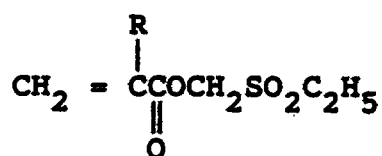
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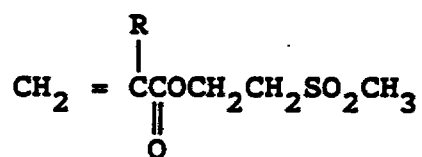
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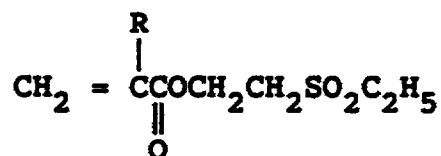
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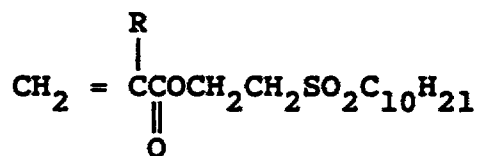
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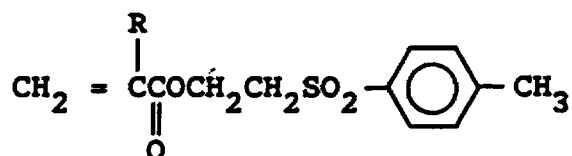
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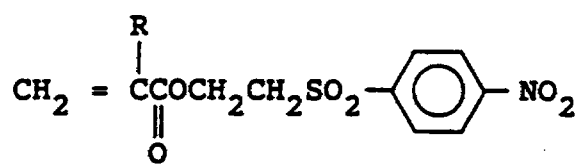
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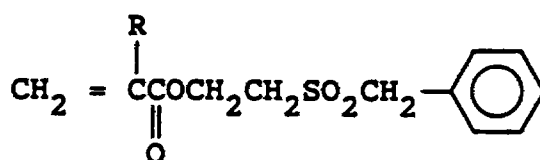
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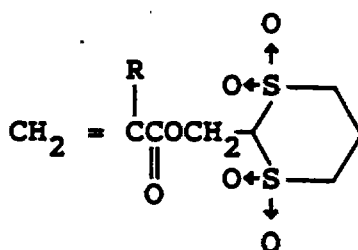
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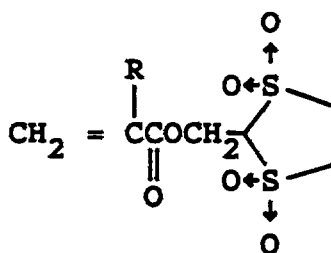
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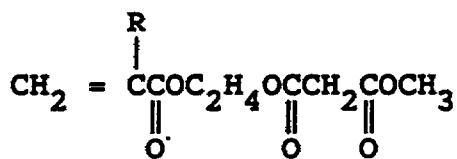
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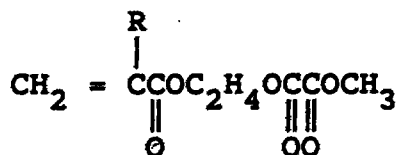
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(17)



(18)



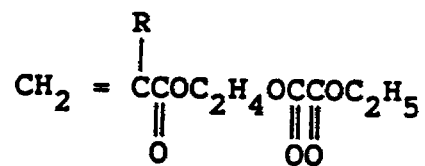
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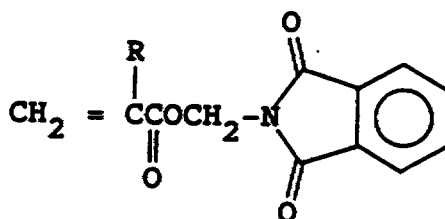
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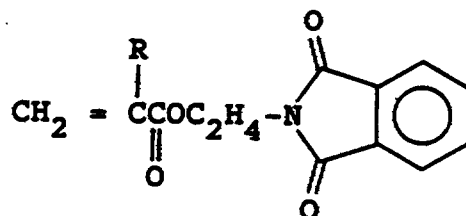
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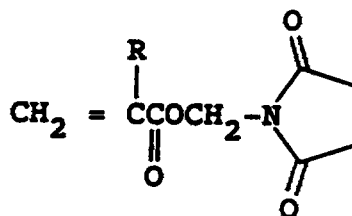
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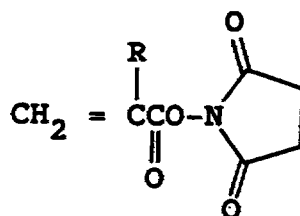
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(23)



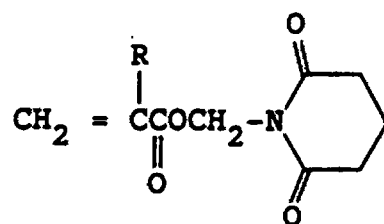
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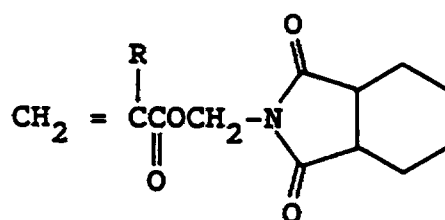
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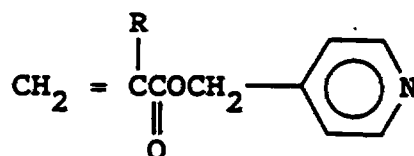
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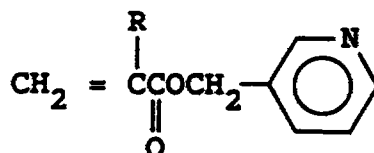
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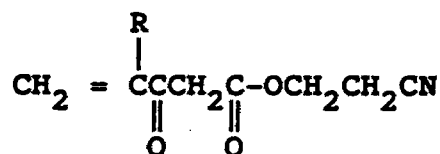
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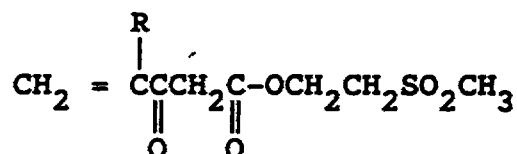
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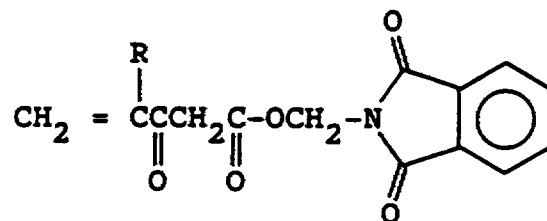


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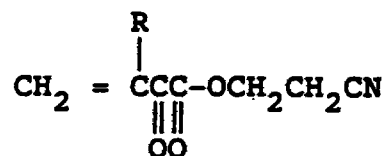
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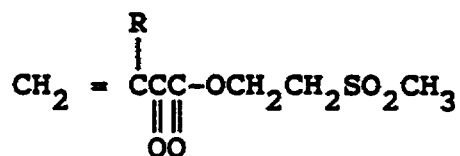
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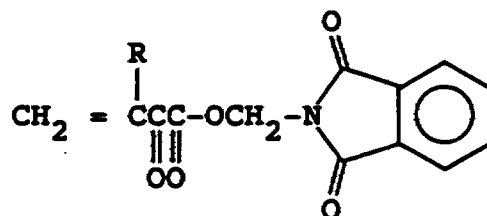
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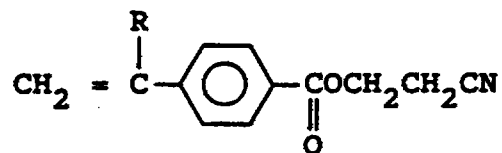
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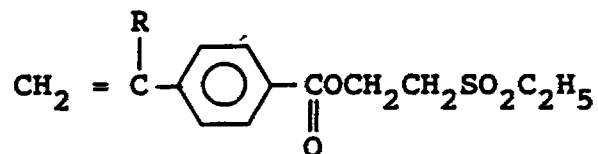
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The compounds of the formula (I) wherein R^3 's represent the hydrocarbon groups forming a cyclic structure with each other are, for example, Compound No. 15 and Compound No. 16 shown in the above list.

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 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 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 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 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



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), 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 aralkyl groups having 3 or more carbon atoms, represented by R^{10} , 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, 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, such as trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, triphenylsilyl, trimethoxysilyl, triethoxysilyl, tripropoxysilyl, tributoxysilyl, triphenoxysilyl, etc.

The unsaturated monomers represented by the 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

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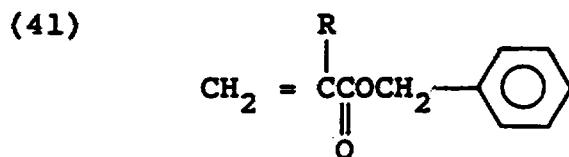
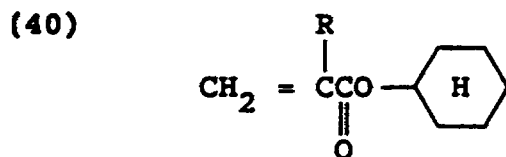
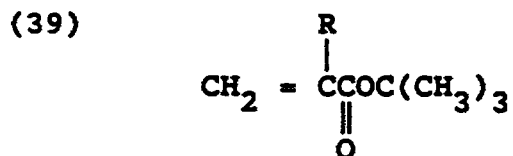
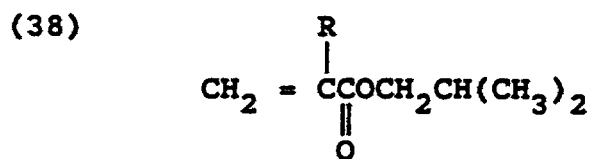
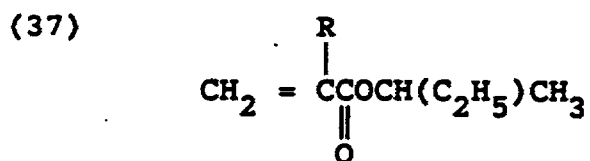
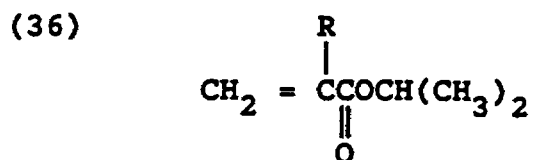


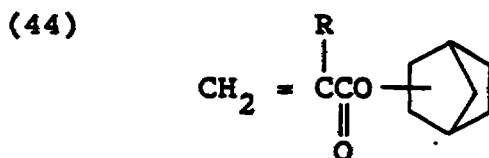
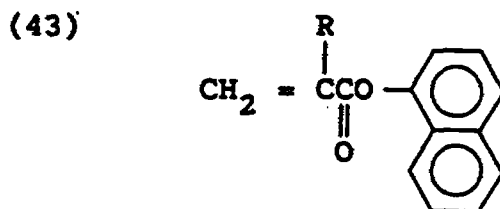
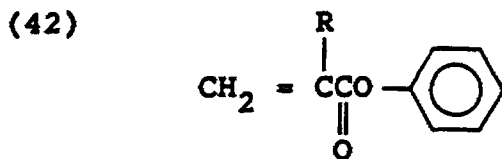
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unsaturated monomers represented by the formula (II) (R in the following formulae is hydrogen atom or methyl group):





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 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 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

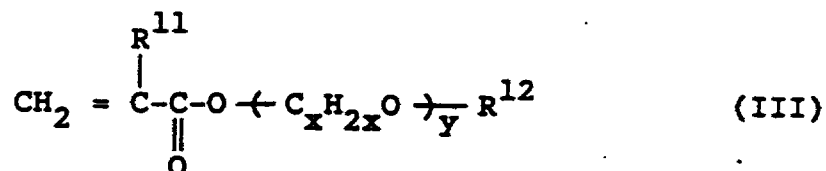
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invention, include unsaturated acid anhydrides or the unsaturated monomers represented by the formula:



wherein R^{11} is hydrogen atom or CH_3 group; x is an 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).

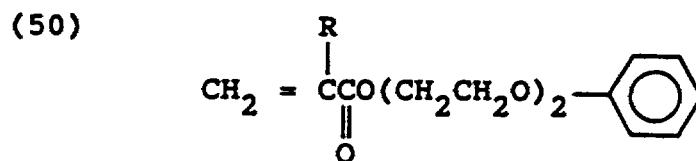
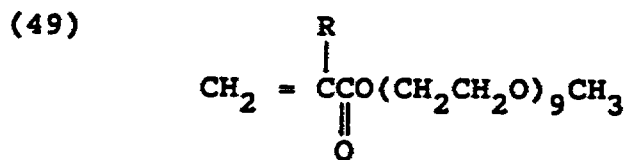
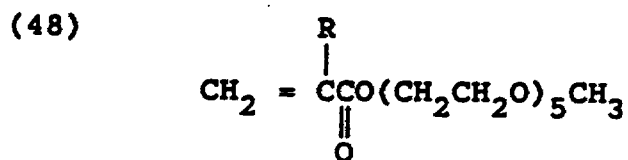
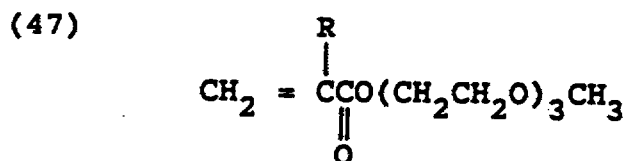
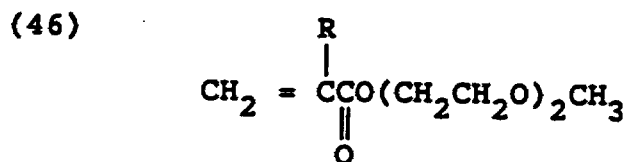
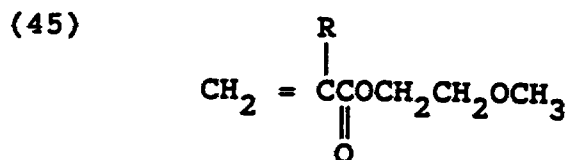
In the unsaturated monomers represented by the formula (III), the straight, branched or cyclic alkyl, aryl or aralkyl groups represented by R^{12} include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, sec-pentyl, tert-pentyl, neopentyl, 2-ethylhexyl, cyclopropyl, cyclobutyl, 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.

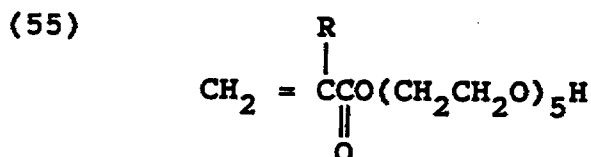
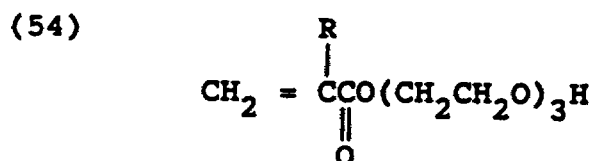
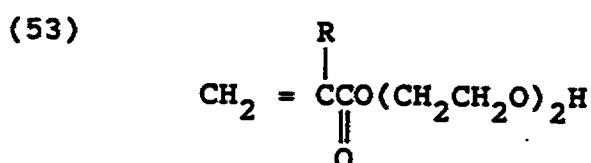
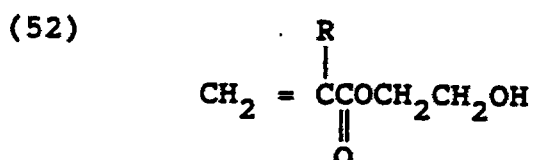
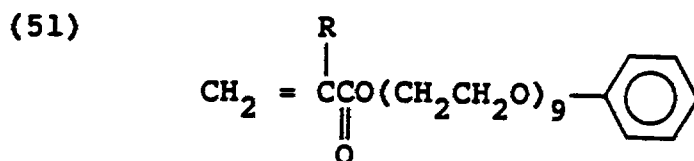
The unsaturated monomers of the formula (III) can be produced by various known synthetic methods. The commercially available unsaturated monomers are also



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):





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



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

The blending ratio of the unsaturated monomer 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%, 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 for antifouling paints.

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

As examples of the unsaturated monomers other 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, 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.



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 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 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 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 (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 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

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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 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 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, when the product is intended to be used as an antifouling 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.

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 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



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 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 methanethiol, ethanethiol, n-propanethiol, isopropanethiol, n-butanethiol, 2-methylpropanethiol, 3-methylpropanethiol, 1,1-dimethylethanethiol, 1-hexanethiol, 1-octanethiol, 1-decanethiol, benzenethiol, 2-methylbenzenethiol, 3-methylbenzenethiol, 4-methylbenzenethiol, 2-ethylbenzenethiol, 3-ethylbenzenethiol, 4-ethylbenzenethiol, bis(4-hydroxydimethylphenyl)disulfide, bis(2-chloromethylphenyl)disulfide, bis(2-bromophenyl)disulfide, dinaphthyl disulfide, di-2-benzothia disulfide, α -methylstyrene 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 appropriate hydrolysis-elution property and can be applied as a coating resin suited for antifouling coating compositions. The coating resin according to

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the present invention may further comprises other polymer(s) within limits not prejudiciary to the effect of the present invention. Such polymers include, for example, vinyl copolymers such as acrylic copolymers, 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 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 ferrocyanate, cupric quinone, cupric 6-hydroquinone, cupric oleate, cupric nitrate, cupric phosphate, cupric tartrate, cuprous oxide, cuprous iodide and cuprous sulfite.

Typical examples of the pigments usable in 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.

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.

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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 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 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 methacrylate, 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 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 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



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):

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),
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

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 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 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



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 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):

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).

(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

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 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



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

(1) ^1H -NMR spectral data (^1H -NMR spectrum as shown 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 Fig. 6):

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

Synthesis Example 4

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

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 dimethyl oxalate was removed by sublimation. The resulting 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 colorless liquid (yield: 64%). From its analytical results shown below, this liquid was confirmed to be 2-methoxalyloxyethyl methacrylate (Compound No. 18, $R = CH_3$).



- (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), 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

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 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 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 = 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



methacrylate (Compound No. 19, R = CH₃).

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

δ(CDCl₃): 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 (Compound No. 20, R = CH₃)

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 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 mixture was poured into icy water and stirred for a while. 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-methacryloyloxymethylphthalimide (Compound No. 20, R = CH₃).

(1) Melting point: 134°C

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(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).

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

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

Synthesis Example 7

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.



- (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),
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 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. 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 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).

- (1) Melting point: 76°C

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(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), 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

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 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 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 colorless crystals (yield: 31%). From the following physical properties, these crystals were confirmed to be N-methacryloyloxysuccinimide (Compound No. 23, R = CH_3).

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- (1) Melting point: 102°C
- (2) ^1H -NMR spectral data (^1H -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).
- (3) IR spectral data (KBr) (IR spectrum as shown in Fig. 17):
1763, 1737 cm^{-1} (C=O).

Synthesis Example 9

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 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 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).

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

$\delta(\text{CDCl}_3)$: 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).

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-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 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 reduced pressure to obtain 130 g of colorless crystals (yield: 64%). From their physical properties, these crystals were confirmed to be 2-methylsulfonylethyl



methacrylate (Compound No. 9, R = CH₃).

(1) Melting point: 48°C

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

δ(CDCl₃): 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):

1710 cm⁻¹ (C=O), 1300, 1140 cm⁻¹ (SO₂).

Examples 1 - 20

Into a four-necked flask equipped with a stirrer, a condenser, an N₂ gas feed pipe, a dropping funnel and a thermometer, a measured amount of a solvent or solvents was supplied and stirred at 95°C. Then a mixed solution comprising monomers, azobisisobutyronitrile (AIBN) and α-methylstyrene dimer (αMSD) was charged into the dropping funnel and added dropwise into the flask in an N₂ gas stream while maintaining the temperature of the reaction mixture at about 95°C and stirring the mixture. After the dropwise addition was completed, the 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 properties of the obtained resins are shown in Tables 1 to 3.



Table 1

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)		NV (%)	Mn
			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

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Table 1 (cont'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN 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

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Table 1 (cont'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Table 2

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Table 2 (comp'd)

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

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Table 2 (comp'd)

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

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Table 3

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)	α MSD (g)	NV (%)	Mn
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

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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 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 a viscous liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 4.

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Table 4

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Table 4 (cont'd)

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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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 N_2 gas feed pipe, a dropping funnel and a thermometer, and the mixture was kept therein with stirring. Then, a mixed solution of other monomers, AIBN and α MSD was supplied into the flask from the dropping funnel in an N_2 gas stream with stirring the mixture and maintaining its temperature at about $95^\circ C$. After completion of the dropwise addition, the reaction mixture was stirred at $95^\circ C$ 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 further stirred at $95^\circ C$ 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.

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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	-			

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Table 5 (cont'd)

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)		
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	-		

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Table 5 (cont'd)

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)	αMSD (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)	-	-			

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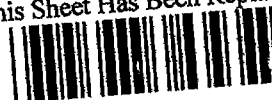
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As seen from Examples 3, 4, 6, 9 - 18 and 27 - 30, the copolymers obtained by using the unsaturated monomers represented by the formula (II) are soluble in solvents, especially aromatic solvents such as xylene and xylene/n-butyl (4/1), and suited for 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 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 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 properties of the obtained resins are shown in Table 6.

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Table 6

Comp. Prep. Ex. No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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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 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 liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 7.

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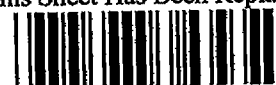
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Table 7

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

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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.

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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

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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 compositions 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.

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. 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 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 periodically. The results are shown in Table 9.

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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

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.

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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 months			
1	2	0	9	17	24
2	3	0	10	19	31

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 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 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 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

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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



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 resin of this invention is soluble in the aromatic solvents, it is very useful for preparing an excellent antifouling paint.

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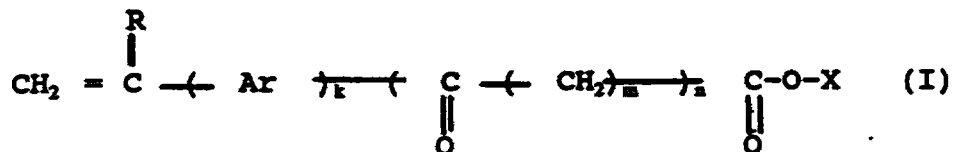


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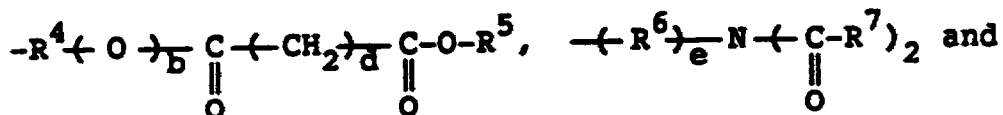
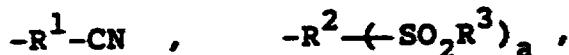
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CLAIMS

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



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:



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

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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.

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 $-R^2-(SO_2R^3)_n$.

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 1 to 5

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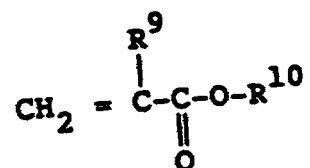


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1 to 5 further comprising as repeating units residues or one or more unsaturated monomer copolymerizable with the unsaturated monomer of the formula (I).

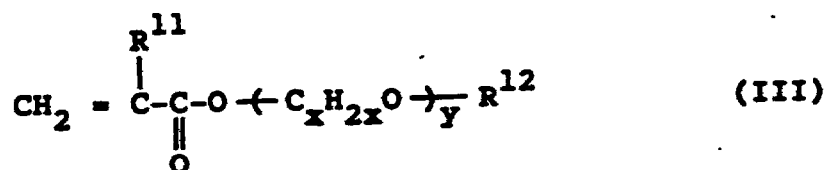
7. A coating resin according to claim 6 comprising as repeating units residues of a copolymerisable unsaturated monomer of formula (II)



wherein R^9 is hydrogen or methyl and R^{10} is branched or alicyclic alkyl, aryl or aralkyl optionally containing one or more hetero atoms and having 3 or more carbon atoms.

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

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)



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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.

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

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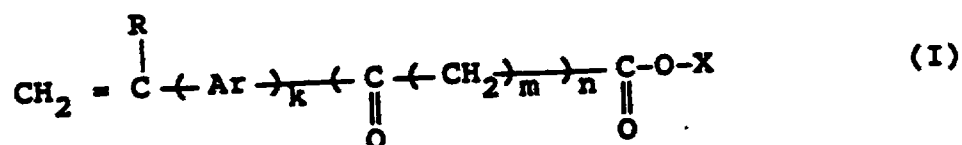
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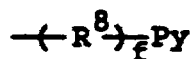
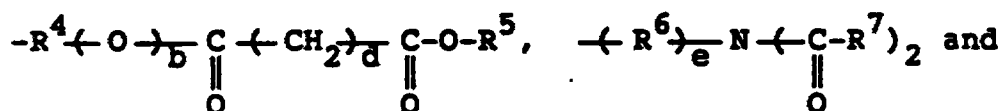
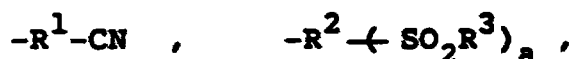
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ABSTRACTCOATING RESIN AND ANTIFOULING COATING COMPOSITION

A coating resin comprising a polymer obtained by polymerising an unsaturated monomer represented by the formula (I):



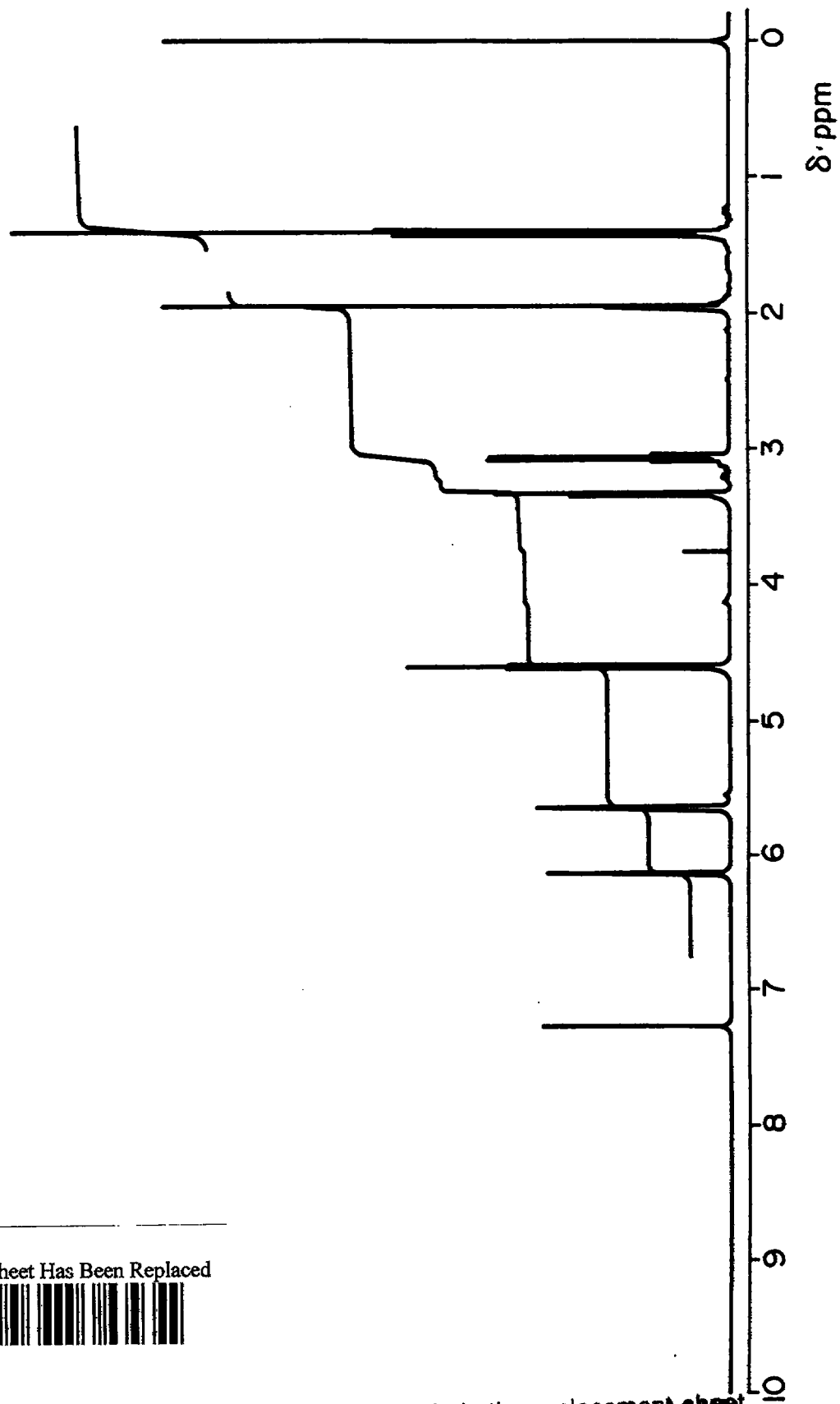
wherein R is H or an alkyl group, and X is selected from:



wherein R¹ to R⁸ represent independently a hydrocarbon group, etc., and Py is a pyridyl group, alone or together with one or more other unsaturated monomers may be used in antifouling coating compositions having no safety problems, good storage stability and excellent antifouling effect for a long period of time.



FIG. 1



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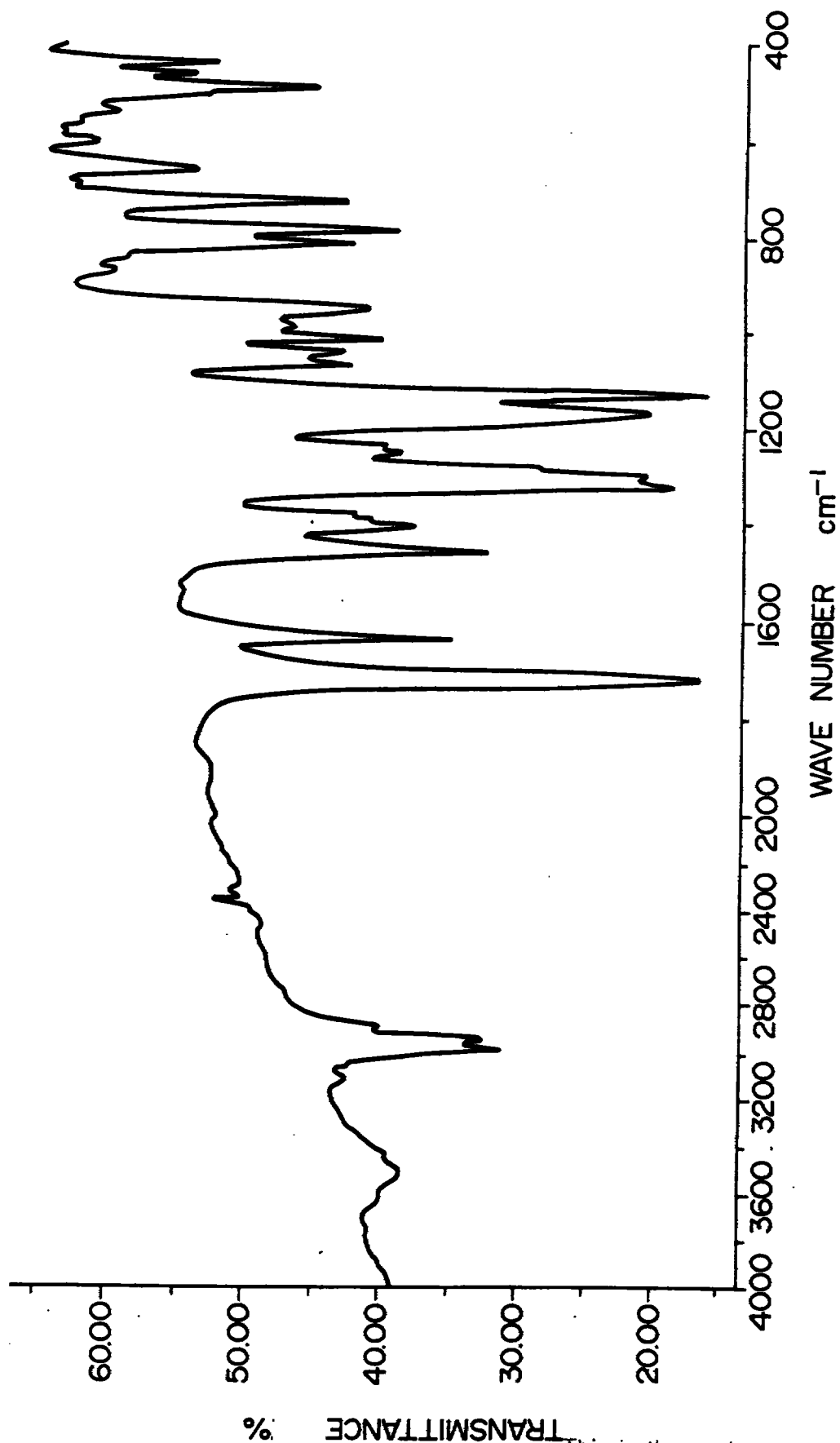


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FIG. 2



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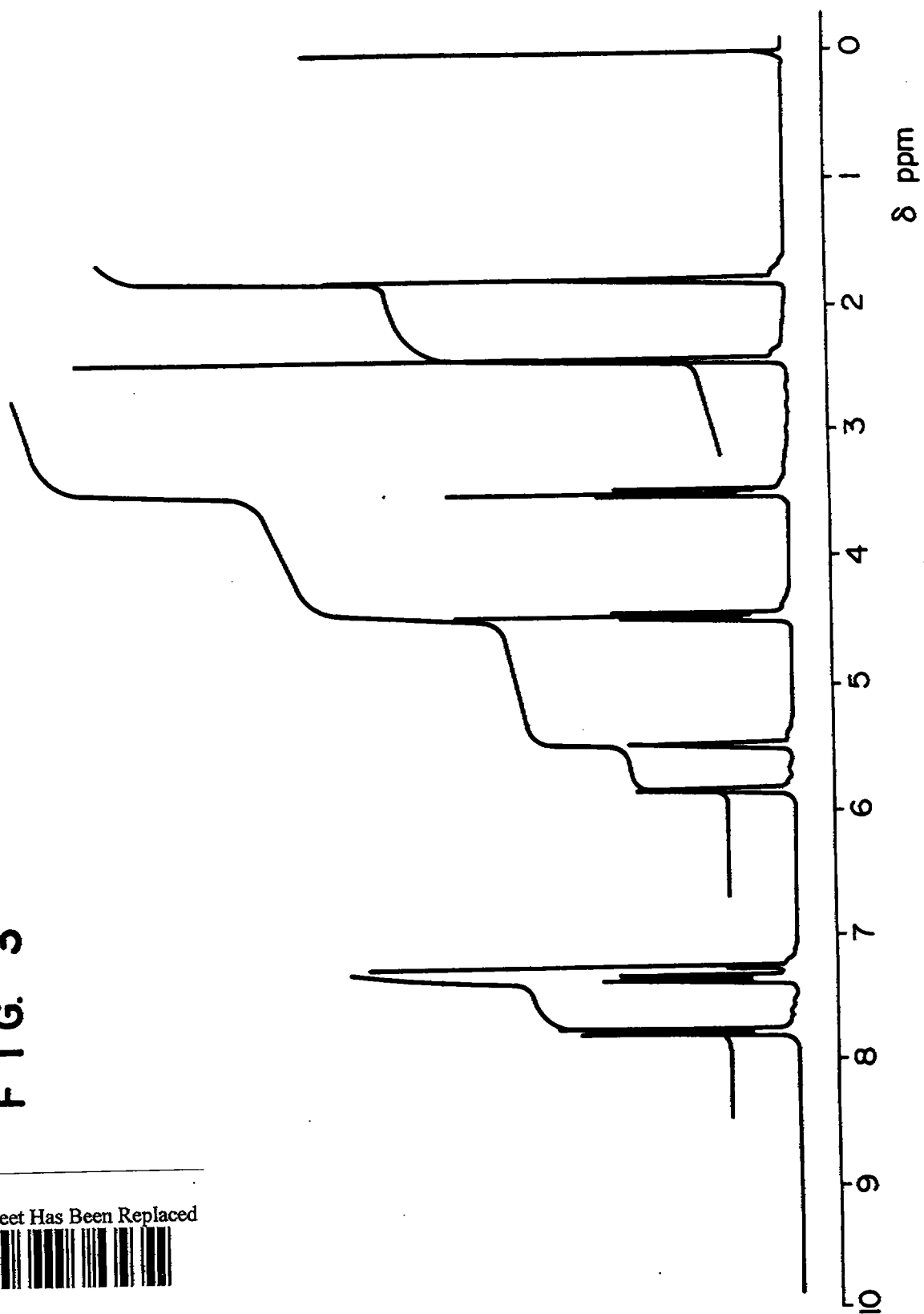
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FIG. 3

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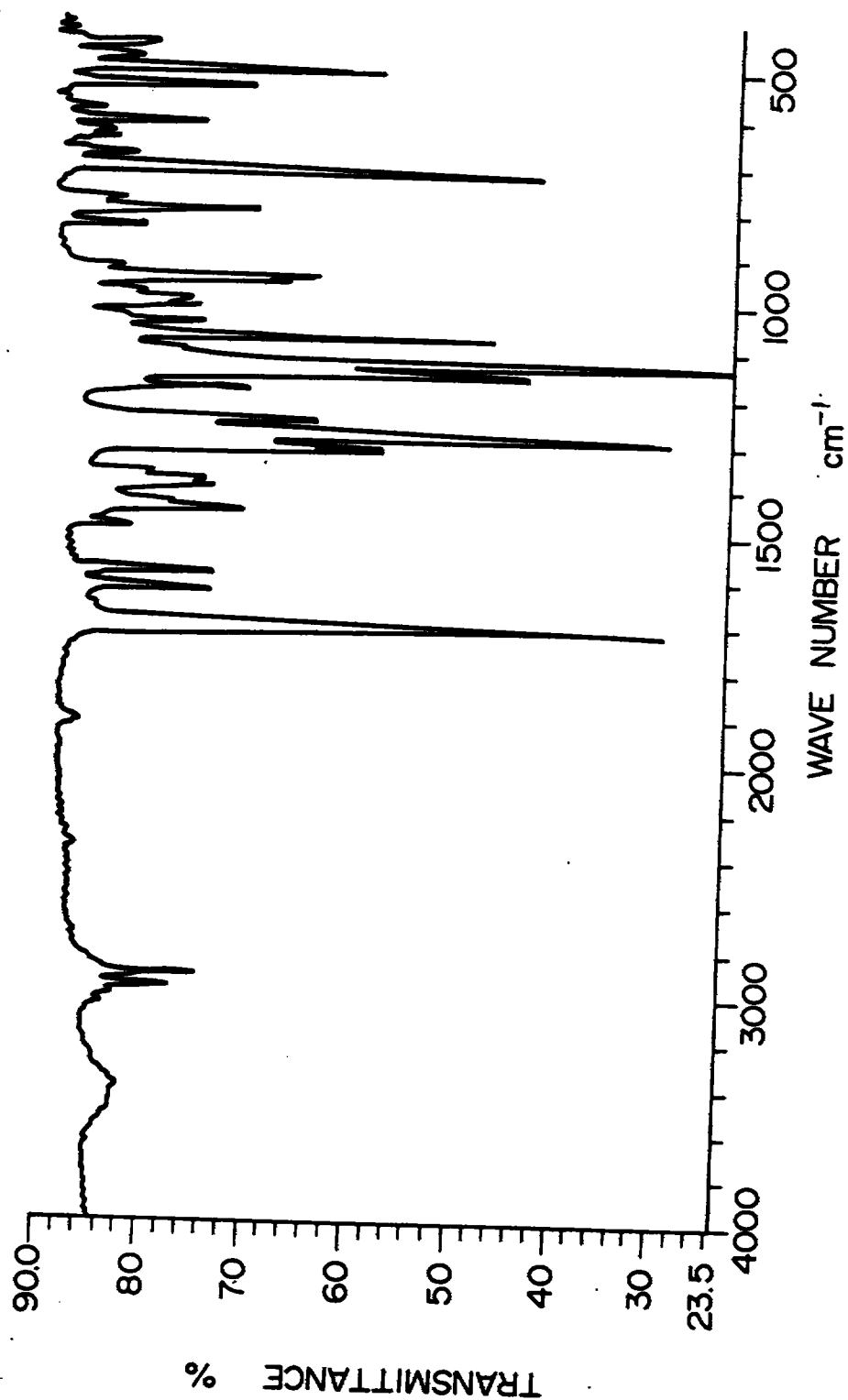
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FIG. 4



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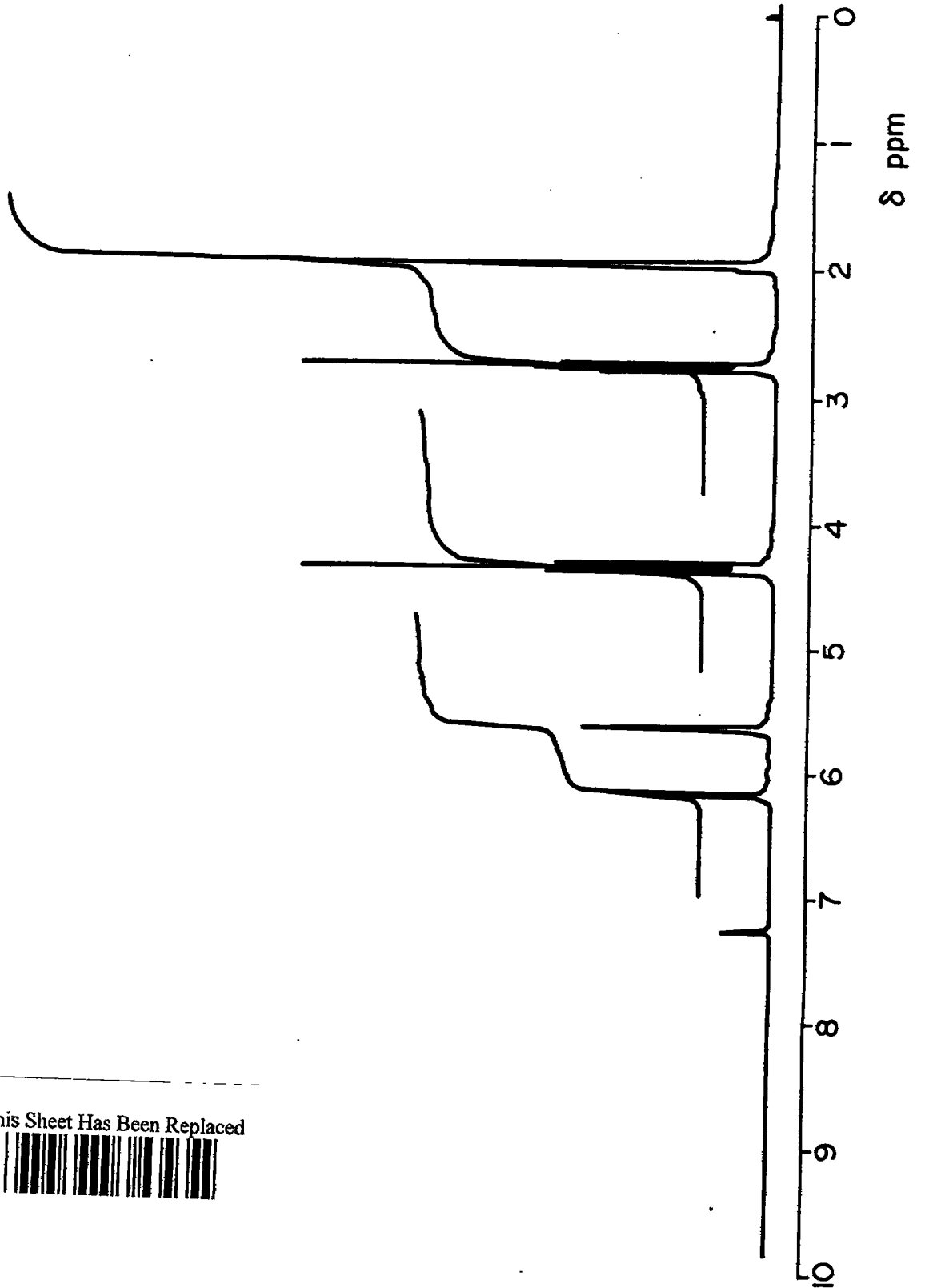


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FIG. 5



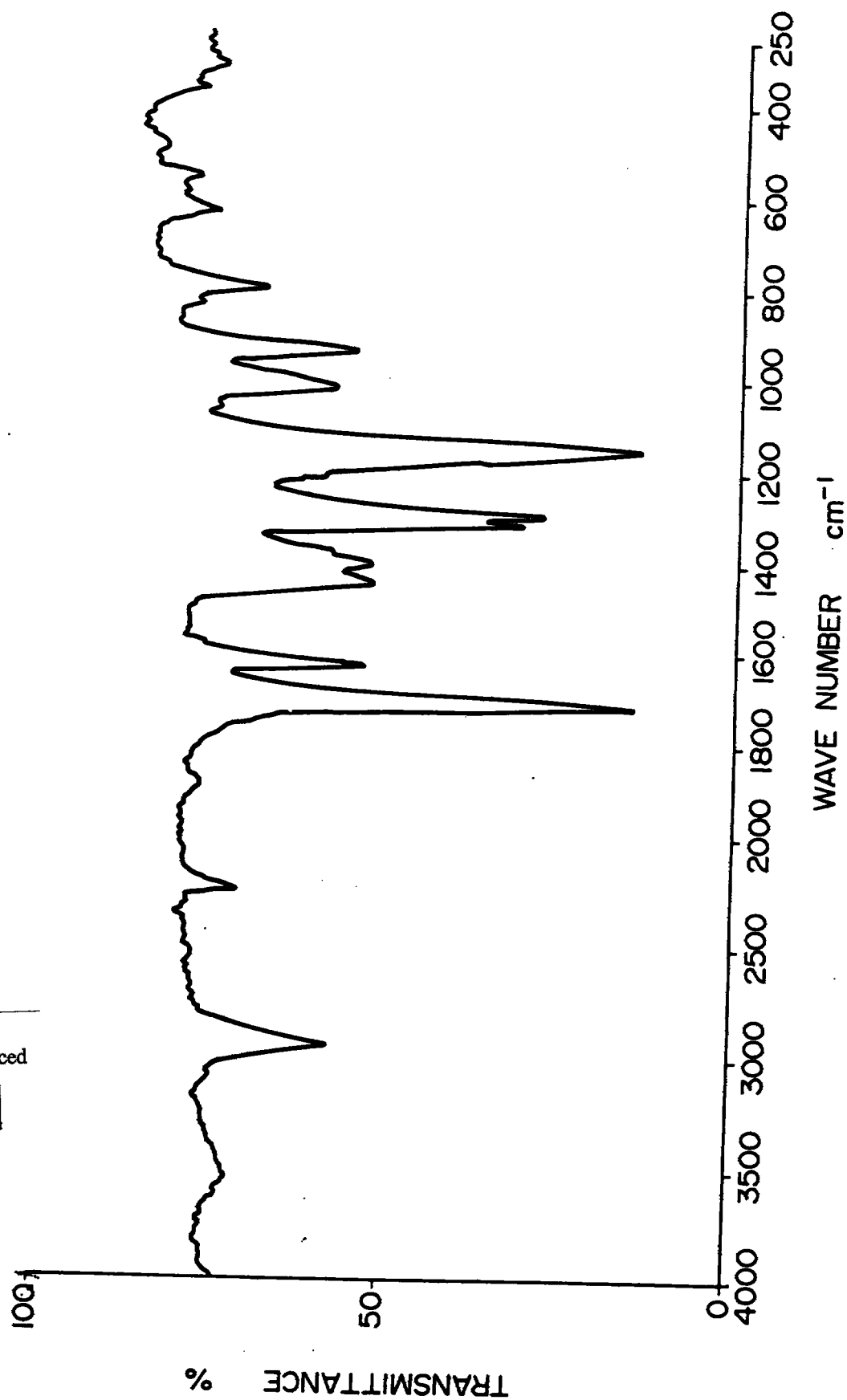
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FIG. 6



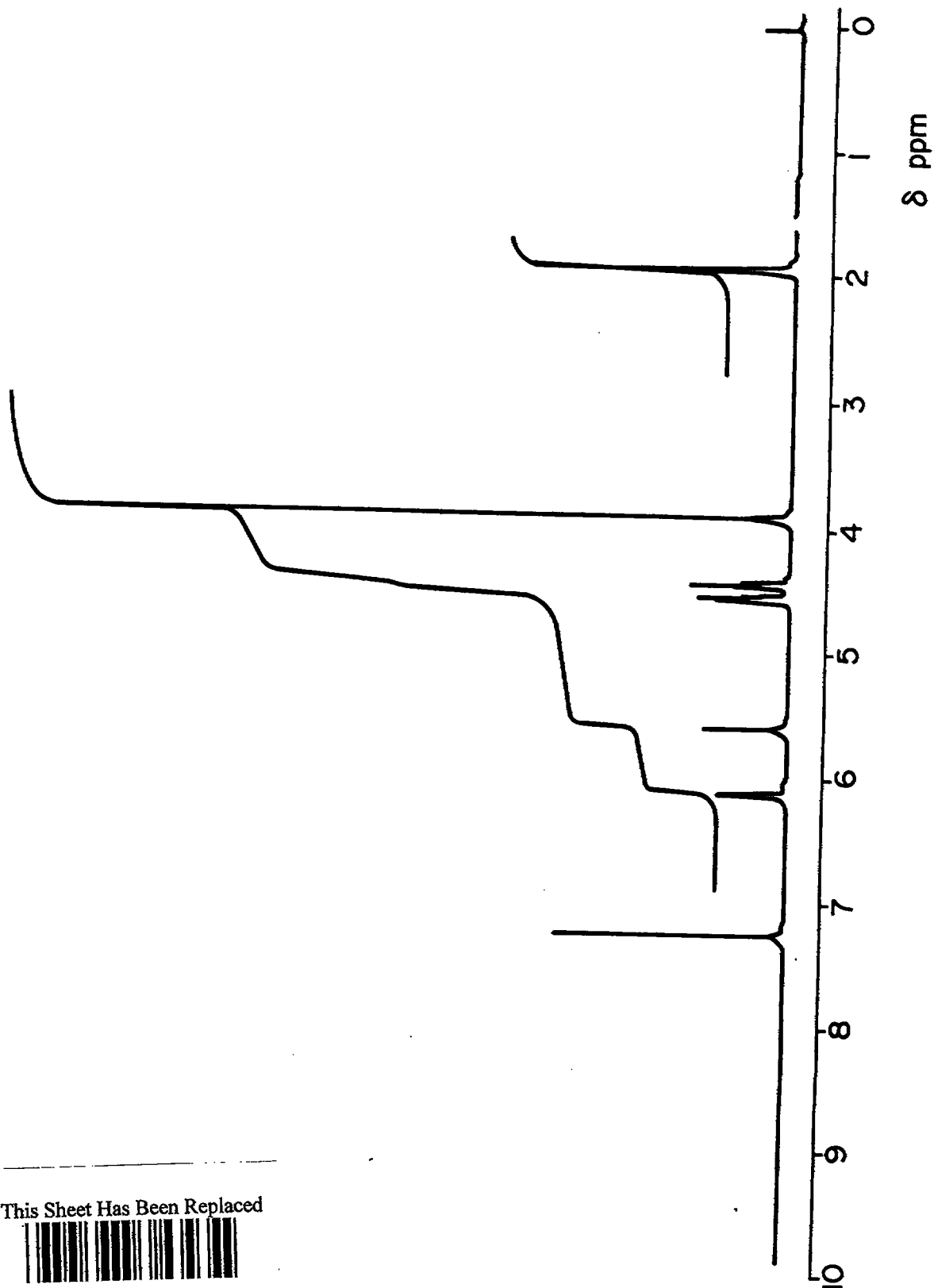
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FIG. 7



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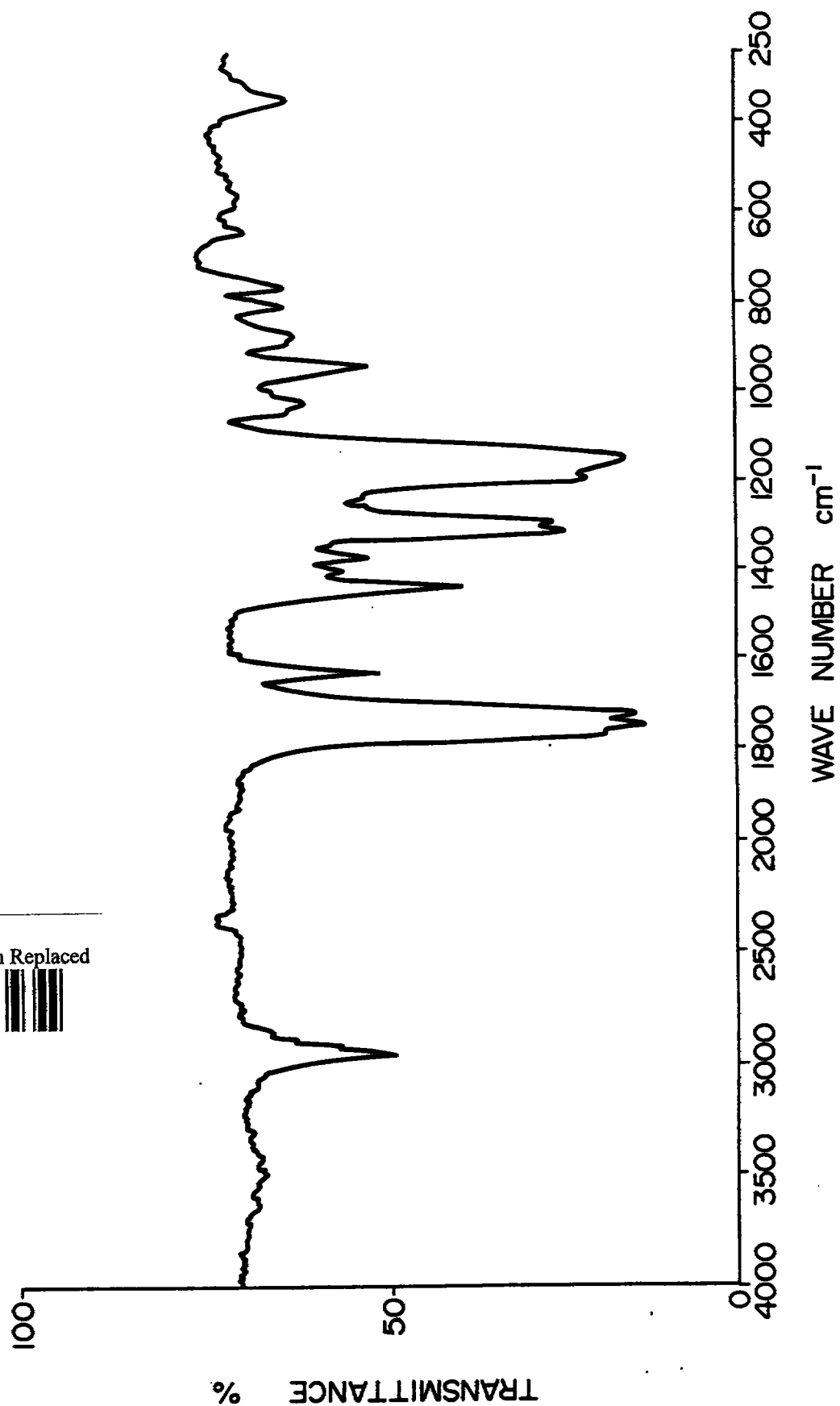
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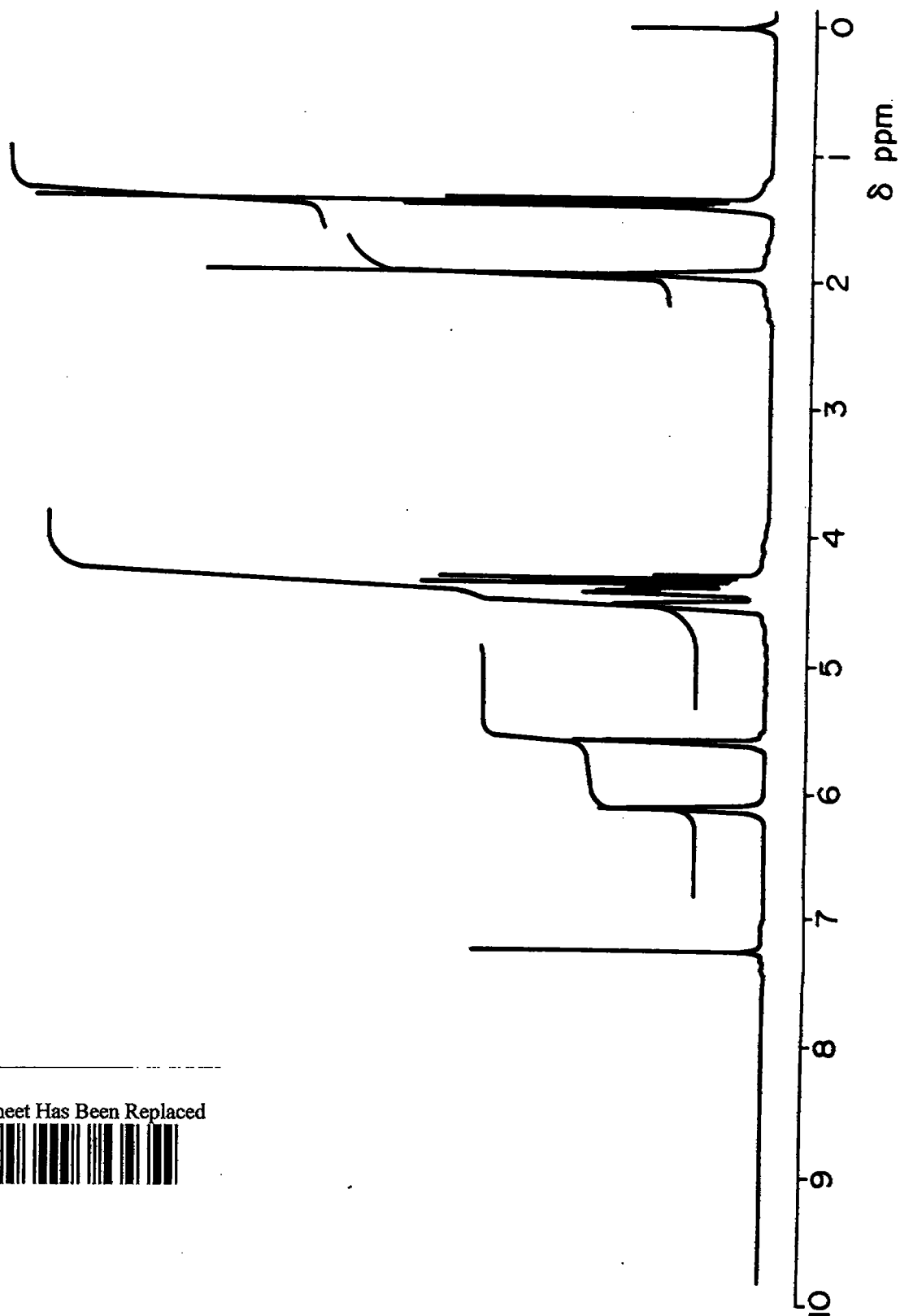
FIG. 8



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FIG. 9



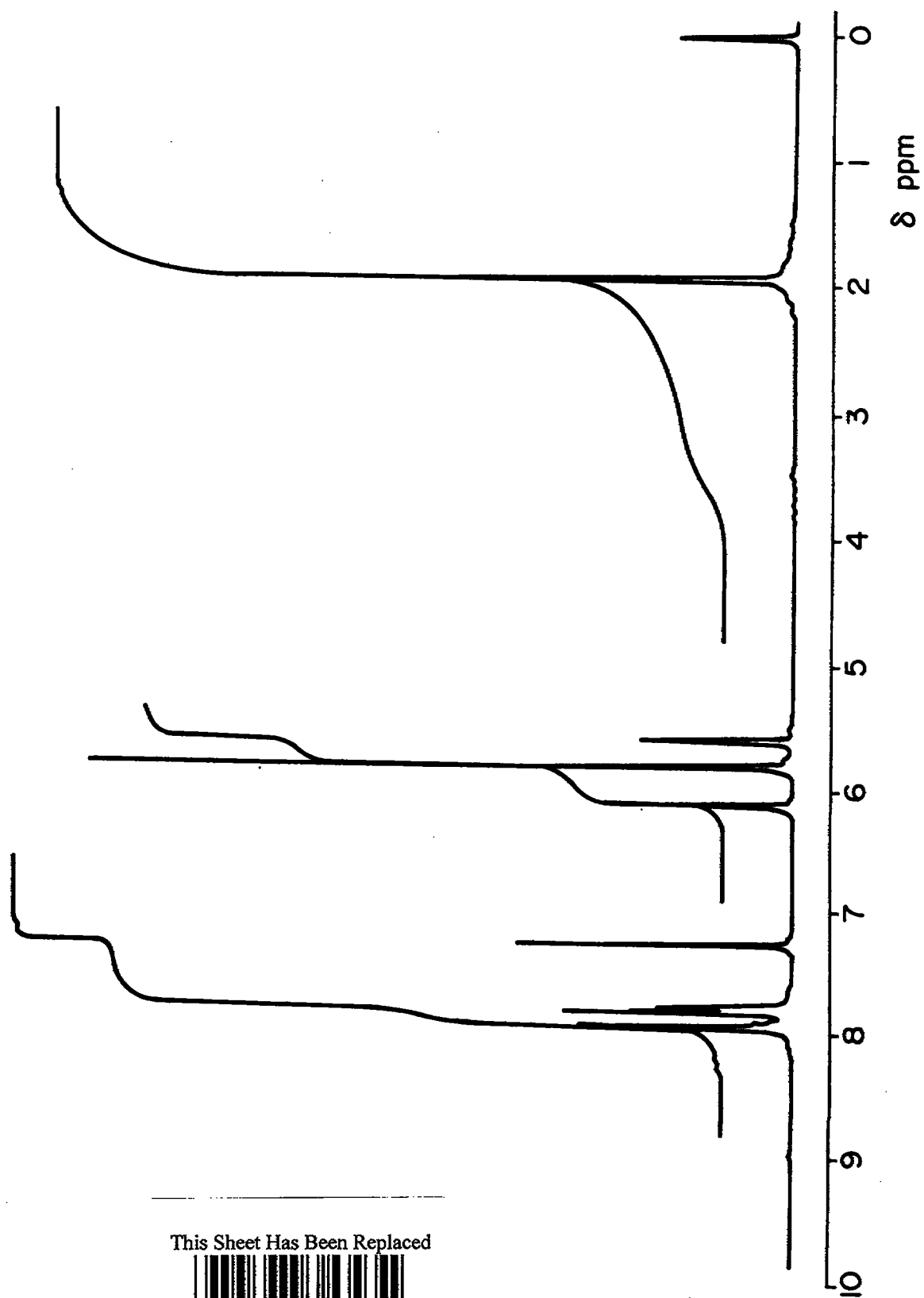
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FIG. 10



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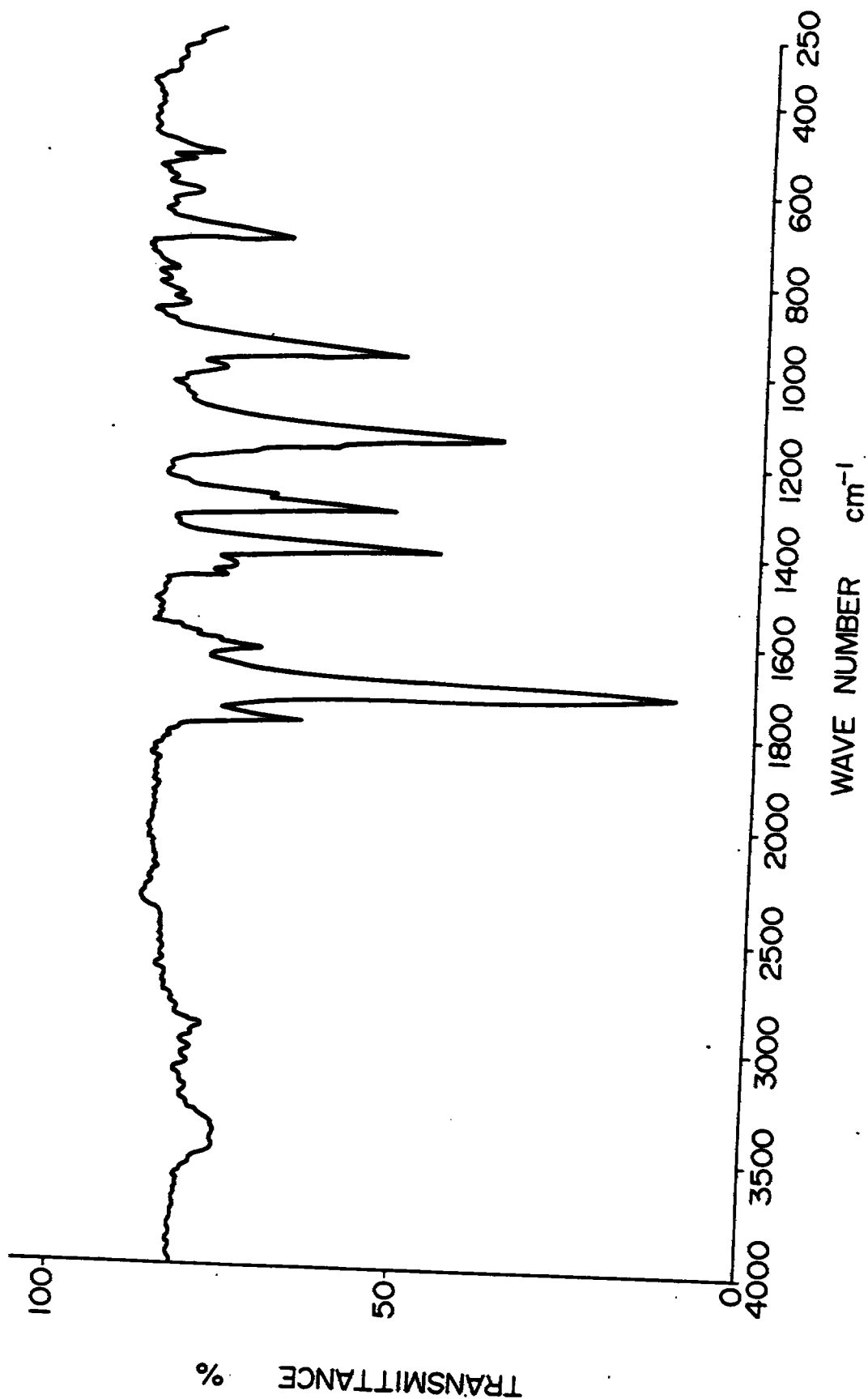


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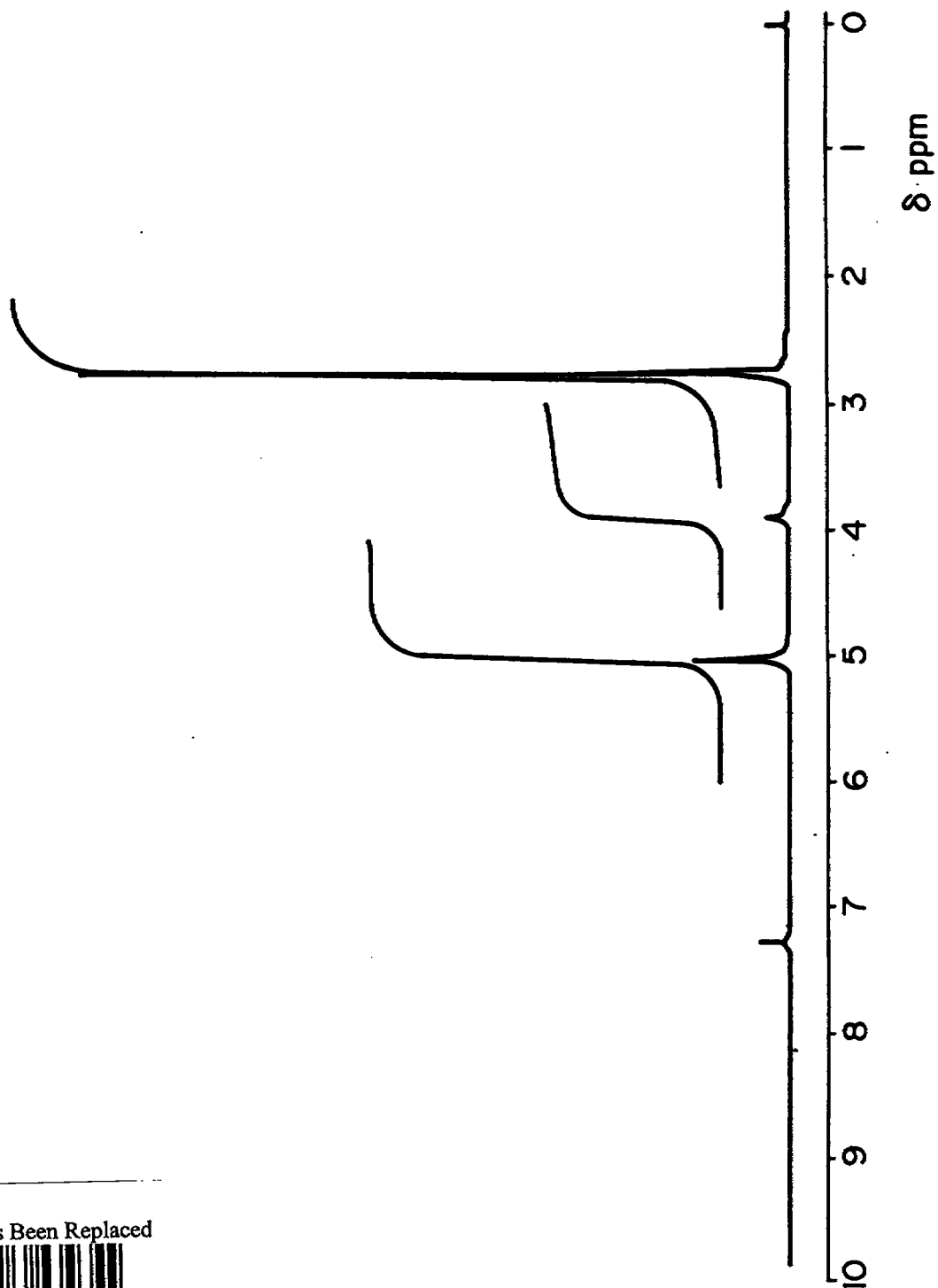
FIG. 11



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FIG. 12



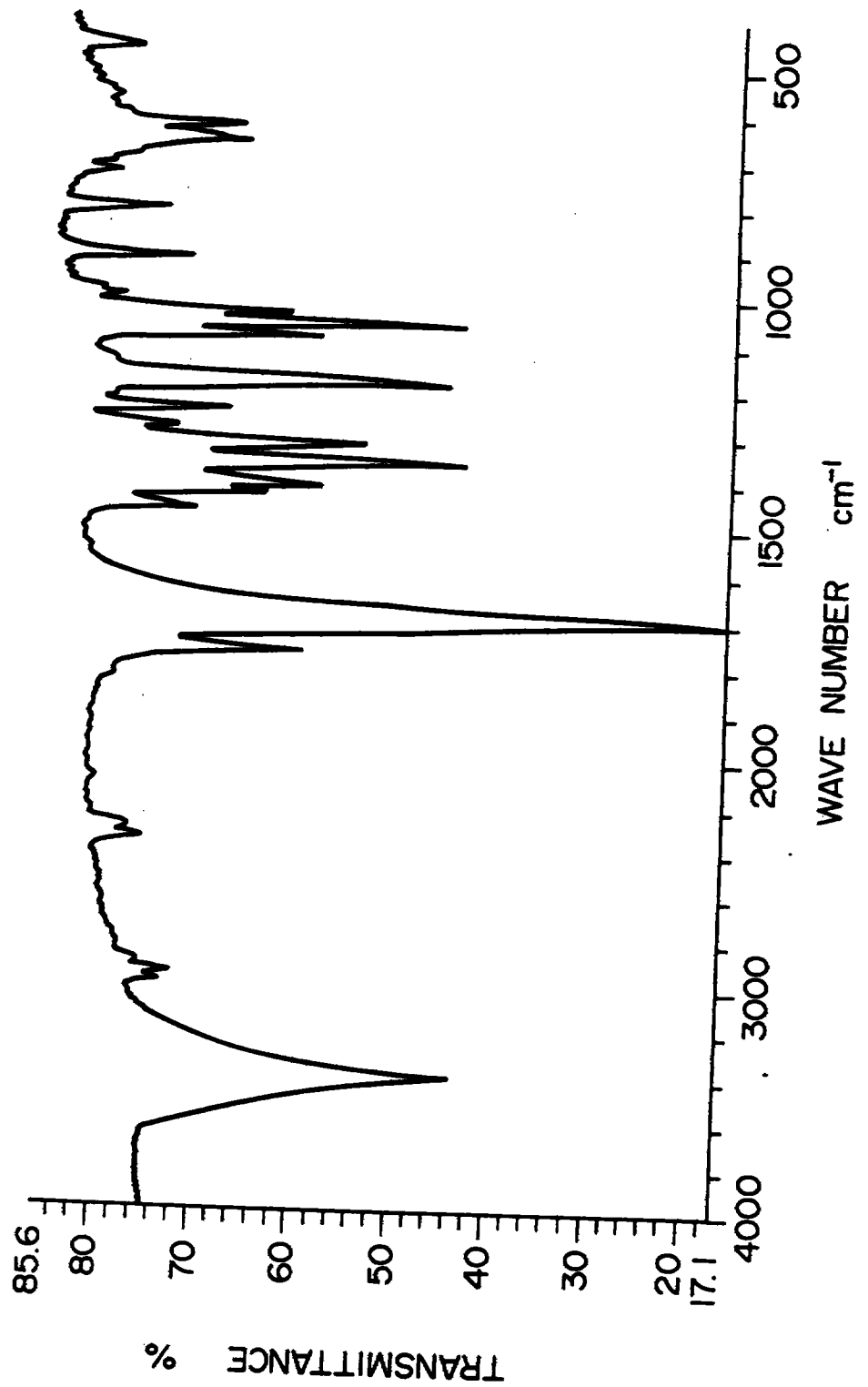
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FIG. 13



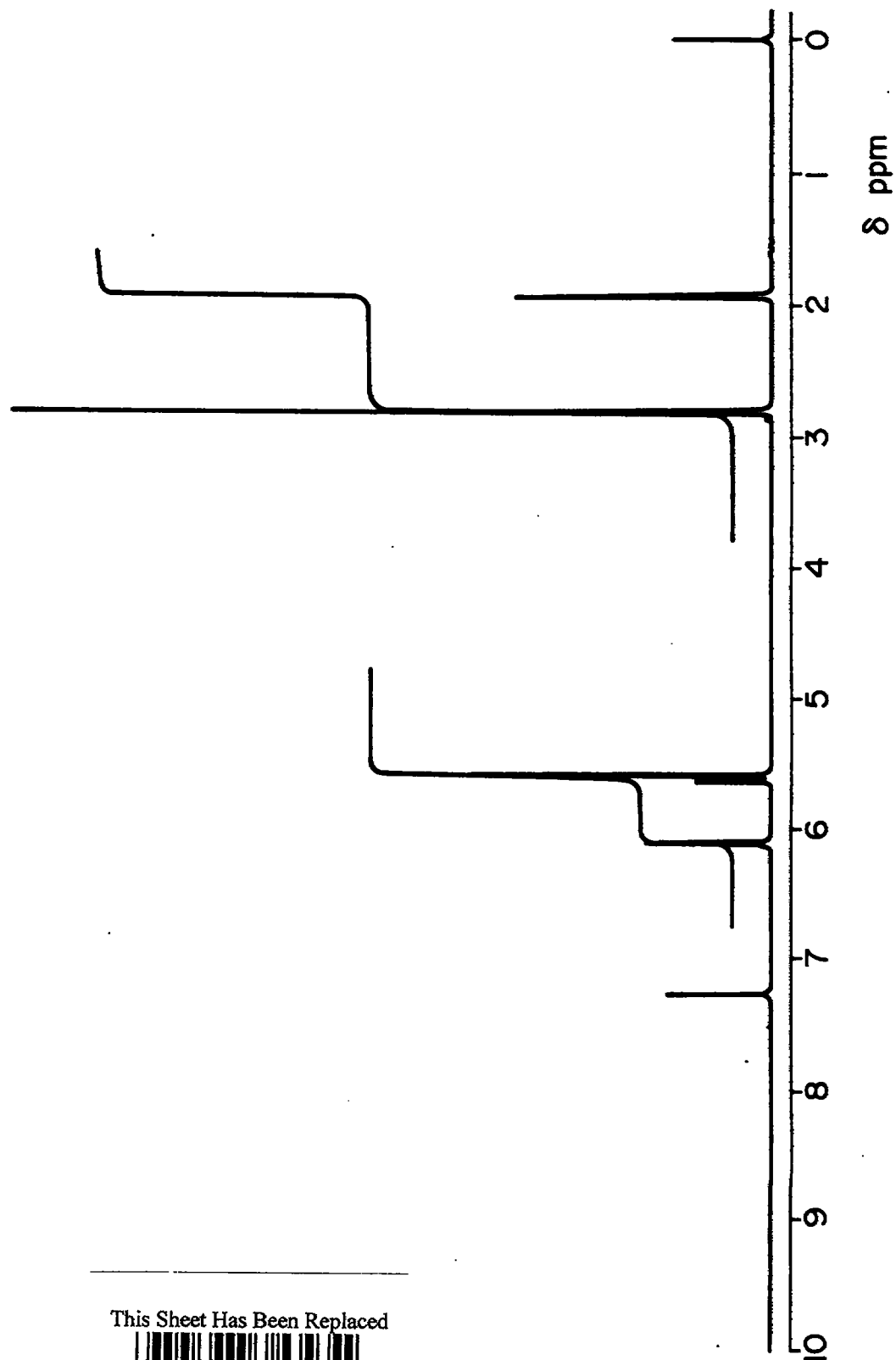
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FIG. 14



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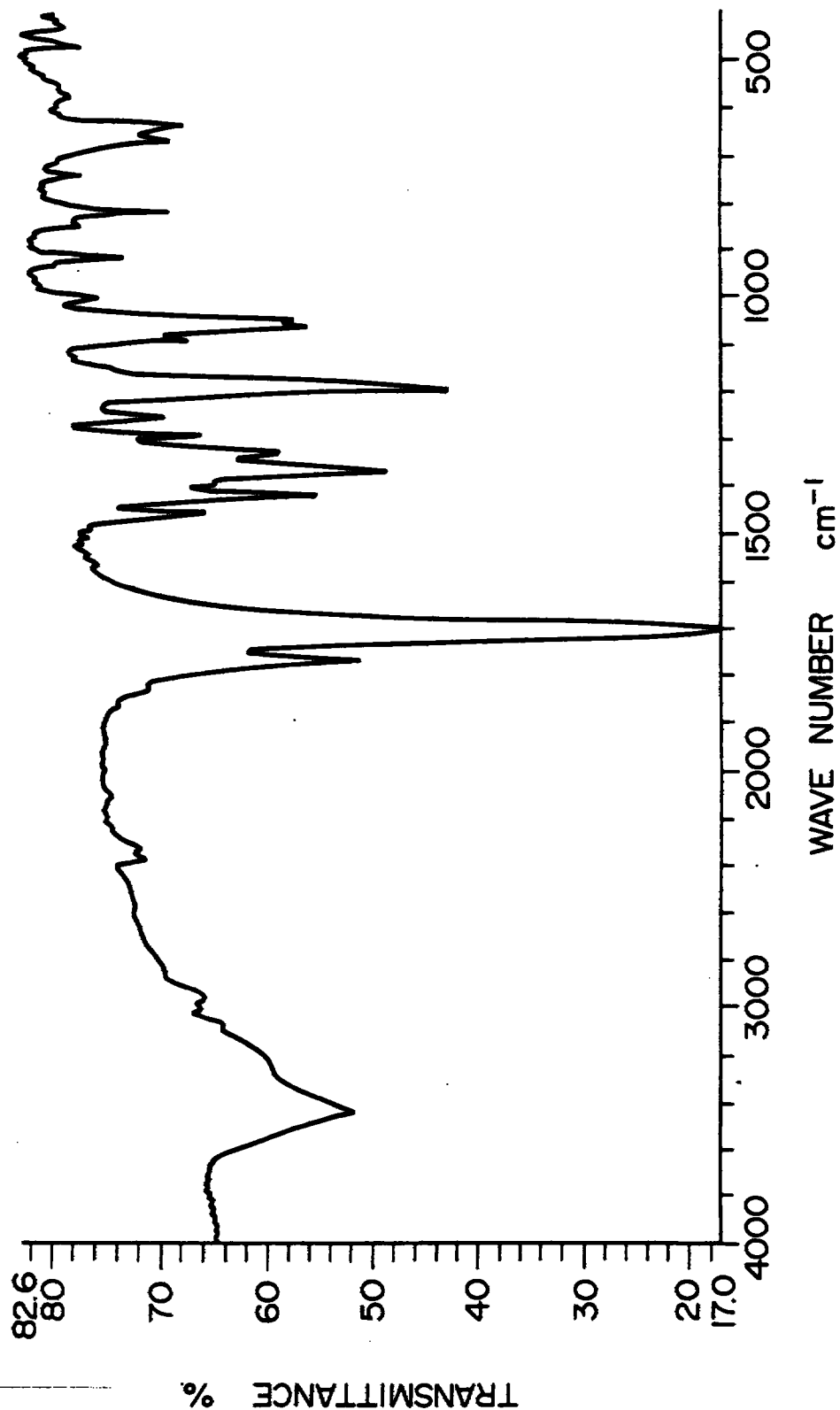


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FIG. 15



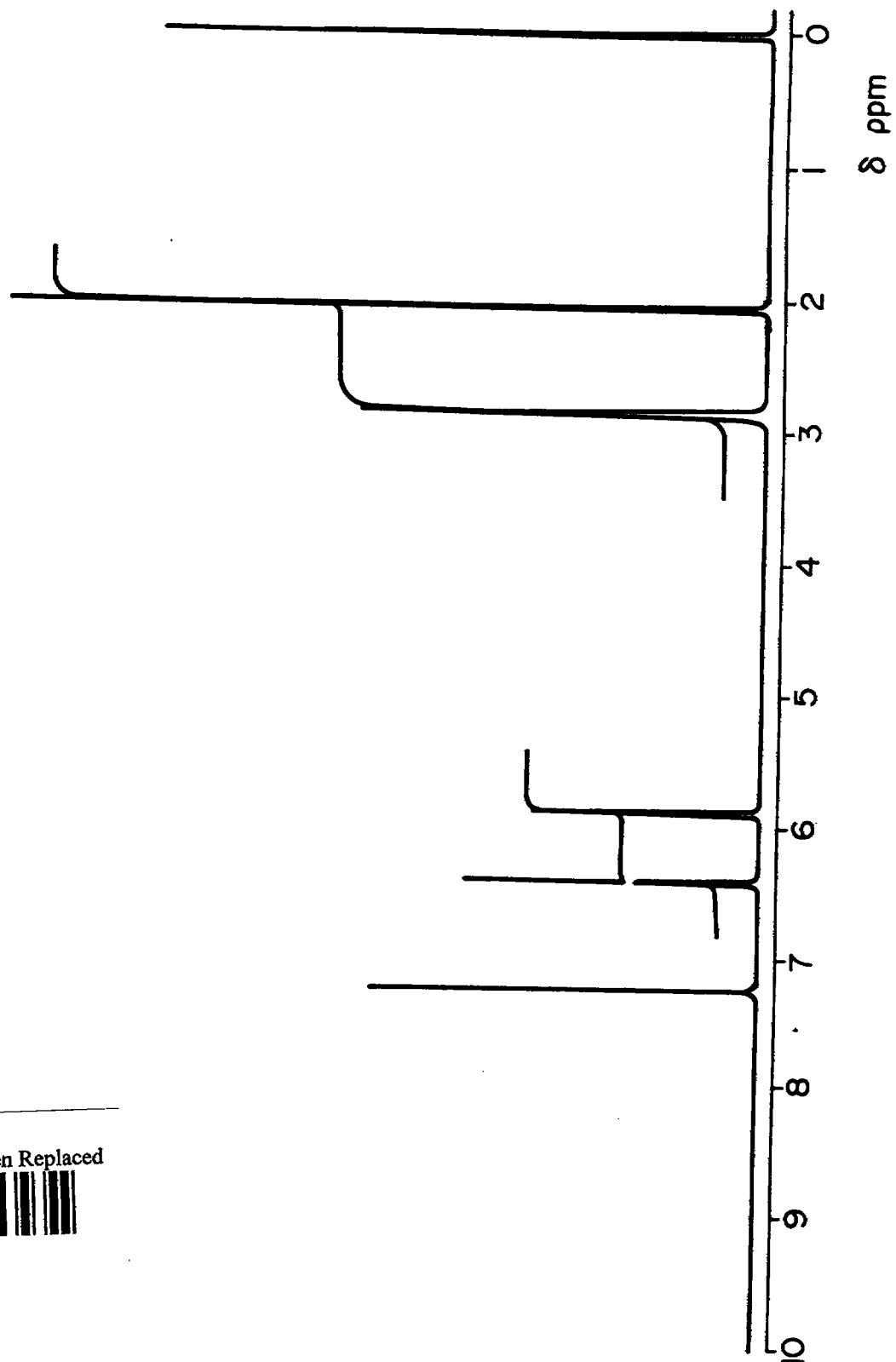
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FIG. 16



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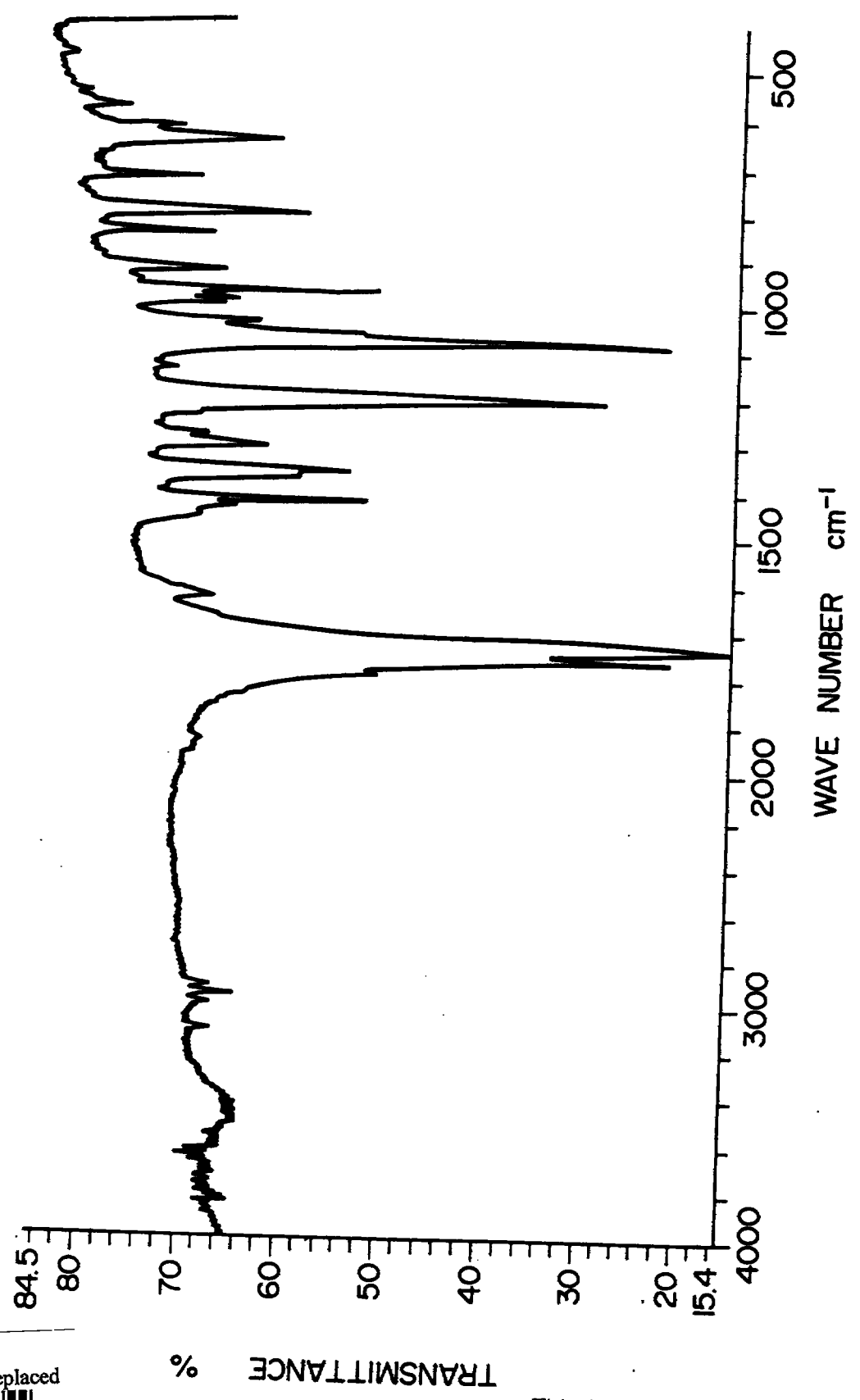


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FIG. 17



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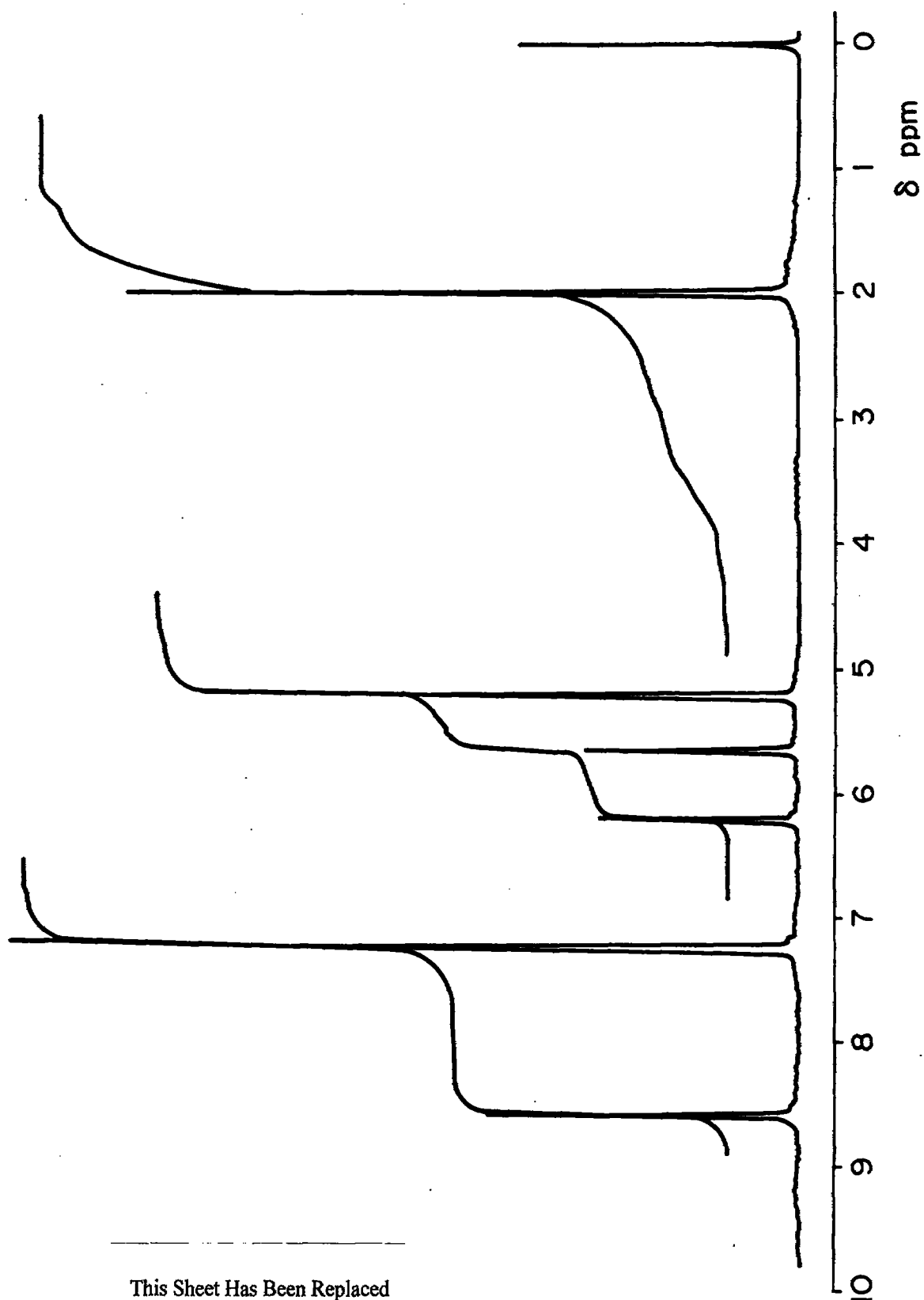


FIG. 18

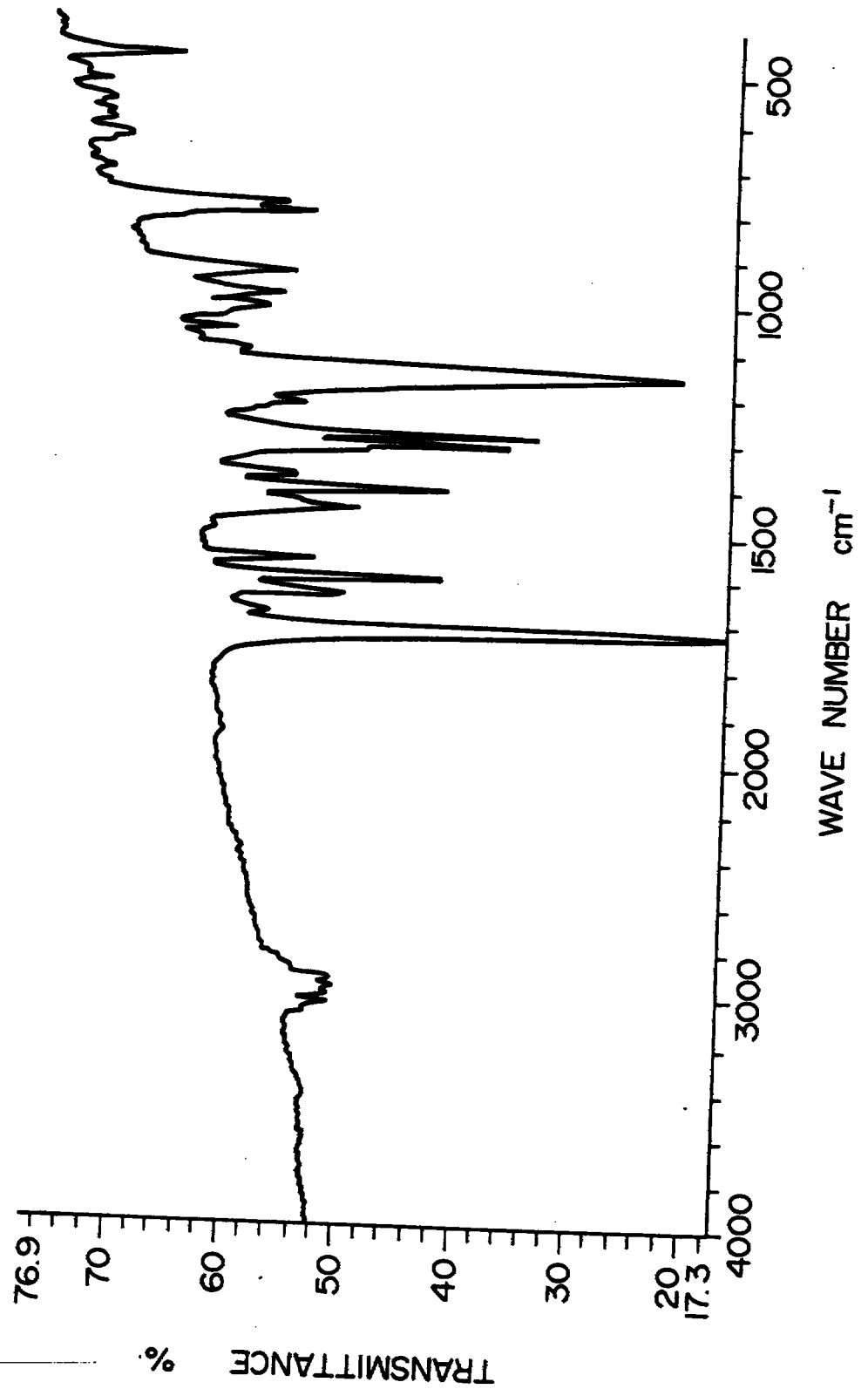
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FIG. 19



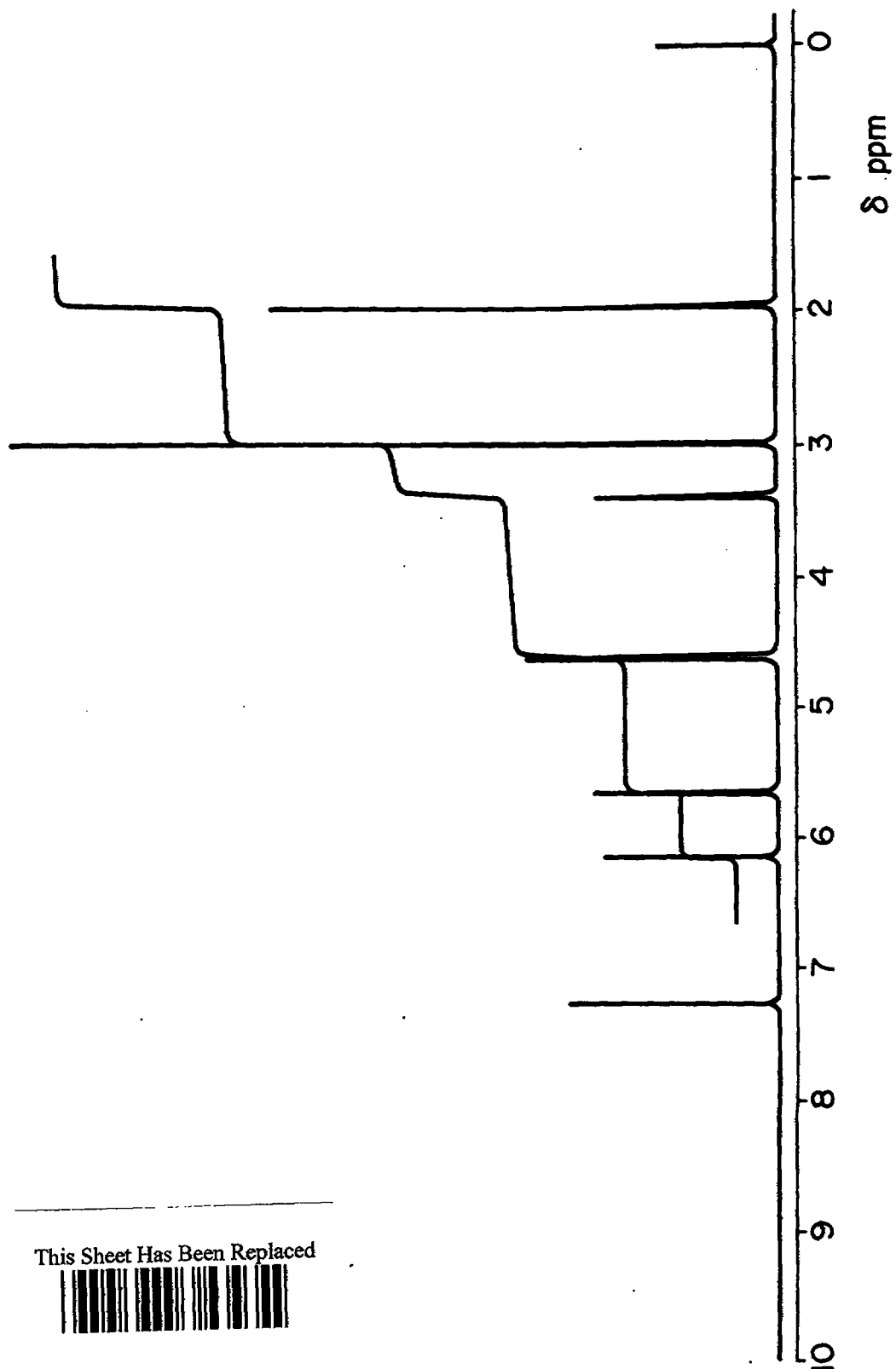
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FIG. 20



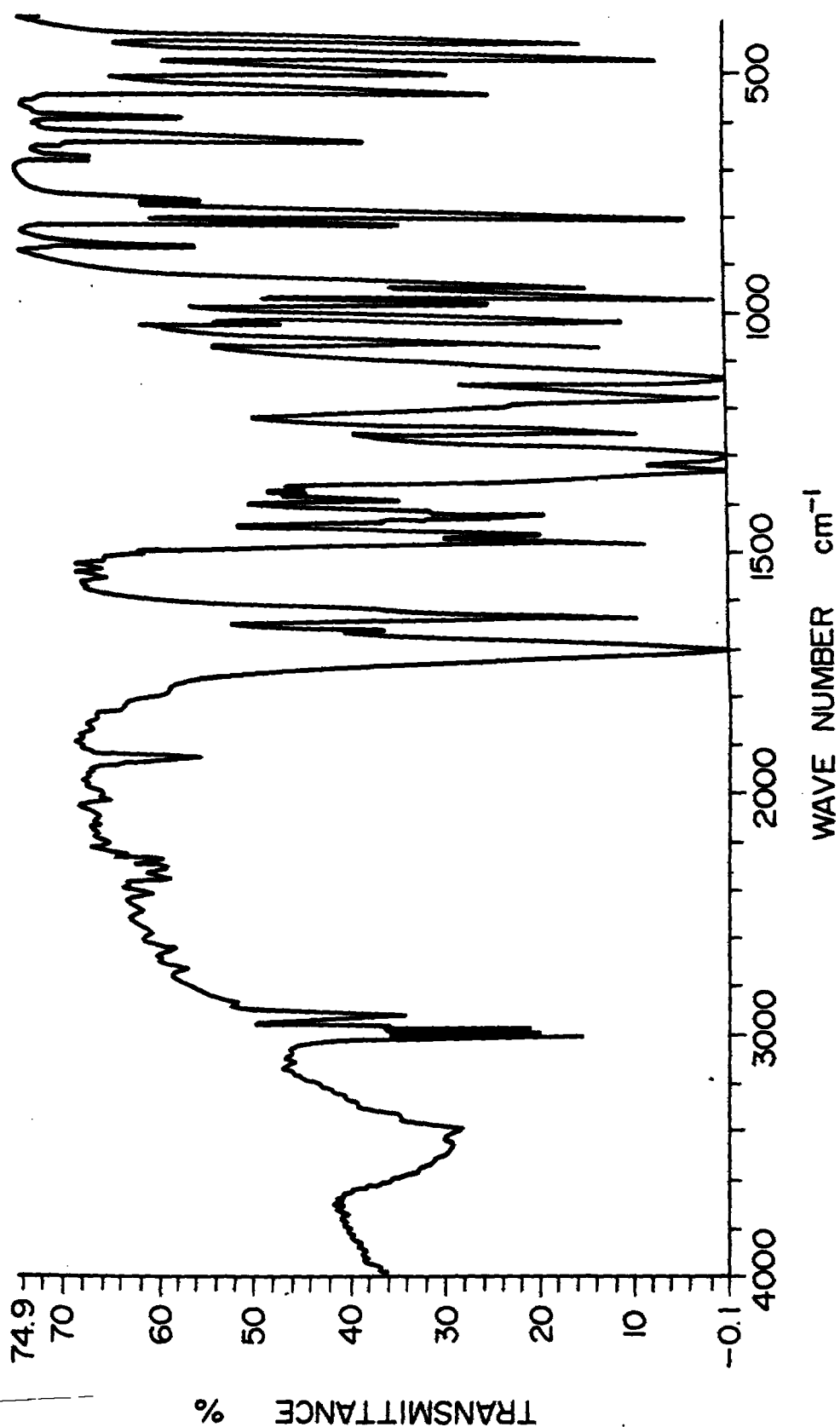
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FIG. 21

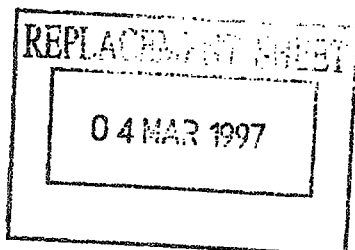


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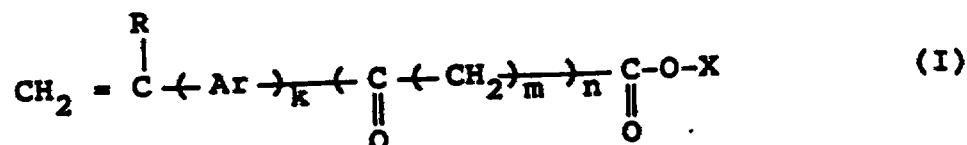
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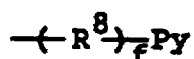
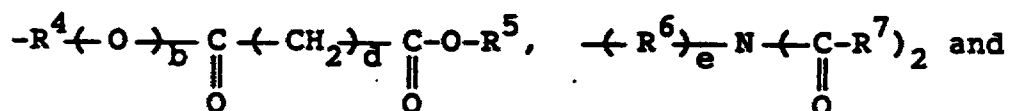
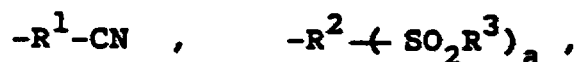
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ABSTRACTTHIS SHEET HAS BEEN
REPLACED**COATING RESIN AND ANTIFOULING COATING COMPOSITION**

A coating resin comprising a polymer obtained by polymerising an unsaturated monomer represented by the formula (I):



wherein R is H or an alkyl group, and X is selected from:



wherein R¹ to R⁵ represent independently a hydrocarbon group, etc., and Py is a pyridyl group, alone or together with one or more other unsaturated monomers may be used in antifouling coating compositions having no safety problems, good storage stability and excellent antifouling effect for a long period of time.

FIGURE 2

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REPLACEMENT SHEETS		SG
☒	Description	: paged 1..... to paged 48.....
☒	Claim(s)	: paged 69..... to paged 72.....
☐	Drawing(s)	: paged to paged
☒	Abstract	: paged 73..... to paged to
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REPLACEMENT SHEETS		SG
☒	Description	: paged 1..... to paged 48.....
☒	Claim(s)	: paged 69..... to paged 72.....
☐	Drawing(s)	: paged to paged
☒	Abstract	: paged 73..... to paged to
DATE OF RECEIPT 24/4/97		

COATING RESIN AND ANTIFOULING COATING

COMPOSITION

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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~~ underwater or submarine structures such as ships, fishing nets, drainage conduits, etc.

Numerous species of marine organisms, such as barnacle, ascidian, serpulula, mussel, laver, etc., live in the sea water. When a structure such as a ship, fishing net, drainage pipe, etc., is set or placed in ⁱⁿ commission 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 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 ^{economic} ~~encomical~~ problem. Also, if the marine 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 the marine organisms to ~~the~~ underwater structures such

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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. 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 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 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 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 antifouling effect, in place of the organotin-based resins 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

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water-repellent resins have also been made (Japanese Patent Application Kokai (Laid-Open) Nos. 62-290768, 62-13471, 58-180565, 57-67672) ~~etc.~~. However, it is hardly possible to realize a long-lasting stabilized 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 Patent Appln. Kokai Nos. 2-69576, 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 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 will not affect the undercoat when coating is performed.

SUMMARY OF THE INVENTION

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

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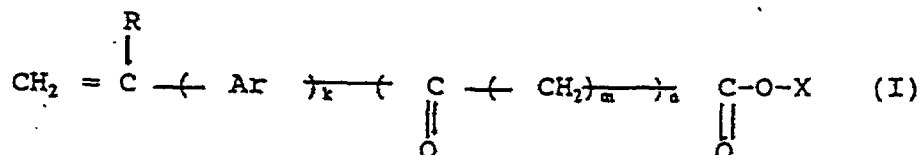
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antifouling coat. This coating resin is also soluble in aromatic solvents.

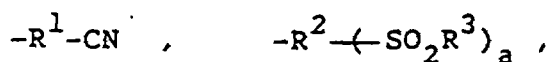
The present inventors have pursued strenuous studies for solving said prior art problems and developing an antifouling coating composition which performs excellently for preventing attachment of the marine organisms to the underwater structures such as mentioned above and has no problem in safety and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

The present invention provides an antifouling coating composition comprising:

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



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:

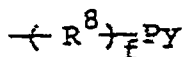
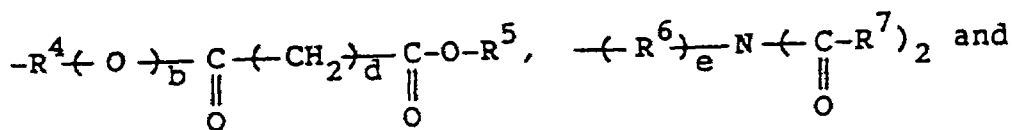


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wherein R^1 , R^4 , R^6 and R^8 are each a straight, branched or alicyclic alkylene group having 1 to 6 carbon atoms; R^2 is a straight, branched or cyclic hydrocarbon group having 1 to 6 carbon atoms and connecting O and SO_2R^3 ; a is an integer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

(b) an antifouling agent.

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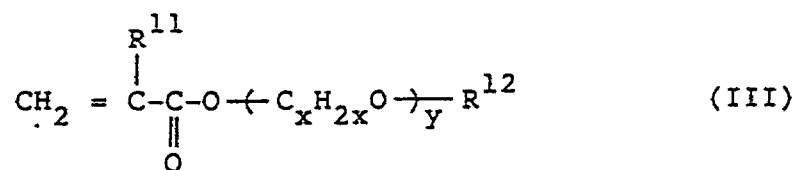


The present invention also provides a coating composition of the type recited, wherein the coating resin further comprises as repeating units residues of a copolymerizable unsaturated monomer of formula:



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.

The present invention also provides a coating composition of the type recited, wherein the coating resin further comprises as repeating units residues of a copolymerizable unsaturated monomer having a hydrophilic functional group. Said monomer may be either an unsaturated acid anhydride or an unsaturated monomer of the formula:



wherein R¹¹ is hydrogen or methyl; x is an integer of 1 to 6; y is an integer of 1 to 10; and R¹² is a hydrogen or a straight, branched or cyclic alkyl, aryl or aralkyl group.

The present invention also provides the use of a coating resin as defined above in an antifouling coating composition.

~~The present invention further provides an
antifouling coating composition comprising said coating
resin.~~

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ^1H -NMR spectrum of Compound No. 10 ($\text{R} = \text{CH}_3$) in the list, given below, of the preferred examples of the unsaturated monomers represented by the formula (I).

Fig. 2 is an IR spectrum of Compound No. 10 ($\text{R} = \text{CH}_3$).

Fig. 3 is a ^1H -NMR spectrum of Compound No. 12 ($\text{R} = \text{CH}_3$).

Fig. 4 is an IR spectrum of Compound No. 12 ($\text{R} = \text{CH}_3$).

Fig. 5 is a ^1H -NMR spectrum of Compound No. 2 ($\text{R} = \text{CH}_3$).

Fig. 6 is an IR spectrum of Compound No. 2 ($\text{R} = \text{CH}_3$).

Fig. 7 is a ^1H -NMR spectrum of Compound No. 18 ($\text{R} = \text{CH}_3$).

Fig. 8 is an IR spectrum of Compound No. 18 ($\text{R} = \text{CH}_3$).

Fig. 9 is a ^1H -NMR spectrum of Compound No. 19 ($\text{R} = \text{CH}_3$).

Fig. 10 is a ^1H -NMR spectrum of Compound No. 20 ($\text{R} = \text{CH}_3$).

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

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

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
(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).

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.
9 (R = CH₃).

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

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The coating resins used in the present invention are preferably those specified below (1) - (9):

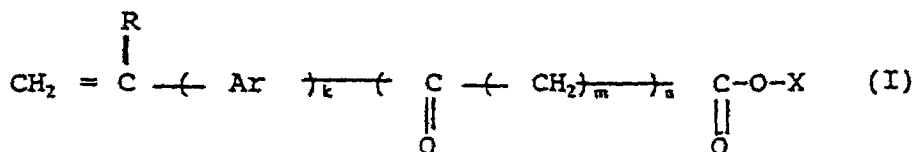
- (1) A coating resin comprising a polymer comprising, as repeating units, the residues of an unsaturated monomer or formula
(I)

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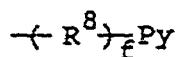
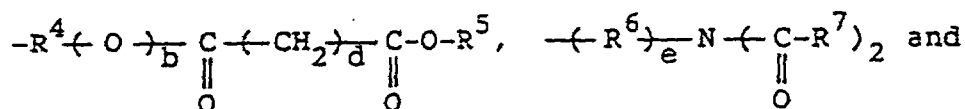


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wherein R is hydrogen or a straight or branched alkyl group having 1 to 4 carbon atoms; Ar is a benzene ring or naphthalene ring; k, m and n represent independently a number of 0 or 1; and X is a substituent selected from the groups:



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 groups R³ 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,

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at least two of the groups R^j may together form a hydrocarbon cyclic structure with each other and R^i ; b, d, e and f are each a number of 0 or 1; R^j is a straight or branched alkyl group having 1-4 carbon atoms; the groups R^i 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^i 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 specified in (1) above wherein k and n are 0.
- (3) A coating resin specified in (1) or (2) above wherein X is $-R^1-CN$.
- (4) A coating resin specified in (1) or (2) above wherein X is $-R^2-(SO_2R^3)_a$.
- (5) A coating resin specified in (1), (2), (3) or (4) above wherein R is H or CH_3 .
- (6) A coating resin specified in (1), (2), (3), (4) or (5) above further comprising as repeating units residues of one or more unsaturated monomer copolymerizable with the unsaturated monomer of the formula (I).
- (7) A coating resin specified in (6) above comprising as repeating units residues of a copolymerizable unsaturated monomer of formula (II):



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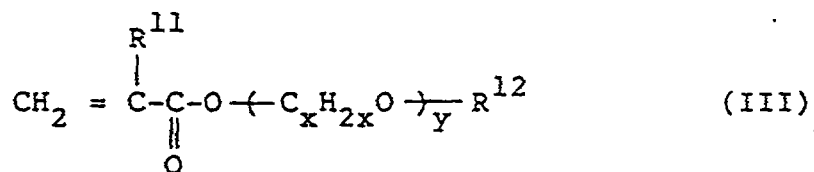
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wherein R^9 is hydrogen or methyl and R^{10} is branched or alicyclic alkyl, aryl or aralkyl optionally containing one or more hetero atoms and having 3 or more carbon atoms.

(8) A coating resin specified in (6) above comprising as repeating units the residues of a copolymerizable unsaturated monomer having a hydrophilic functional group.

(9) A coating resin specified in (8) above wherein the unsaturated monomer having a hydrophilic functional group is a monomer of formula (III):



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wherein R^{11} is ~~a~~ hydrogen atom or a ^{methyl} ~~CH₃ 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.

~~(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 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, ^{and} tert-butyl, etc. 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-cyclopentylene, 1,3-cyclopentylene, 1,2-cyclohexylene, 1,3-cyclohexylene, ^{and} 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, cyclobutyl, 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,

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tert-tetradecyl, hexadecyl, tert-hexadecyl, octadecyl, tert-octadecyl, ^{and} eicosyl, docodyl ~~etc.~~. The C_{6-10} aryl groups or C_{7-18} aralkyl groups which may have a substituent include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, sulfonylphenyl, acylphenyl, naphthyl, benzyl, phenethyl, ^{and} 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, ^{and} tetramethylene ~~etc.~~. The C_{1-4} straight or branched alkyl groups represented by R^5 include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, ^{and} tert-butyl ~~etc.~~. The C_{1-22} straight, branched or alicyclic alkyl groups represented by R^7 include methyl, ethyl, 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, ^{and} docosyl ~~etc.~~. The C_{6-10} aryl groups or C_{7-10} aralkyl groups represented by R^7 include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, naphthyl, benzyl, phenethyl, ^{and} benzhydryl ~~etc.~~. The groups forming a cyclic structure, represented by two R^7 , include methylene, ethylene, trimethylene, o-phenylene, 1,2-naphthylene, ^{and} 2,3-naphthylene ~~etc.~~

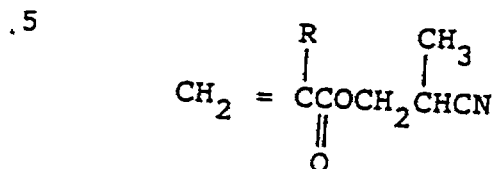
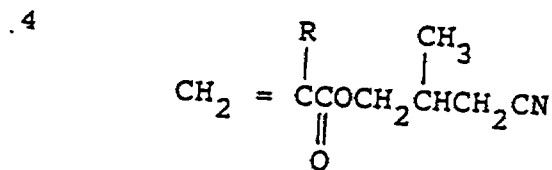
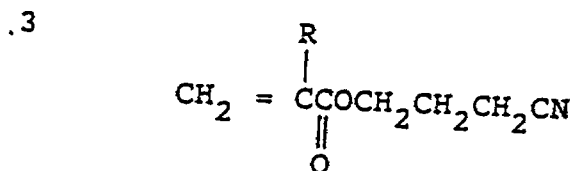
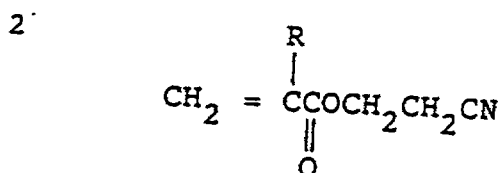
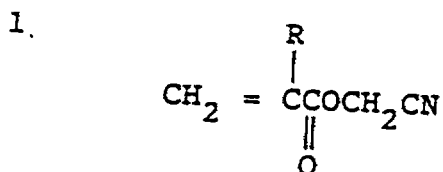
The unsaturated monomers represented by the formula (I) can be produced by various known processes of synthesis. It is possible to use the pertinent

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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):



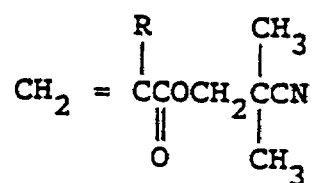
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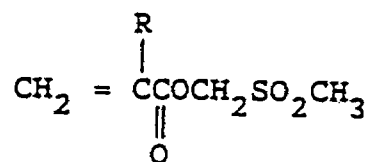
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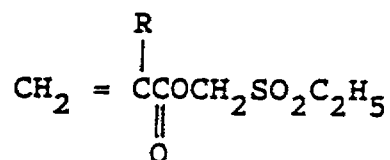
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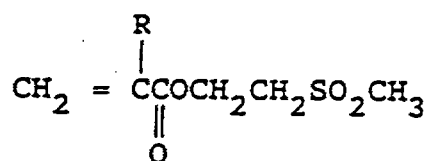
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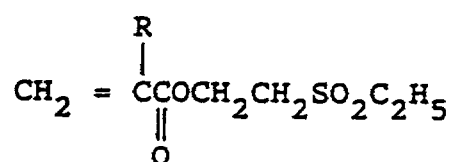
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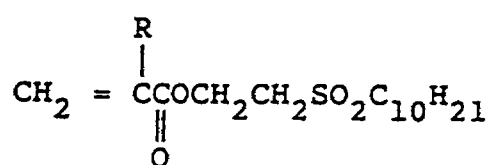
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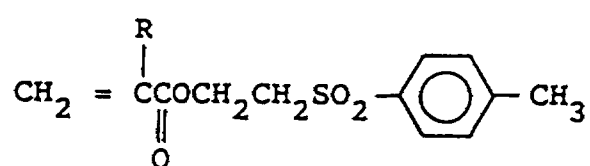
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12.



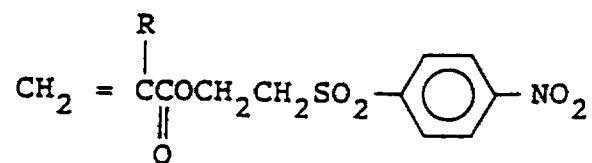
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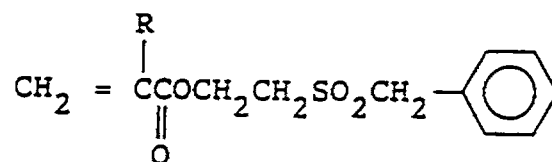
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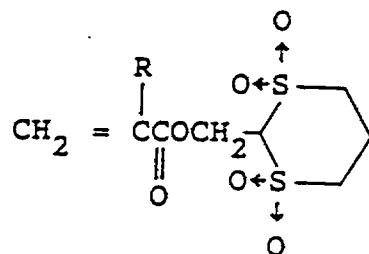
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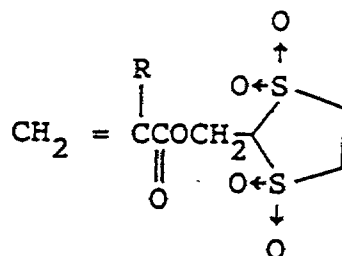
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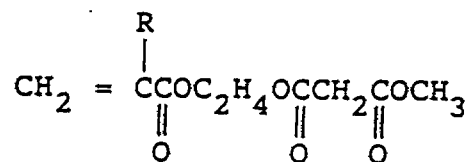
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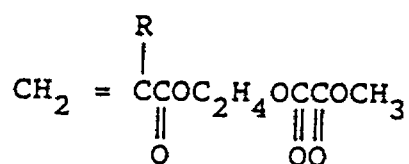
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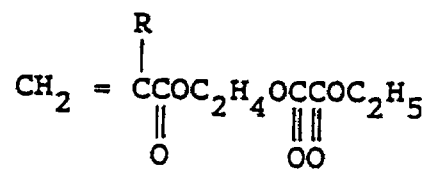
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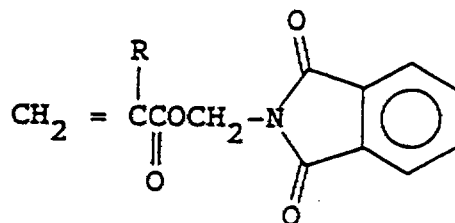
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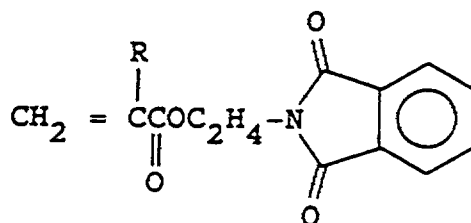
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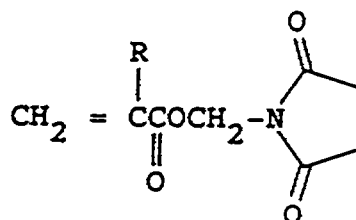
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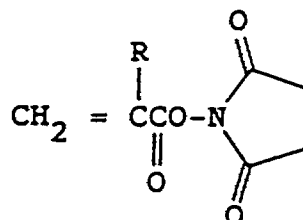
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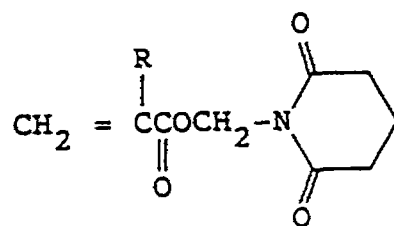
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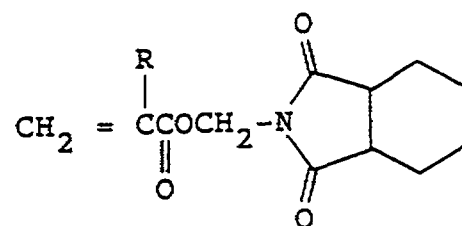
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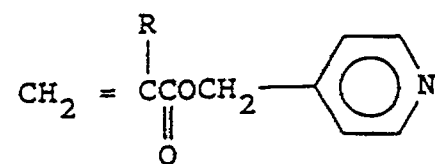
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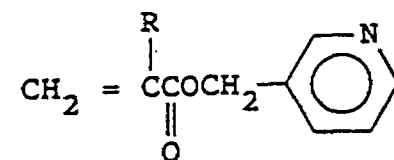
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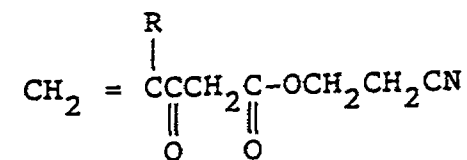
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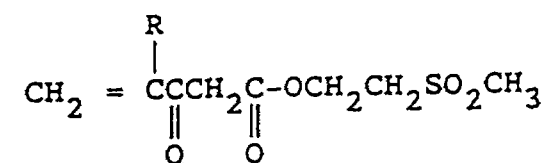
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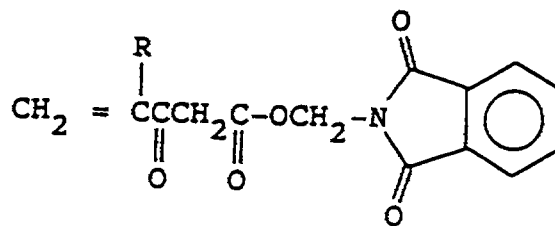
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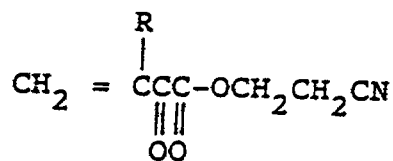
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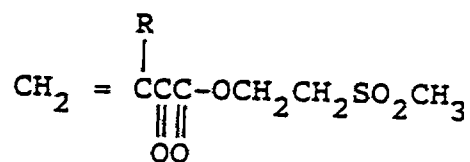
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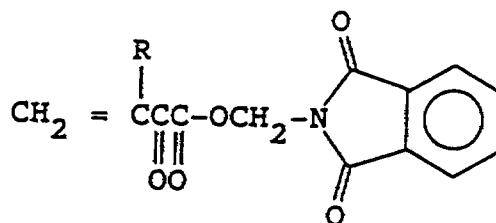
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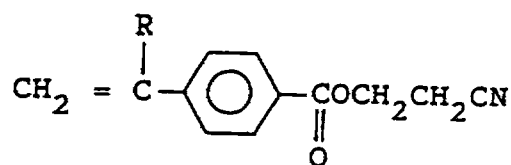
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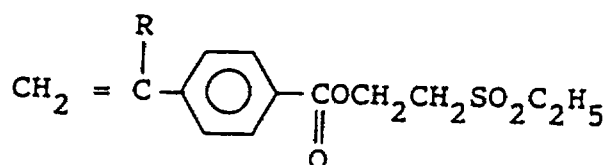
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The compounds of the formula (I) wherein R^3 's represent the hydrocarbon groups forming a cyclic structure with each other are, for example, Compound No. 15 and Compound No. 16 shown in the above list.

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 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 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; ~~pre-~~
~~ferred that~~ ^{preferably} it is not less than 0.1 mol% based on the 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 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

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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), the unsaturated monomers represented by the formula (II) and the unsaturated monomers having a hydrophilic functional group are preferably used.

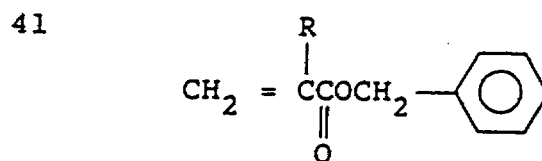
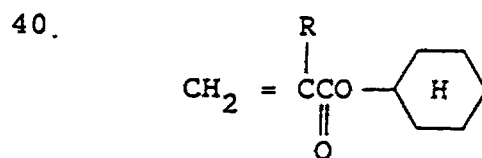
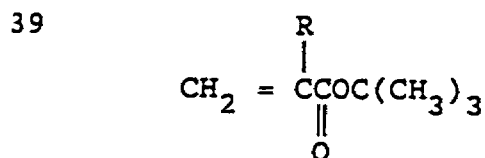
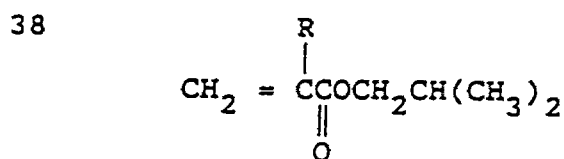
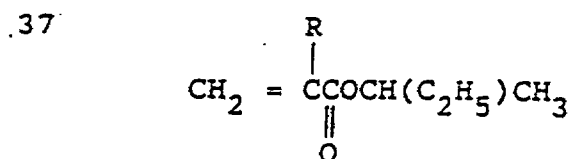
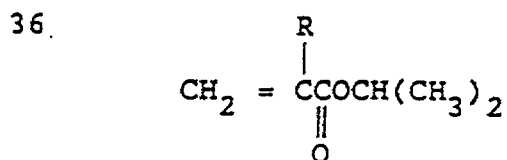
In the unsaturated monomers represented by the formula (II), the branched or alicyclic alkyl, aryl or aralkyl groups having 3 or more carbon atoms, represented by R^{10} , include isopropyl, isobutyl, sec-butyl, tert-butyl, sec-pentyl, tert-pentyl, neopentyl, 2-ethylhexyl, cyclopropyl, cyclobutyl, cyclopentyl,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

The unsaturated monomers represented by the 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



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

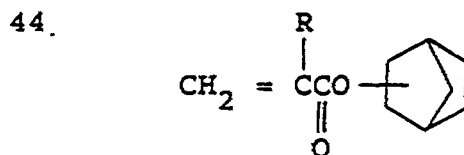
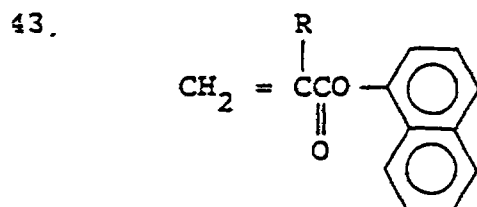
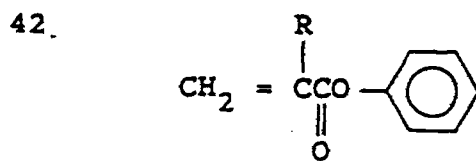


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An unsaturated monomer of the formula (II) can be blended for the purpose of increasing solubility in the solvents, especially aromatic solvents. The blending ratio of this unsaturated monomer is preferably from 5 to 95 mol%. A too low blending ratio 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 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

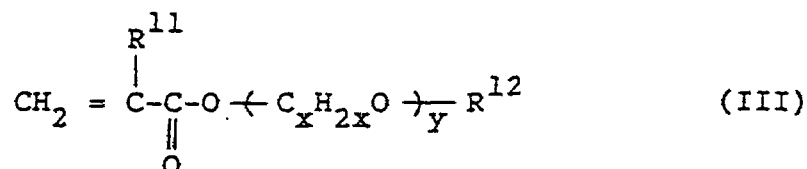
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invention, include unsaturated acid anhydrides or the unsaturated monomers represented by the formula:



wherein R^{11} is hydrogen atom or CH_3 group; x is an integer of 1 to 6; y is an integer of 1 to 10; 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).

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, 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, and norbonyl etc.

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

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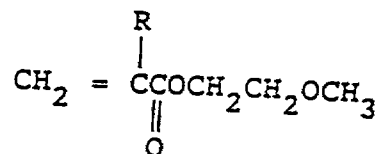
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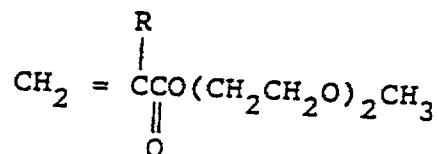
usable.

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):

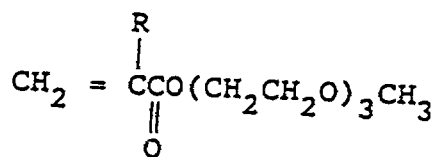
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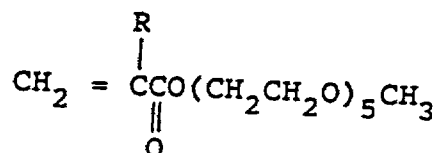
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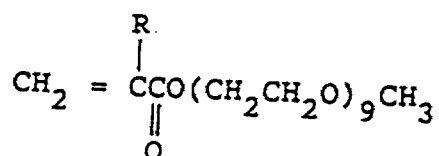
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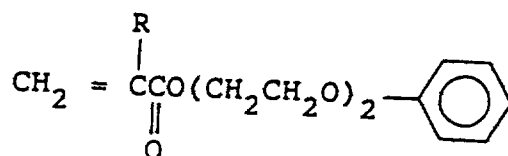
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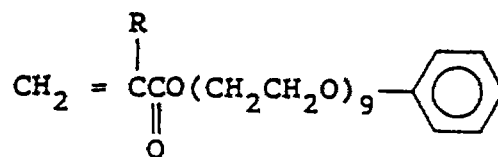
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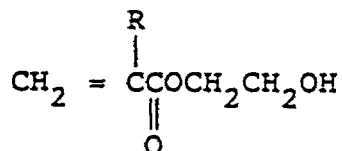
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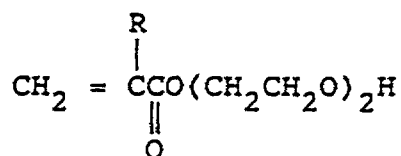
51.



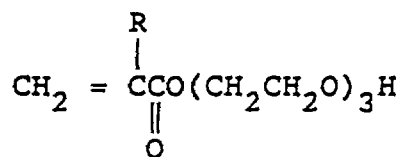
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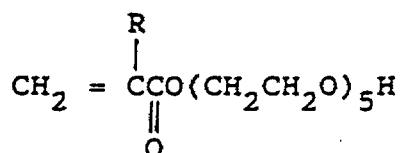
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Examples of the unsaturated acid anhydrides usable as an unsaturated monomer having a hydrophilic functional group include maleic anhydride, methylmaleic anhydride, dimethylmaleic anhydride, ethylmaleic anhydride, phenylmaleic anhydride, chloromaleic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

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itaconic anhydride, 1-chloroitaconic anhydride, endomethylenetetrahydrophthalic anhydride, chlorendic anhydride, ^{and} tetrahydrophthalic anhydride ~~etc.~~

The blending ratio of the unsaturated monomer having a hydrophilic ^f 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 ^e effect of addition of this unsaturated monomer is almost nil. On the other hand, when the blending ratio exceeds 70 mol%, 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 for antifouling paints.

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

As examples of the unsaturated monomers other 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, ^{and} n-butyl ester, ~~etc.~~, styrene monomers such as styrene, ^{and} α -methylstyrene, ^{and} p-t-butylstyrene, ~~etc.~~, polyolefin monomers such as butadiene, isoprene, ^{and} chloroprene, ~~etc.~~, vinyl monomers such as vinyl chloride, ^{and} vinyl acetate, ~~etc.~~, acrylonitrile, ^{and} methacrylonitrile, ~~and the like.~~



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 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 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 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 ^{homopolymer} ~~polymer~~ or copolymer (hereinafter simply referred ^{red} 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 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



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 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 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, since ~~when~~ the product is ~~intended to be~~ used as an antifouling 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.

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, ~~and~~ peroxide compounds ~~and the like~~. The number-average 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



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 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 methanethiol, ethanethiol, n-propanethiol, isopropanethiol, n-butanethiol, 2-methylpropanethiol, 3-methylpropanethiol, 1,1-dimethylethanethiol, 1-hexanethiol, 1-octanethiol, 1-decanethiol, benzenethiol, 2-methylbenzenethiol, 3-methylbenzenethiol, 4-methylbenzenethiol, 2-ethylbenzenethiol, 3-ethylbenzenethiol, 4-ethylbenzenethiol, bis(4-hydroxydimethylphenyl)disulfide, bis(2-chloromethylphenyl)disulfide, bis(2-bromophenyl)disulfide, dinaphthyl disulfide, di-2-benzothia disulfide, α -methylstyrene 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 appropriate hydrolysis-elution property and can be applied as a coating resin suited for antifouling coating compositions. The coating resin ^{used in} ~~according to~~

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the present invention may further comprise^L other polymer(s) within limits not prejudicial^L to the effect of the present invention. Such polymers include, for example, vinyl copolymers such as acrylic copolymers, styrene-acrylic copolymers^{and} polyvinyl chloride~~etc~~; polyesters;^{and} polysiloxanes~~etc~~.

The coating resin^{used in} of this invention, if necessary, may be blended with a known coloring matter, a known antifouling agent and various other additives in 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 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 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.

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



It is also possible to use rosin, gum rosin, wood rosin, ^{or} tall oil rosin ~~or the like~~ as elution assistant.

The antifouling coating composition of this invention obtained in the manner described above is useful as bottom paint, ^{and} 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 invention in any way.

Synthesis Example 1

Synthesis of 2-ethylsulfonylethyl methacrylate

(Compound No. 10, R = CH₃)

A mixture of 315 g (3.15 mol) of methyl methacrylate, 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 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 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



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):

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),
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

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 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 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



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 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):

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).

(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

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 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



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

(1) ^1H -NMR spectral data (^1H -NMR spectrum as shown 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 Fig. 6):

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

Synthesis Example 4

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

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 dimethyl oxalate was removed by sublimation. The resulting 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 colorless liquid (yield: 64%). From its analytical results shown below, this liquid was confirmed to be 2-methoxalyloxyethyl methacrylate (Compound No. 18, $R = CH_3$).

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- (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), 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

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 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 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 = 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



methacrylate (Compound No. 19, R = CH₃).

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

δ(CDCl₃): 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 (Compound No. 20, R = CH₃)

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 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 mixture was poured into icy water and stirred for a while. 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-methacryloyloxymethylphthalimide (Compound No. 20, R = CH₃).

(1) Melting point: 134°C

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- (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).

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

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

Synthesis Example 7

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.



- (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),
2.75 (4H, s).

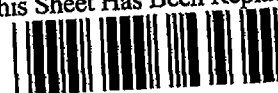
- (3) IR spectral data (KBr) (IR spectrum as shown in Fig. 13):

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

To a 236 ml methylene chloride solution of 30 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. 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 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).

- (1) Melting point: 76°C

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- (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), 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

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 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 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 colorless crystals (yield: 31%). From the following physical properties, these crystals were confirmed to be N-methacryloyloxysuccinimide (Compound No. 23, R = CH_3).

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- (1) Melting point: 102°C
- (2) ^1H -NMR spectral data (^1H -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).

- (3) IR spectral data (KBr) (IR spectrum as shown in Fig. 17):

1763, 1737 cm^{-1} (C=O).

Synthesis Example 9

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

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

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

$\delta(\text{CDCl}_3)$: 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).

Synthesis Example 10

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

A mixture of 315 g (3.15 mol) of methyl methacrylate, 130 g (1.05 mol) of 2-methylsulfonyl-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 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 reduced pressure to obtain 130 g of colorless crystals (yield: 64%). From their physical properties, these crystals were confirmed to be 2-methylsulfonylethyl



- methacrylate (Compound No. 9, R = CH₃).

(1) Melting point: 48°C

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

δ(CDCl₃): 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):

1710 cm⁻¹ (C=O), 1300, 1140 cm⁻¹ (SO₂).

Examples 1 - 20

Into a four-necked flask equipped with a stirrer, a condenser, an N₂ gas feed pipe, a dropping funnel and a thermometer, a measured amount of a solvent or solvents was supplied and stirred at 95°C. Then a mixed solution comprising monomers, azobisisobutyronitrile (AIBN) and α-methylstyrene dimer (αMSD) was charged into the dropping funnel and added dropwise into the flask in an N₂ gas stream while maintaining the temperature of the reaction mixture at about 95°C and stirring the mixture. After the dropwise addition was completed, the 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 properties of the obtained resins are shown in Tables 1 to 3.

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Table 1

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		αMSD (g)	NV (%)	Mn
			(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	

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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

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Table 1 cont'd

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN α MSD (g)		NV (%)	Mn
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

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Table 2

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)	α MSD (g)	NV (%)	Mn
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

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Table 2 ^{of} cont'd

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

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Table 2 ^{at} comp'd.

Exam- ple No.	Solvent w. (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

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Table 3

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Examples 21 - 26

A solvent, monomers, AIBN and α MSD were put into a four-necked flask equipped with a stirrer, a condenser, an N₂ gas feed pipe, and a thermometer, and the mixture was stirred while bubbling with N₂ 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 a viscous liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 4.

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Table 4

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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Table 4 cont'd

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)		α MSD (g)	NV (%)	Mn
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

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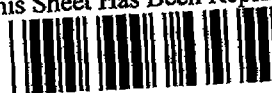
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Examples 27 - 30

Measured amounts of a solvent and a lowly reactive monomer were placed in a four-necked flask equipped with a stirrer, a condenser, an N_2 gas feed pipe, a dropping funnel and a thermometer, and the mixture was kept therein with stirring. Then, a mixed solution of other monomers, AIBN and α MSD was supplied into the flask from the dropping funnel in an N_2 gas stream with stirring the mixture and maintaining its 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 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.

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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	-			

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Table 5 cont'd

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

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Table 5 cont'd

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)	αMSD (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)	-	-			

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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 and xylene/n-butanol^{no} (4/1), and suited for use as a resin for antifouling paints.

Comparative Preparation Examples 1 and 2

A determined amount of a solvent was put into a four-necked flask equipped with a stirrer, a condenser, an N₂ 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 αMSD was supplied into the dropping funnel and added dropwise into the flask under N₂ gas stream with 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 properties of the obtained resins are shown in Table 6.

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Table 6

Comp. Prep. Ex. No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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

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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 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 liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 7.

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Table 7

Comp. Prep. Ex. No.	Solvent (g)	Formulation Monomers (g)			NV (%)	Mn
		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

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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 JP-T-60 500 452 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.

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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 ^{used in} ~~according to~~ the present ~~sheet~~ ^{This is the replacement sheet}

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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 compositions ^{used in} ~~of~~ this invention are superior to the resins disclosed in Japanese Patent Application Publication No. JP-T-60 500 452 ~~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.

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. 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 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 periodically. The results are shown in Table 9.

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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

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.

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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

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 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 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 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



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 ^{used in} ~~of~~ this invention.

The coating resin ^{used in} ~~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

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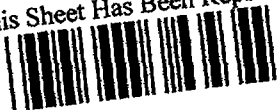
with the organotin-containing resins, so that ^{it} ~~the~~
~~coating resin of this invention~~ is capable of forming a
coat which can maintain an excellent antifouling effect
for a long period of time. Further, since the coating
resin ^{used in} ~~of~~ this invention is soluble in ~~the~~ aromatic
solvents,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

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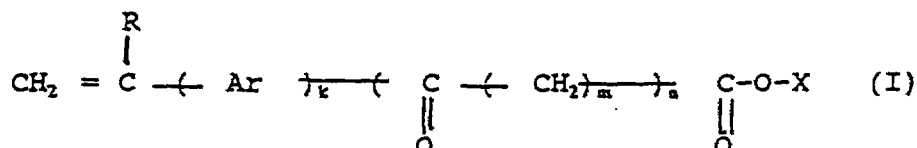
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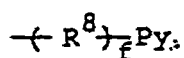
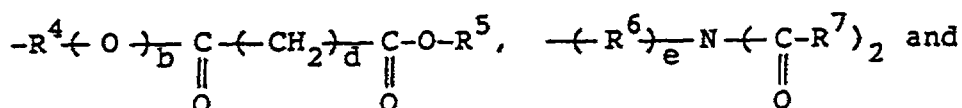
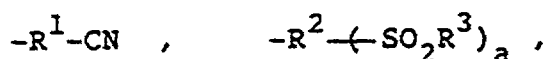
CLAIMS

1. An antifouling coating composition comprising:

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



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:



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





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groups R^j 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^j 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; and

(b) an antifouling agent.

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

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

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

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

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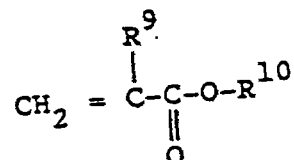
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1 to 5 wherein the coating resin further comprises as repeating units residues of one or more unsaturated monomers copolymerizable with the unsaturated monomer of formula (I).

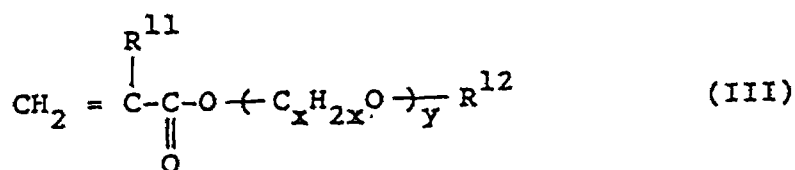
7. A composition according to claim 6 wherein the coating resin comprises as repeating units residues of a copolymerisable unsaturated monomer of formula (II)



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.

8. A composition according to claim 6 wherein the coating resin comprises as repeating units the residues of a copolymerizable unsaturated monomer having a hydrophilic functional group.

9. A composition according to claim 8 wherein the unsaturated monomer having a hydrophilic functional group is a monomer of formula (III)



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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.

10. A composition according to any one of the preceding claims wherein the unsaturated monomer of formula (I) is present in the resin in an amount of not less than 0.1 mol% based on the total amount of monomers.

11. A composition according to any one of the preceding claims wherein the polymer has a number-average molecular weight of from 3,000 to 200,000.

12. Use of a coating resin as defined in claim 1 in an antifouling coating composition.

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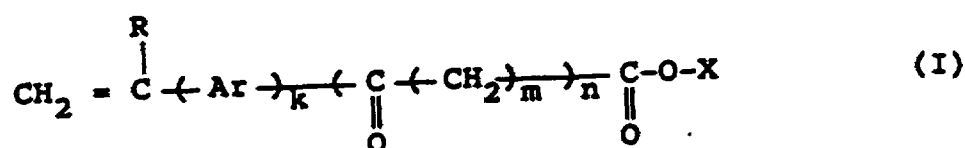
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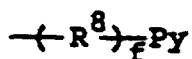
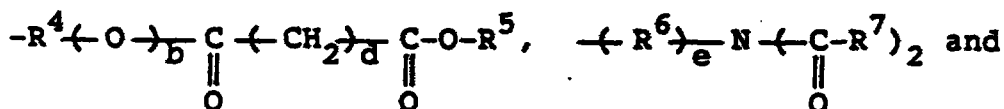
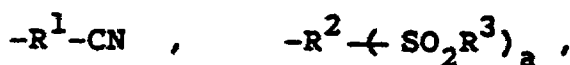
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ABSTRACTCOATING RESIN AND ANTIFOULING COATING COMPOSITION

A coating resin comprising a polymer obtained by polymerising an unsaturated monomer represented by the formula (I):



wherein R is H or an alkyl group, and X is selected from:



wherein R¹ to R⁵ represent independently a hydrocarbon group, etc., and Py is a pyridyl group, alone or together with one or more other unsaturated monomers may be used in antifouling coating compositions having no safety problems, good storage stability and excellent antifouling effect for a long period of time.

FIGURE 2

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REPLACEMENT SHEETS 8G
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☒ Claim(s) : pages 69 to page 72
☒ Drawing(s) : pages 74 to page 74
☒ Abstract : pages 73 to page 74
DATE OF RECEIPT 3/5/91

COATING RESIN AND ANTIFOULING COATING
COMPOSITION

BACKGROUND OF THE INVENTION

This invention relates to
an antifouling coating composition to be used for
preventing attachment of marine organisms to under-
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,
fishing net, drainage pipe, etc., is set or placed in
commission 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
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 economic problem. Also, if the marine
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
the marine organisms to underwater structures such

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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. 40-21426, 44-9579, 46-13392, 49-20491, 51-11647, 51-12049, 52-48170) 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 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 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 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 antifouling effect, in place of the organotin-based resins 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

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water-repellent resins have also been made (Japanese Patent Application Kokai (Laid-Open) Nos. 62-290768, 62-13471, 58-180565, 57-67672). However, it is hardly possible to realize a long-lasting stabilized 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 Patent Appln. Kokai Nos. 2-69576, 63-215780, 62-57464, Japanese Patent Appln. Kokoku Nos. 55-39271, 61-3830), 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 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 will not affect the undercoat when coating is performed.

SUMMARY OF THE INVENTION

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

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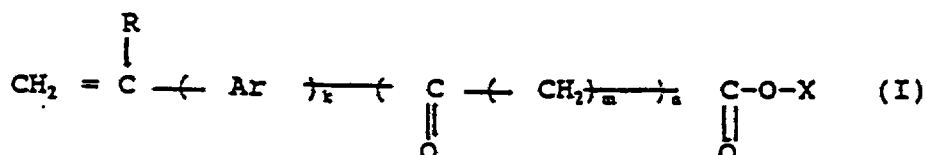
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antifouling coat. This coating resin is also soluble in aromatic solvents.

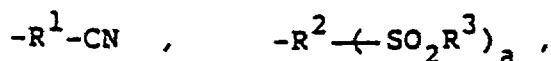
The present inventors have pursued strenuous studies for solving said prior art problems and developing an antifouling coating composition which performs excellently for preventing attachment of the marine organisms to the underwater structures such as mentioned above and has no problem in safety and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

The present invention provides an antifouling coating composition comprising:

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

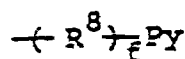
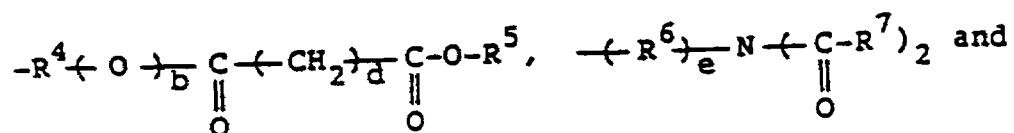


wherein R is hydrogen or a straight or branched alkyl group having 1 to 4 carbon atoms; Ar is a benzene ring or naphthalene ring; k, m and n represent independently a number of 0 or 1; and X is a substituent selected from the groups:



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

(b) an antifouling agent.

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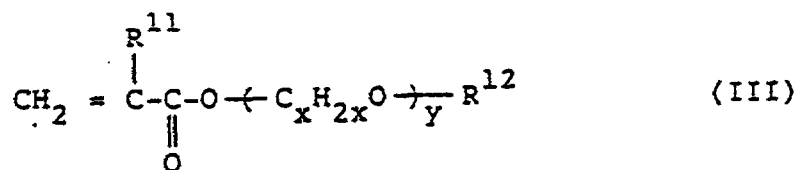
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The present invention also provides a coating composition of the type recited, wherein the coating resin further comprises as repeating units residues of a copolymerizable unsaturated monomer of formula:



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.

The present invention also provides a coating composition of the type recited, wherein the coating resin further comprises as repeating units residues of a copolymerizable unsaturated monomer having a hydrophilic functional group. Said monomer may be either an unsaturated acid anhydride or an unsaturated monomer of the formula:



wherein R¹¹ is hydrogen or methyl; x is an integer of 1 to 6; y is an integer of 1 to 10; and R¹² is hydrogen or a straight, branched or cyclic alkyl, aryl or aralkyl group.

The present invention also provides the use of a coating resin as defined above in an antifouling coating composition.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ^1H -NMR spectrum of Compound No. 10 ($\text{R} = \text{CH}_3$) in the list, given below, of the preferred examples of the unsaturated monomers represented by the formula (I).

Fig. 2 is an IR spectrum of Compound No. 10 ($\text{R} = \text{CH}_3$).

Fig. 3 is a ^1H -NMR spectrum of Compound No. 12 ($\text{R} = \text{CH}_3$).

Fig. 4 is an IR spectrum of Compound No. 12 ($\text{R} = \text{CH}_3$).

Fig. 5 is a ^1H -NMR spectrum of Compound No. 2 ($\text{R} = \text{CH}_3$).

Fig. 6 is an IR spectrum of Compound No. 2 ($\text{R} = \text{CH}_3$).

Fig. 7 is a ^1H -NMR spectrum of Compound No. 18 ($\text{R} = \text{CH}_3$).

Fig. 8 is an IR spectrum of Compound No. 18 ($\text{R} = \text{CH}_3$).

Fig. 9 is a ^1H -NMR spectrum of Compound No. 19 ($\text{R} = \text{CH}_3$).

Fig. 10 is a ^1H -NMR spectrum of Compound No. 20 ($\text{R} = \text{CH}_3$).

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

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

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
(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).

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.
9 (R = CH₃).

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

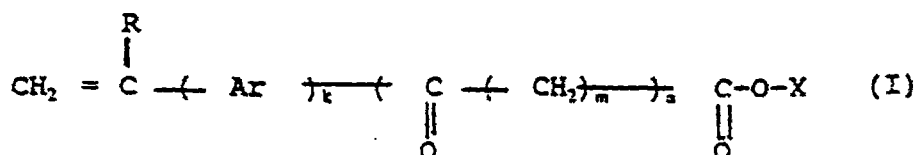
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The coating resins used in the present invention are preferably those specified below (1) - (9):

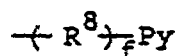
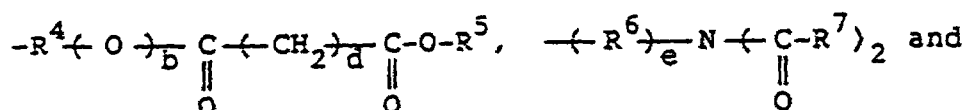
- (1) A coating resin comprising a polymer comprising, as repeating units, the residues of an unsaturated monomer or formula (I)

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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:



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 groups R³ 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,

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at least two of the groups R^1 may together form a hydrocarbon cyclic structure with each other and R^1 ; b, d, e and f are each a number of 0 or 1; R^2 is a straight or branched alkyl group having 1-4 carbon atoms; the groups R^3 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^3 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 specified in (1) above wherein k and n are 0.
- (3) A coating resin specified in (1) or (2) above wherein X is $-R^1-CN$.
- (4) A coating resin specified in (1) or (2) above wherein X is $-R^2 + SO_2R^3)_a$.
- (5) A coating resin specified in (1), (2), (3) or (4) above wherein R is H or CH_3 .
- (6) A coating resin specified in (1), (2), (3), (4) or (5) above further comprising as repeating units residues of one or more unsaturated monomer copolymerizable with the unsaturated monomer of the formula (I).
- (7) A coating resin specified in (6) above comprising as repeating units residues of a copolymerizable unsaturated monomer of formula (II):



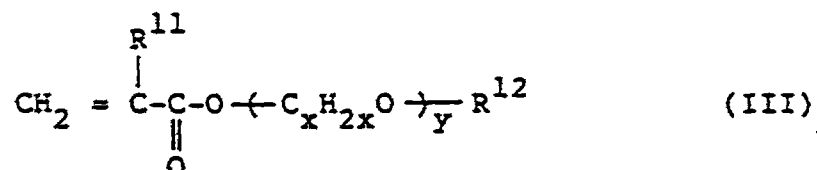
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wherein R^1 is hydrogen or methyl and R^{10} is branched or alicyclic alkyl, aryl or aralkyl optionally containing one or more hetero atoms and having 3 or more carbon atoms.

(8) A coating resin specified in (6) above comprising as repeating units the residues of a copolymerizable unsaturated monomer having a hydrophilic functional group.

(9) A coating resin specified in (8) above wherein the unsaturated monomer having a hydrophilic functional group is a monomer of formula (III):



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.

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 and tert-butyl.

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,

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ethylene, trimethylene, tetra-methylene, penta-methylene, neopentylene, hexamethylene, cyclopropylene, 1,2-cyclobutylene, 1,3-cyclobutylene, 1,2-cyclopentylene, 1,3-cyclopentylene, 1,2-cyclohexylene, 1,3-cyclohexylene and 1,4-cyclohexylene. 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, cyclobutyl, 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, tert-tetradecyl, hexadecyl, tert-hexadecyl, octadecyl, tert-octadecyl and eicosyl, docodyl. The C_{6-10} aryl groups or C_{7-18} aralkyl groups which may have a substituent include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, sulfonylphenyl, acylphenyl, naphthyl, benzyl, phenethyl and benzhydryl. 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 and tetramethylene. The C_{1-4} straight or branched alkyl groups represented by R^5 include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and tert-butyl. The C_{1-22} straight, branched or alicyclic

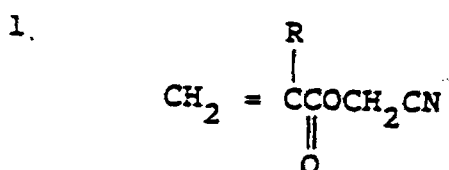
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alkyl groups represented by R^7 include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, cyclopropyl, cyclobutyl, pentyl, sec-pentyl, tert-pentyl, neo-pentyl, cyclopentyl, hexyl, cyclohexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, and docosyl. The C_{6-10} aryl groups or C_{7-10} aralkyl groups represented by R^7 include phenyl, tolyl, anisyl, cyanophenyl, nitrophenyl, naphthyl, benzyl, phenethyl and benzhydryl. The groups forming a cyclic structure, represented by two R^7 , include methylene, ethylene, trimethylene, o-phenylene, 1,2-naphthylene and 2,3-naphthylene.

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

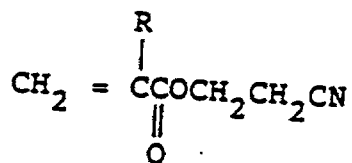
Listed below are the preferred examples of the unsaturated monomers represented by the formula (I) (R in the following formulae is hydrogen atom or methyl group):



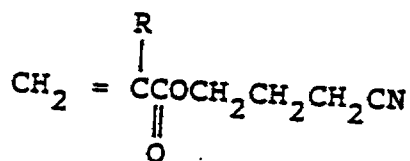
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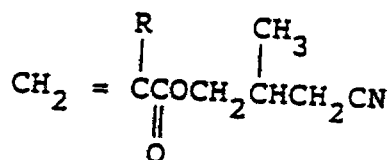
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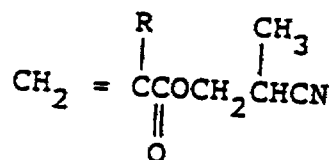
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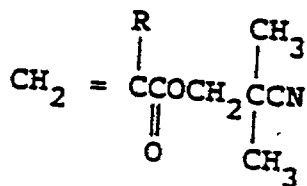
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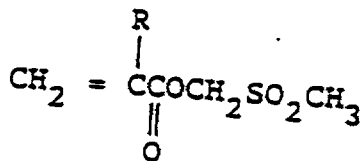
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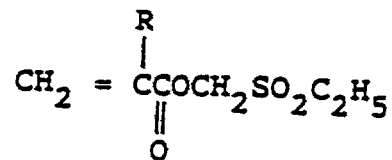
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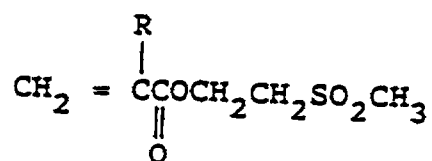
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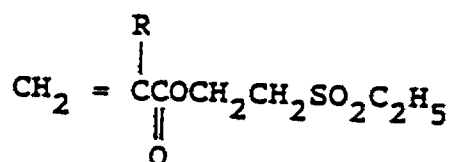
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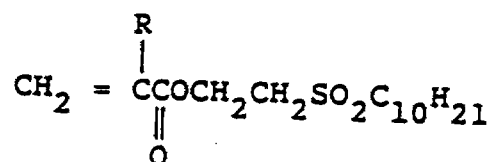
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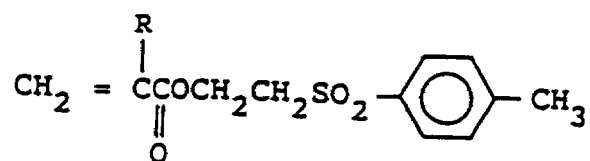
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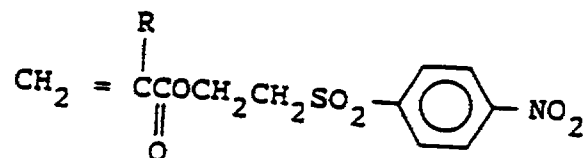
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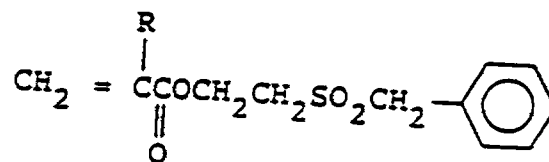
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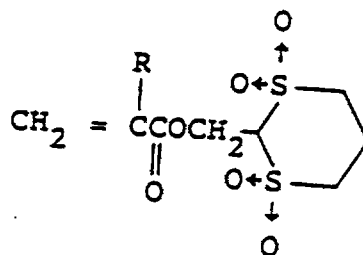
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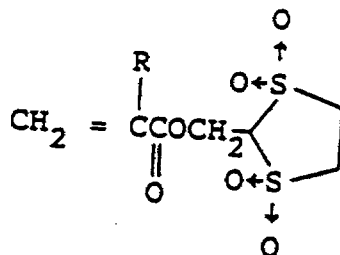
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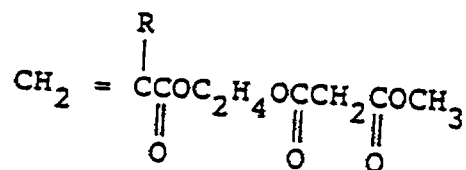
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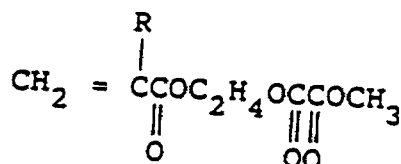
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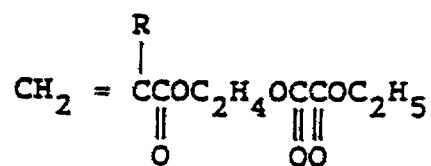
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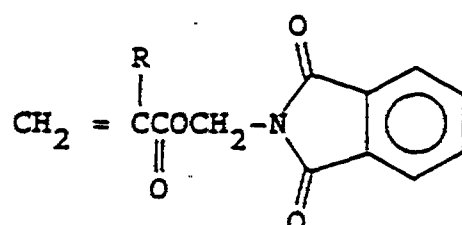
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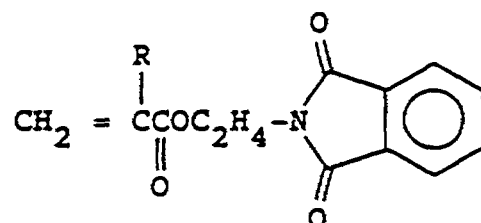
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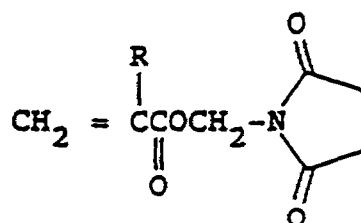
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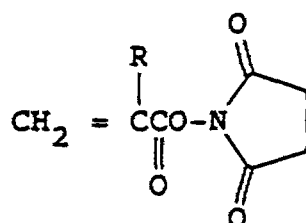
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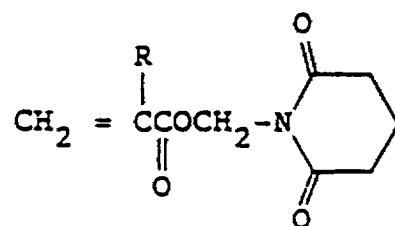
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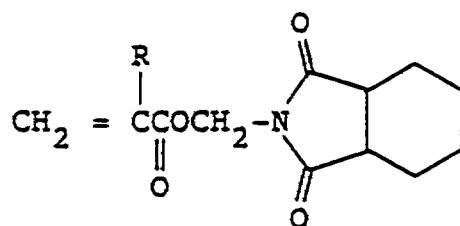
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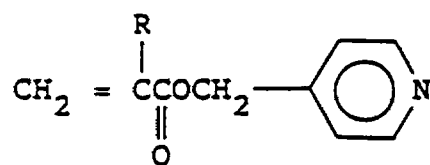
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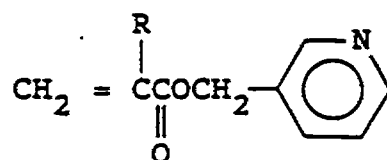
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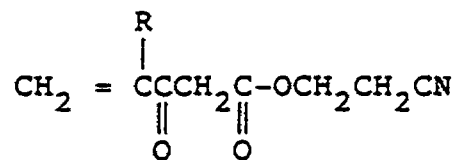
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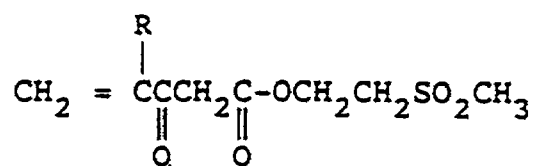
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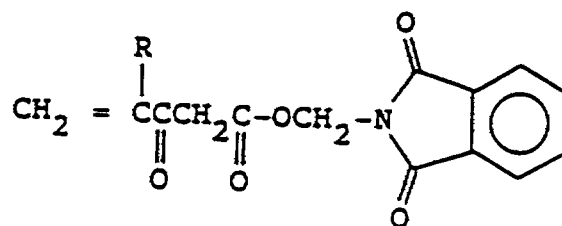
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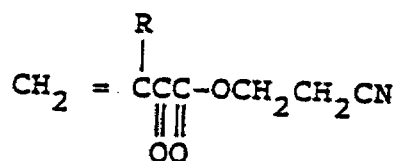
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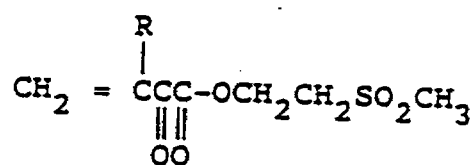
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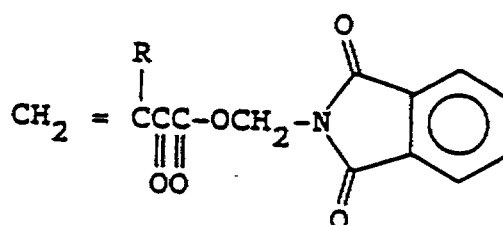
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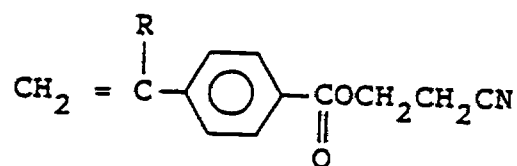
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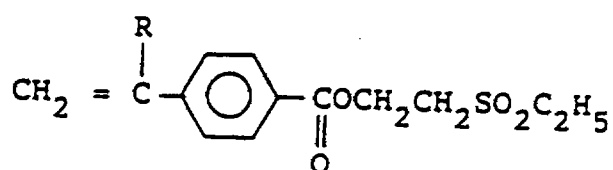
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The compounds of the formula (I) wherein R^3 's represent the hydrocarbon groups forming a cyclic structure with each other are, for example, Compound No. 15 and Compound No. 16 shown in the above list.

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 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 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; preferably it is not less than 0.1 mol% based on the 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 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

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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), 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 aralkyl groups having 3 or more carbon atoms, represented by R^{10} , 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, 2,3-xylyl, 2,4-xylyl, o-cumenyl, m-cumenyl, p-cumenyl, mesityl, benzyl, phenethyl, trityl, naphthyl, norbornyl and adamantyl. The organic substituents having a similar structure but containing other atoms than carbon include the compounds having silicon instead of carbon, such as trimethylsilyl, triethylsilyl, tripropylsilyl, tributylsilyl, triphenylsilyl, trimethoxysilyl, triethoxysilyl, tripropoxysilyl, tributoxysilyl and triphenoxysilyl.

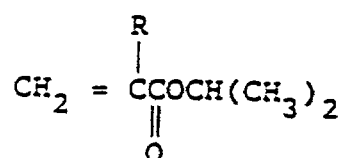
The unsaturated monomers represented by the formula (II) can be produced by various known synthetic methods. The pertinent commercially available unsaturated monomers are also usable.

Listed below are the preferred examples of the

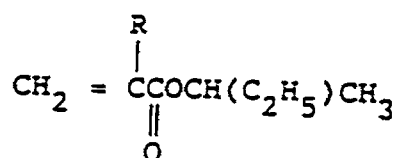
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unsaturated monomers represented by the formula (II) (R in the following formulae is hydrogen atom or methyl group):

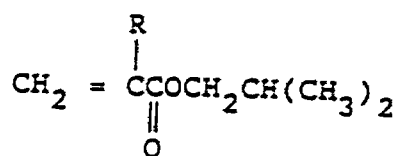
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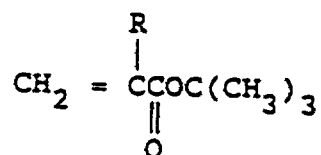
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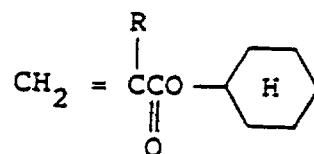
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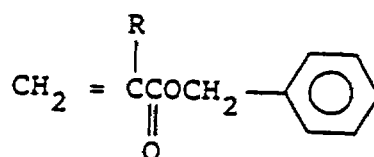
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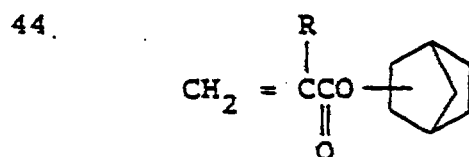
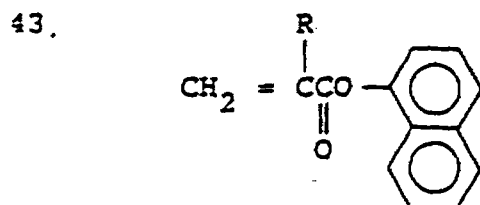
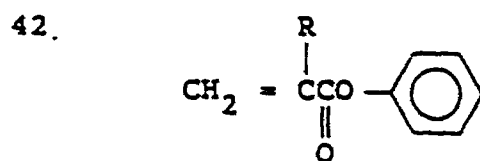


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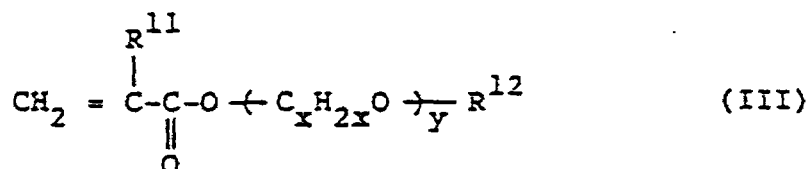
An unsaturated monomer of the formula (II) can be blended for the purpose of increasing solubility in the solvents, especially aromatic solvents. The blending ratio of this unsaturated monomer is preferably from 5 to 95 mol%. A too low blending ratio results in a poor solubility in the aromatic solvents, 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 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

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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 integer of 1 to 6; y is an integer of 1 to 10; 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).

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, 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 and norbonyl.

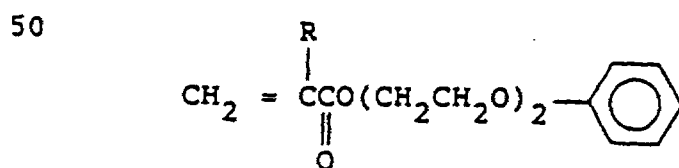
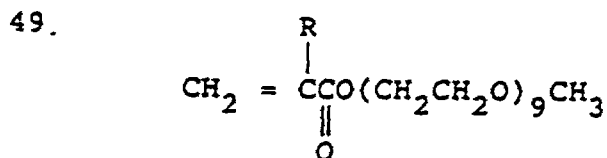
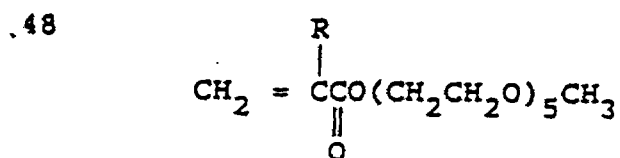
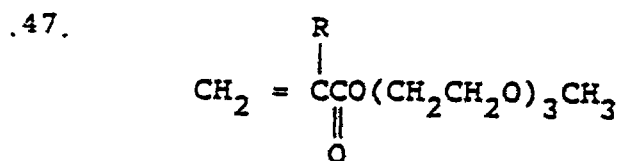
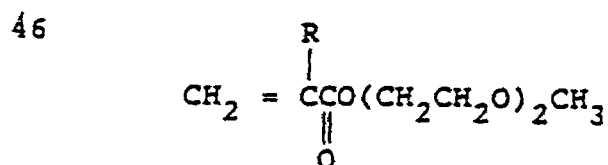
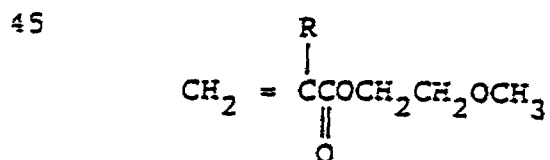
The unsaturated monomers of the formula (III) can be produced by various known synthetic methods. The commercially available unsaturated monomers are also

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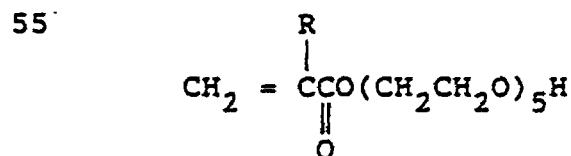
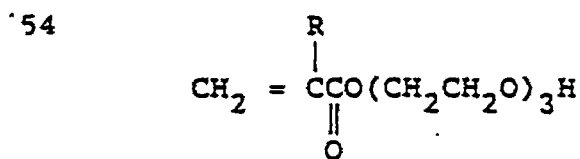
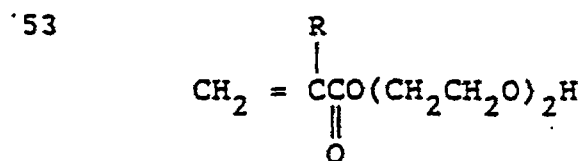
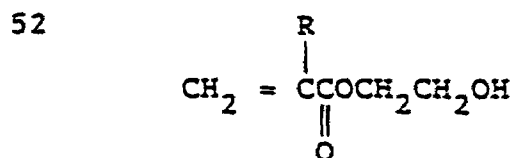
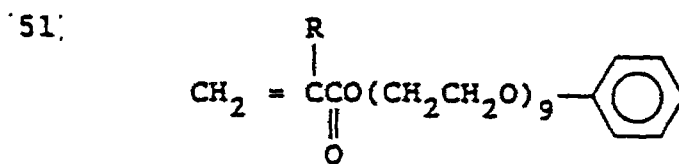
usable.

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):



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

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

The blending ratio of the unsaturated monomer 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%, 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 for antifouling paints.

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

As examples of the unsaturated monomers other 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 and n-butyl ester, styrene monomers such as styrene, α -methylstyrene and p-t-butylstyrene, polyolefin monomers such as butadiene, isoprene and chloroprene, vinyl monomers such as vinyl chloride and vinyl acetate acrylonitrile and methacrylonitrile.

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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 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. The blending ratio of this monomer is 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 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 homopolymer or copolymer (hereinafter simply referred 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 polymerization catalyst at a temperature of 0 to 180°C, preferably 40 to 170°C, for a period of one to 20 hours, preferably 4 to 10 hours.

As for the organic solvent used for the

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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 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 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, since the product is used as an antifouling 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.

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 and peroxide compounds.

The number-average 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

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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 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 methanethiol, ethanethiol, n-propanethiol, isopropanethiol, n-butanethiol, 2-methylpropanethiol, 3-methylpropanethiol, 1,1-dimethylethanethiol, 1-hexanethiol, 1-octanethiol, 1-decanethiol, benzenethiol, 2-methylbenzenethiol, 3-methylbenzenethiol, 4-methylbenzenethiol, 2-ethylbenzenethiol, 3-ethylbenzenethiol, 4-ethylbenzenethiol, bis(4-hydroxydimethylphenyl)disulfide, bis(2-chloromethylphenyl)disulfide, bis(2-bromophenyl)disulfide, dinaphthyl disulfide, di-2-benzothia disulfide, α -methylstyrene 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 appropriate hydrolysis-elution property and can be applied as a coating resin suited for antifouling coating compositions. The coating resin used in

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the present invention may further comprise 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, styrene-acrylic copolymers and polyvinyl chloride: polyesters; and polysiloxanes.

The coating resin used in this invention, if necessary, may be blended with a known coloring matter, a known antifouling agent and various other additives in 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 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 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.

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

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

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

The present invention is further described below with reference to the Examples of the invention, which Examples however do not limit the present 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 methacrylate, 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 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 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

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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):

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),
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

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 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 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

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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 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):

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).

(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

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 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

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

(1) ^1H -NMR spectral data (^1H -NMR spectrum as shown 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 Fig. 6):

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

Synthesis Example 4

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

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 dimethyl oxalate was removed by sublimation. The resulting 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 colorless liquid (yield: 64%). From its analytical results shown below, this liquid was confirmed to be 2-methoxalyloxyethyl methacrylate (Compound No. 18, $R = CH_3$).

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- (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), 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

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 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 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 = 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

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methacrylate (Compound No. 19, R = CH₃).

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

δ(CDCl₃): 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 (Compound No. 20, R = CH₃)

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 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 mixture was poured into icy water and stirred for a while. 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-methacryloyloxymethylphthalimide (Compound No. 20, R = CH₃).

(1) Melting point: 134°C

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- (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).

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

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

Synthesis Example 7

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.

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- (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),
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 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. 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 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).

- (1) Melting point: 76°C

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(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), 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

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 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 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 colorless crystals (yield: 31%). From the following physical properties, these crystals were confirmed to be N-methacryloyloxysuccinimide (Compound No. 23, R = CH_3).

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- (1) Melting point: 102°C
- (2) ^1H -NMR spectral data (^1H -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).
- (3) IR spectral data (KBr) (IR spectrum as shown in Fig. 17):
1763, 1737 cm^{-1} (C=O).

Synthesis Example 9

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

$\delta(\text{CDCl}_3)$: 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).

Synthesis Example 10

Synthesis of 2-methylsulfonylethyl methacrylate

(Compound No. 9, $\text{R} = \text{CH}_3$)

A mixture of 315 g (3.15 mol) of methyl methacrylate, 130 g (1.05 mol) of 2-methylsulfonyl-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 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 reduced pressure to obtain 130 g of colorless crystals (yield: 64%). From their physical properties, these crystals were confirmed to be 2-methylsulfonylethyl

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methacrylate (Compound No. 9, R = CH₃).

(1) Melting point: 48°C

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

δ(CDCl₃): 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):

1710 cm⁻¹ (C=O), 1300, 1140 cm⁻¹ (SO₂).

Examples 1 - 20

Into a four-necked flask equipped with a stirrer, a condenser, an N₂ gas feed pipe, a dropping funnel and a thermometer, a measured amount of a solvent or solvents was supplied and stirred at 95°C. Then a mixed solution comprising monomers, azobisisobutyronitrile (AIBN) and α-methylstyrene dimer (αMSD) was charged into the dropping funnel and added dropwise into the flask in an N₂ gas stream while maintaining the temperature of the reaction mixture at about 95°C and stirring the mixture. After the dropwise addition was completed, the 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 properties of the obtained resins are shown in Tables 1 to 3.

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Table 1

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		αMSD (g)	NV (%)	Mn
			(g)	(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	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	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	0.55	50	7000

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Table 1 cont'd

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIDN		NV (%)	Mn
			(g)	α MSD (g)		
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

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Table 1 cont'd

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)	α MSD (g)	NV (%)	Mn
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

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Table 2

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN (g)		αMSD (g)	NV (%)	Mn
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

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Table 2 cont'd

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

- cont'd -

Table 2 (cont'd)

Exam- ple No.	Solvent ω. (g)	Formulation Monomers (g)	AIBN αMSD		NV (%)	Mn
			(g)	(g)		
17	Xylene (40) n-Butanol (10)	Compound No. 2, R=H (25.9)	1.66	1.2	50	6400
		Compound No. 39, R=CH ₃ (11.8)				
		Methyl methacrylate (12.4)				
18	Xylene (40) n-Butanol (10)	Compound No. 2, R=H (25.9)	1.66	1.66	50	5000
		Compound No. 39, R=CH ₃ (11.8)				
		Methyl methacrylate (12.4)				

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Table 3

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		αMSD (g)	NV (%)	Mn
			(g)	(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	

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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 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 a viscous liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 4.

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Table 4

Exam- ple No.	Solvent (g)	Formulation Monomers (g)	AIBN		NV (%)	Mn
			(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 Monomers (g)	AIBN		α MSD (g)	NV (%)	Mn
			(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

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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 N_2 gas feed pipe, a dropping funnel and a thermometer, and the mixture was kept therein with stirring. Then, a mixed solution of other monomers, AIBN and α MSD was supplied into the flask from the dropping funnel in an N_2 gas stream with stirring the mixture and maintaining its temperature at about $95^\circ C$. After completion of the dropwise addition, the reaction mixture was stirred at $95^\circ C$ 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 further stirred at $95^\circ C$ 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.

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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	-			

Table 5 cont'd

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)			
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				

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Table 5 cont'd

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)			
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)	-	-			

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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 and xylene/n-butanol(4/1), and suited for use as a resin for antifouling paints.

Comparative Preparation Examples 1 and 2

A determined amount of a solvent was put into a four-necked flask equipped with a stirrer, a condenser, an N₂ 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 N₂ gas stream with 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 properties of the obtained resins are shown in Table 6.

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Table 6

Comp. Prep. Ex. No.	Solvent (g)	Formulation Monomers (g)	AIBN		αMSD (g)	NV (%)	Mn
			(g)	(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

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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 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 liquid with a specified solid content. The detailed experimental conditions and the properties of the obtained resins are shown in Table 7.

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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

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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. JP-T-60 500 452 (Comparative Preparation Examples 2 and 3) proposed as a substitute for said organotin-containing resin. The test results are shown in Table 8.

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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 used in the present

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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 compositions used in this invention are superior to the resins disclosed in Japanese Patent Application Publication No. JP-T-60 500 452, 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.

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. 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 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 periodically. The results are shown in Table 9.

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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

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.

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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

As noted from the results of the antifouling performance tests shown above, any of the paints prepared according to the present invention showed excellent antifouling 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 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 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

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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 when mixed with cuprous oxide, is slight, indicating excellent storage stability of the coating resin used in this invention.

The coating resin used in 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

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

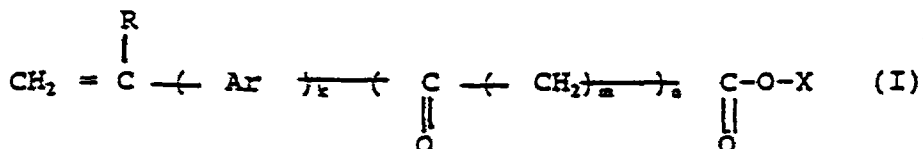
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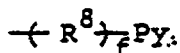
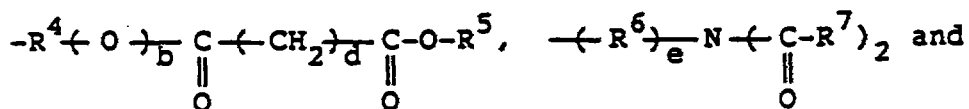
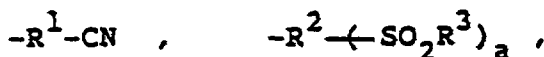
CLAIMS

1. An antifouling coating composition comprising:

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



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:



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



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groups R^j 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^j may together form a hydrocarbon cyclic structure with each other and R^i ; b , d , e and f are each a number of 0 or 1; R^j is a straight or branched alkyl group having 1-4 carbon atoms; the groups R^j 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^j together with the carbonyl carbon form a cyclic structure; and Py is a substituted or unsubstituted 2-, 3- or 4-pyridyl group; and

(b) an antifouling agent.

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

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

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

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

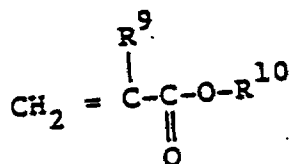
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6. A composition according to any one of claims 1 to 5 wherein the coating resin further comprises as repeating units residues of one or more unsaturated monomers copolymerizable with the unsaturated monomer of formula (I).

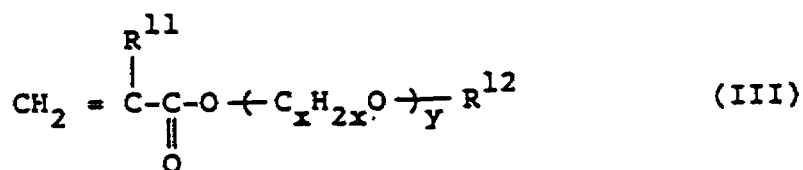
7. A composition according to claim 6 wherein the coating resin comprises as repeating units residues of a copolymerisable unsaturated monomer of formula (II)



wherein R^9 is hydrogen or methyl and R^{10} is branched or alicyclic alkyl, aryl or aralkyl optionally containing one or more hetero atoms and having 3 or more carbon atoms.

8. A composition according to claim 6 wherein the coating resin comprises as repeating units the residues of a copolymerizable unsaturated monomer having a hydrophilic functional group.

9. A composition according to claim 8 wherein the unsaturated monomer having a hydrophilic functional group is a monomer of formula (III)



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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.

10. A composition according to any one of the preceding claims wherein the unsaturated monomer of formula (I) is present in the resin in an amount of not less than 0.1 mol% based on the total amount of monomers.

11. A composition according to any one of the preceding claims wherein the polymer has a number-average molecular weight of from 3,000 to 200,000.

12. Use of a coating resin as defined in claim 1 in an antifouling coating composition.



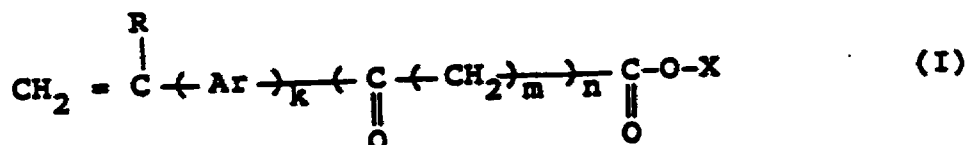
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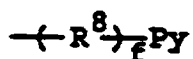
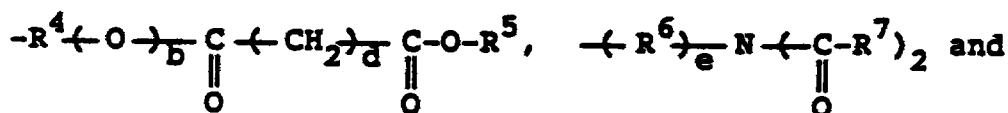
ABSTRACT

COATING RESIN AND ANTIFOULING COATING COMPOSITION

A coating resin comprising a polymer obtained by polymerising an unsaturated monomer represented by the formula (I):



wherein R is H or an alkyl group, and X is selected from:



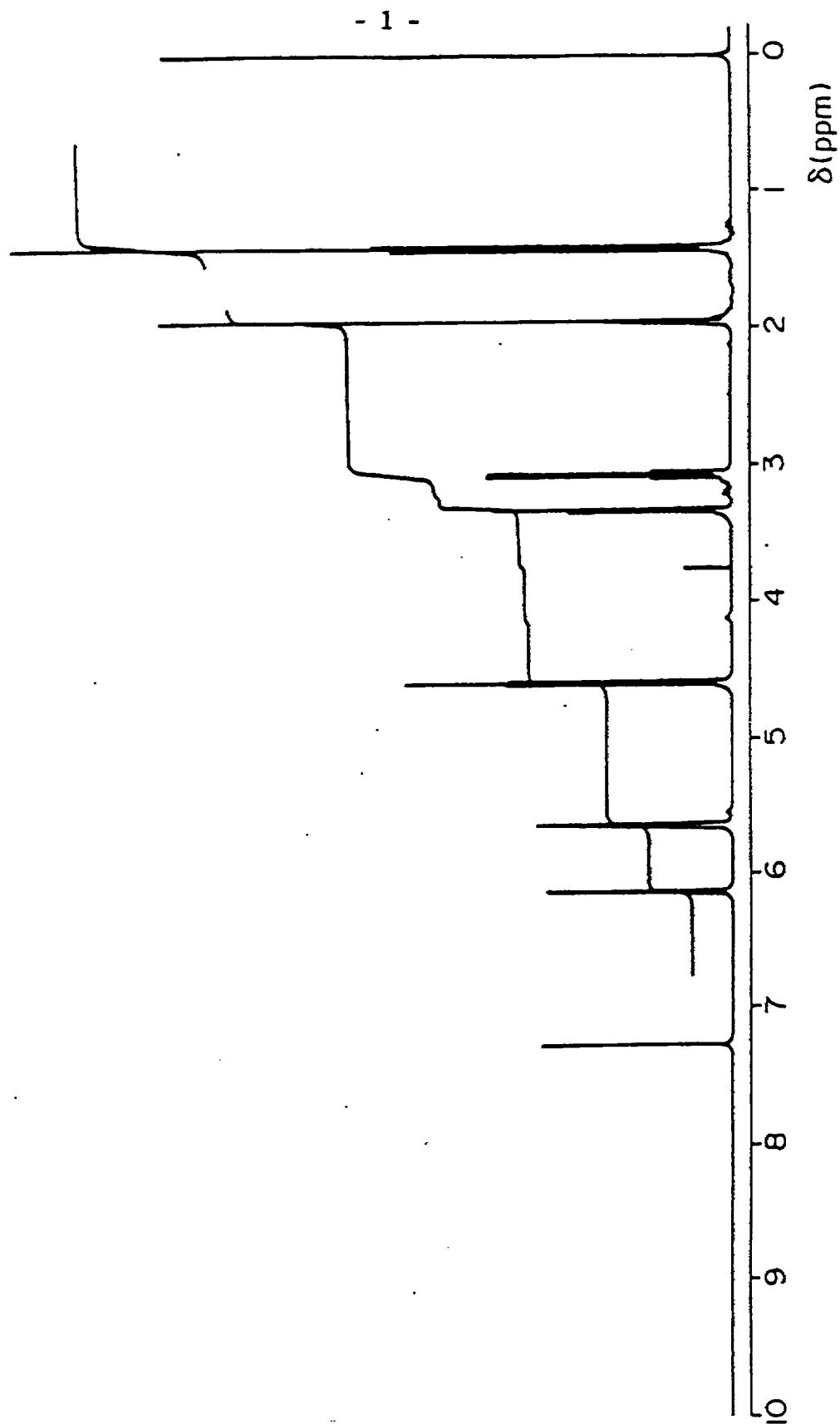
wherein R¹ to R⁸ represent independently a hydrocarbon group, etc., and Py is a pyridyl group, alone or together with one or more other unsaturated monomers may be used in antifouling coating compositions having no safety problems, good storage stability and excellent antifouling effect for a long period of time.

FIGURE 2

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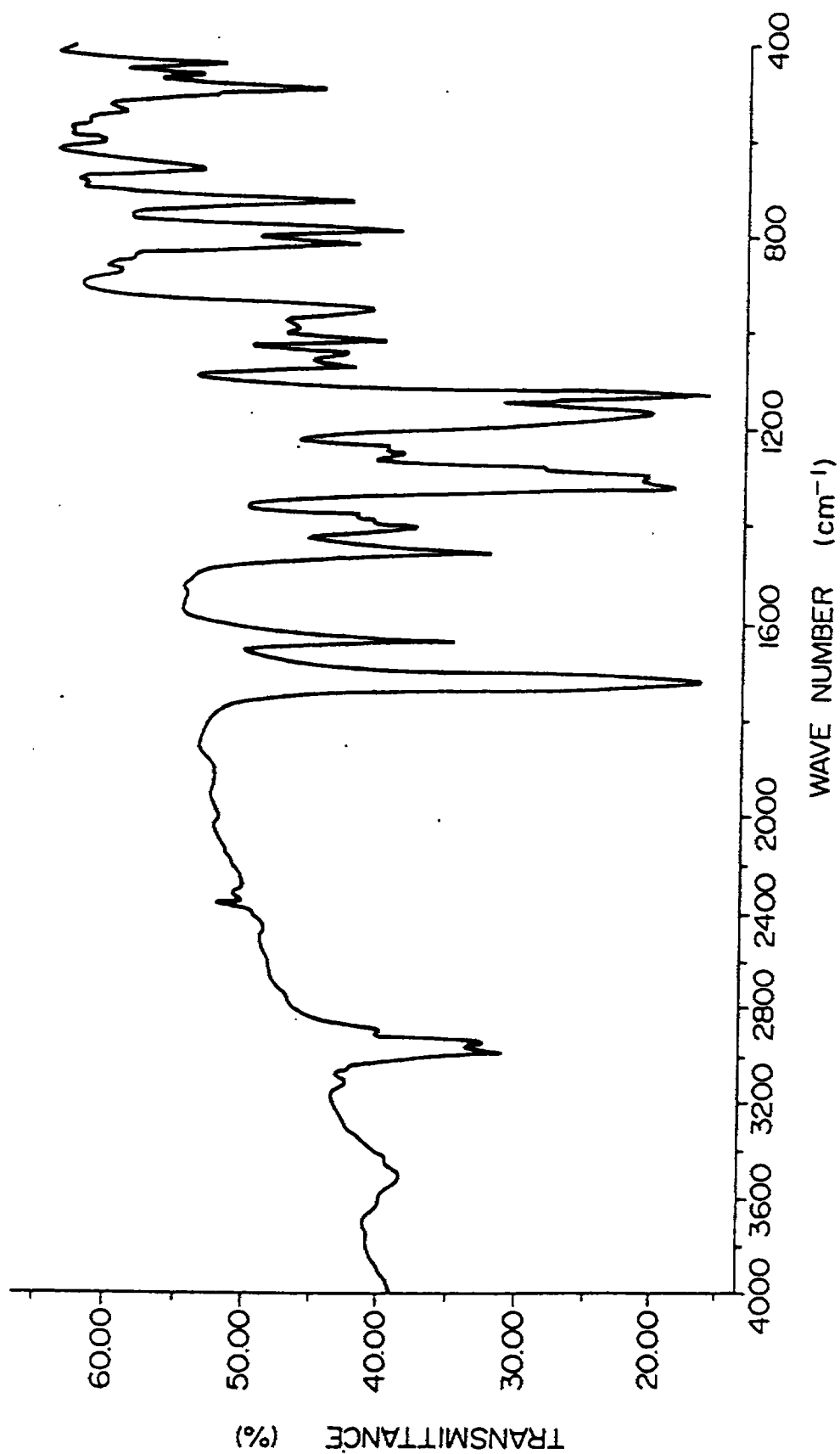
FIG. 1



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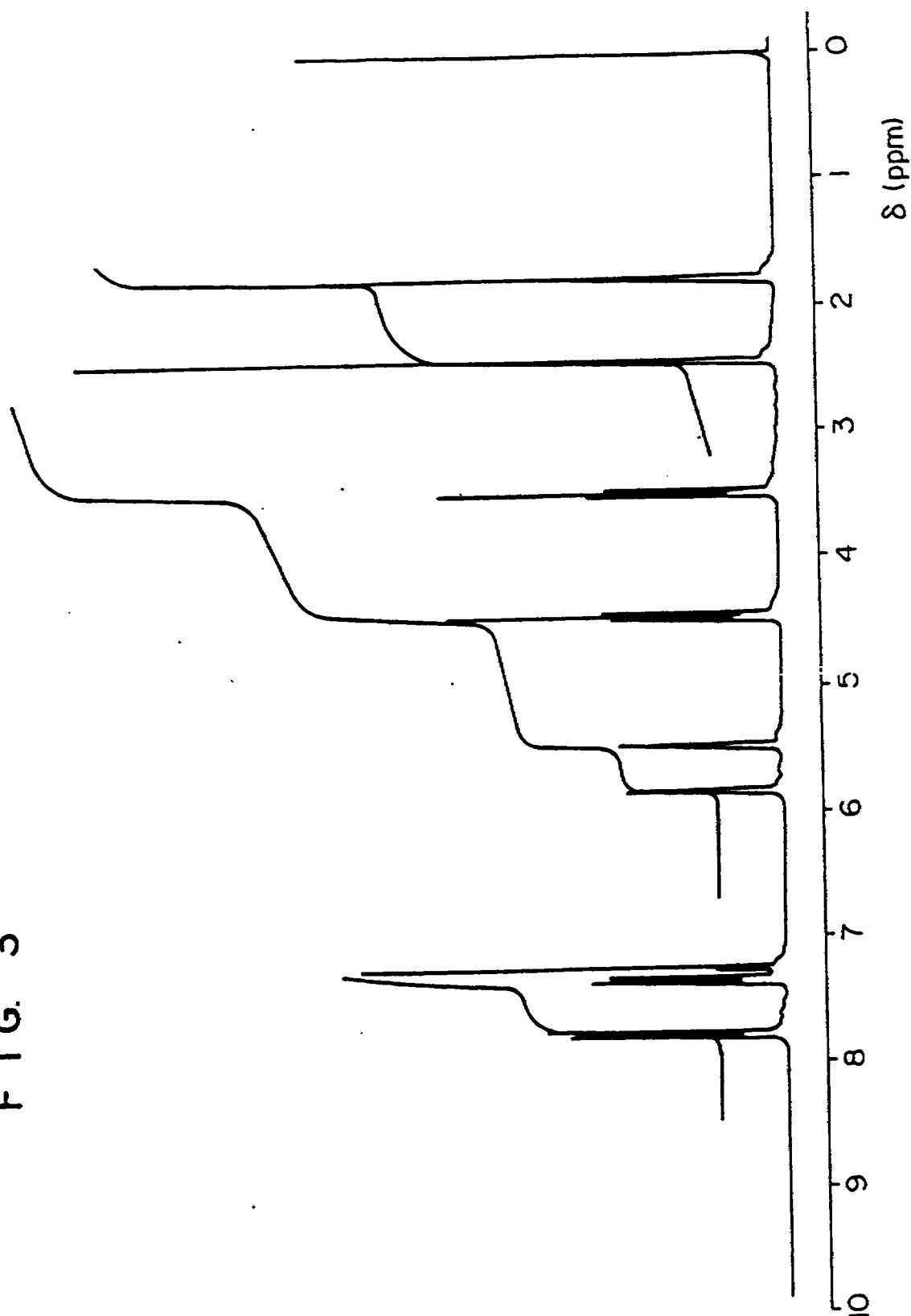
FIG. 2



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Date: 31 MAY 1999

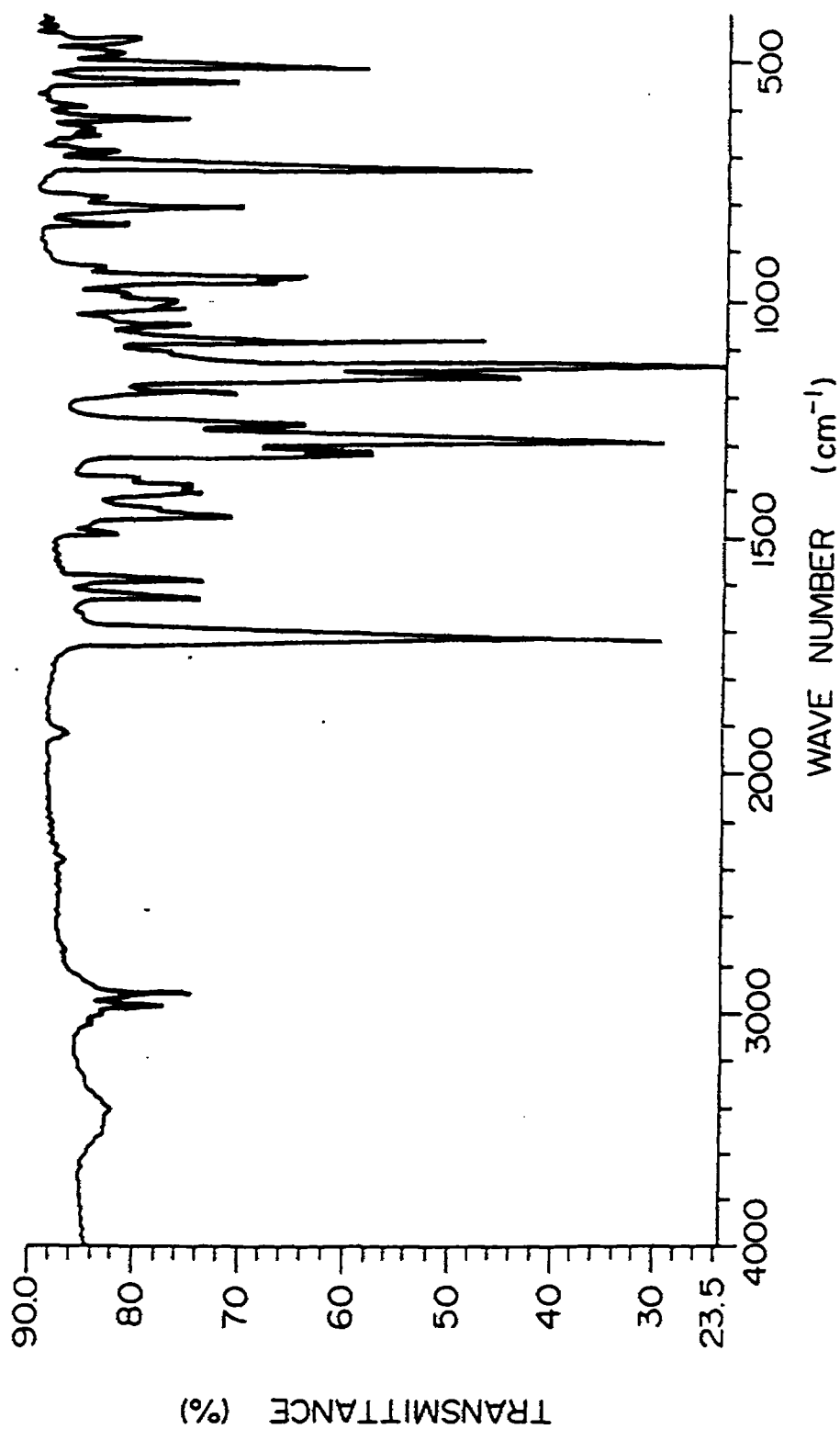
FIG. 3



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Date: 31 MAY 1999

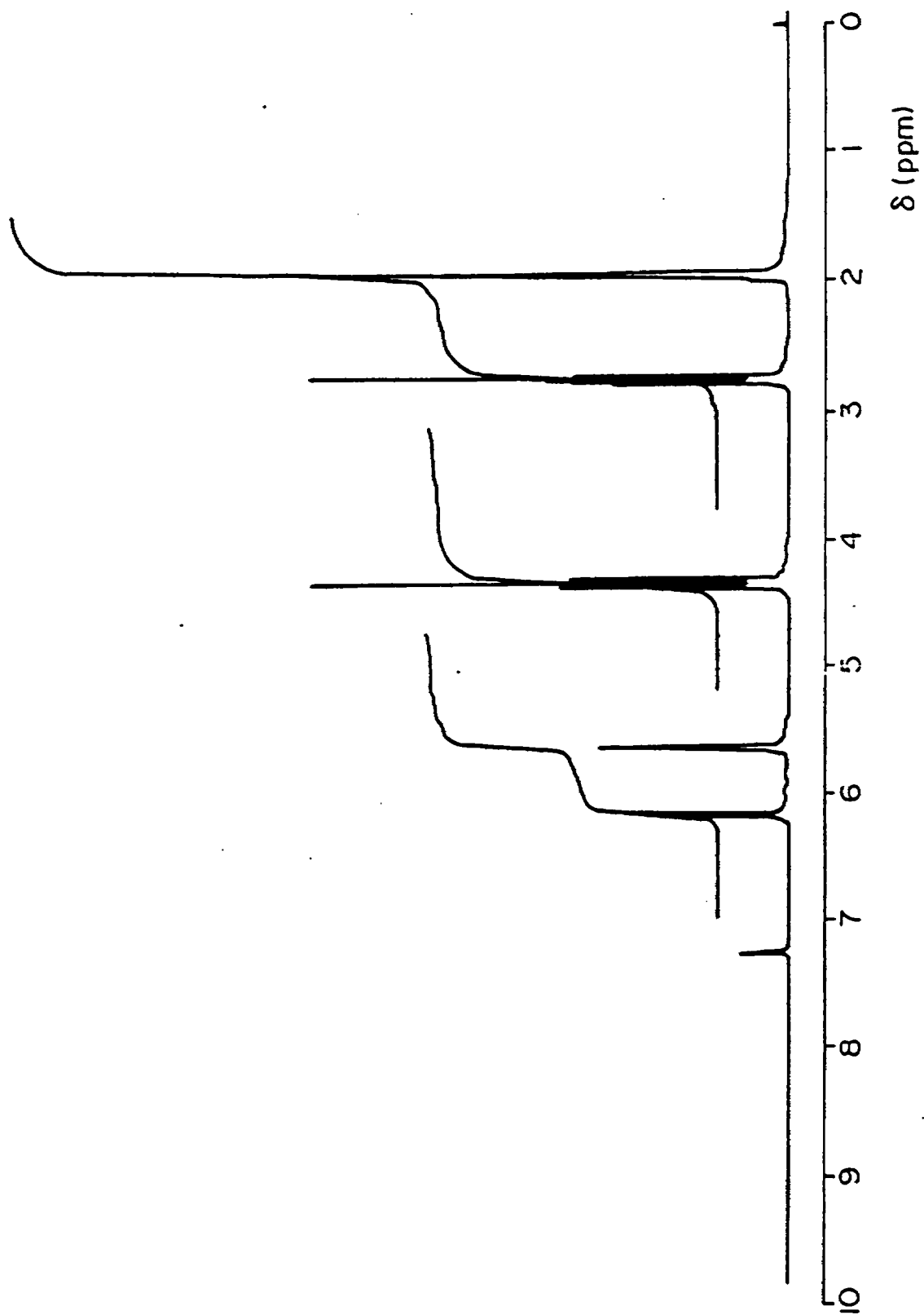
FIG. 4



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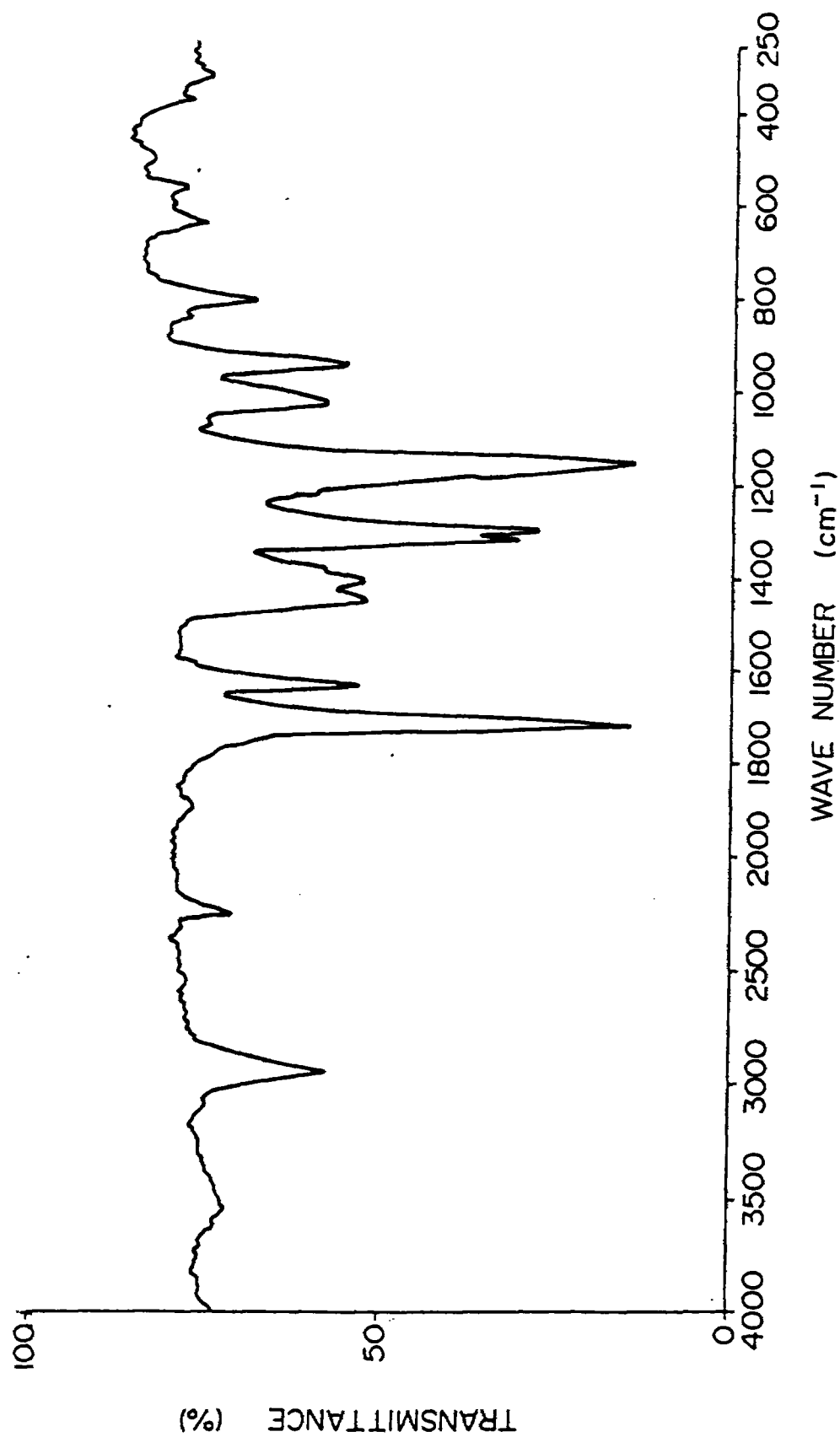
FIG. 5



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Date: 31 MAY 1999

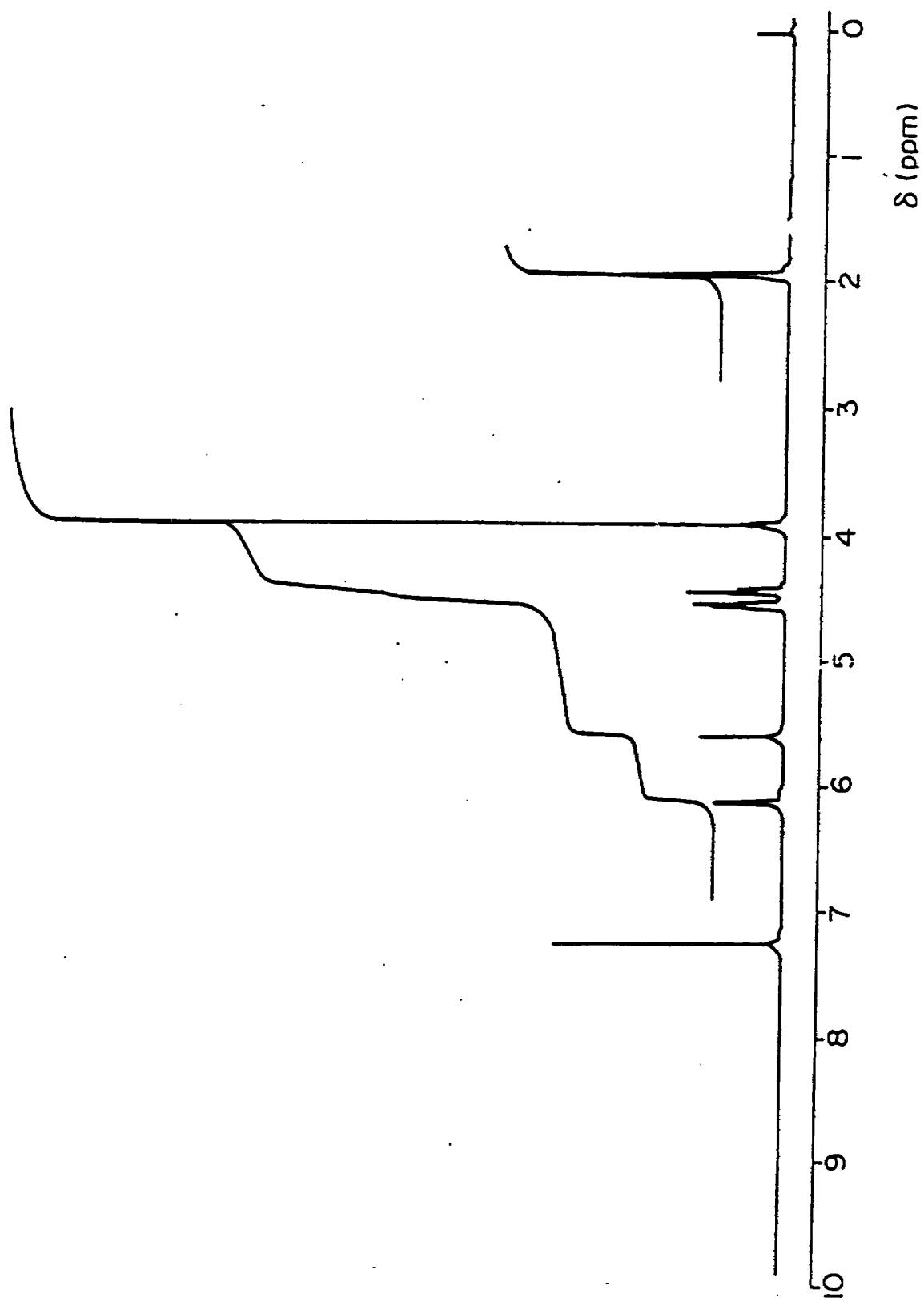
FIG. 6



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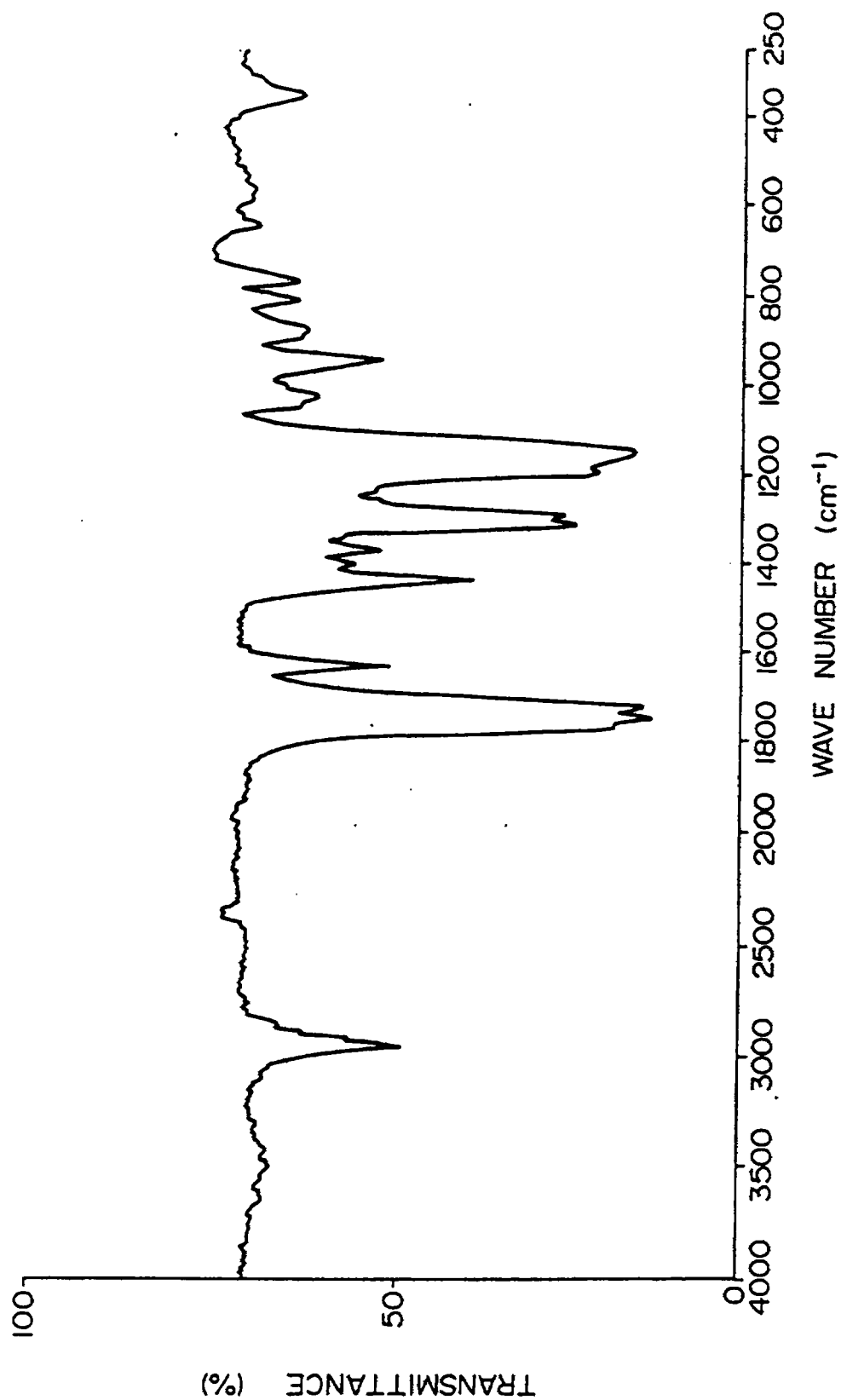
FIG. 7



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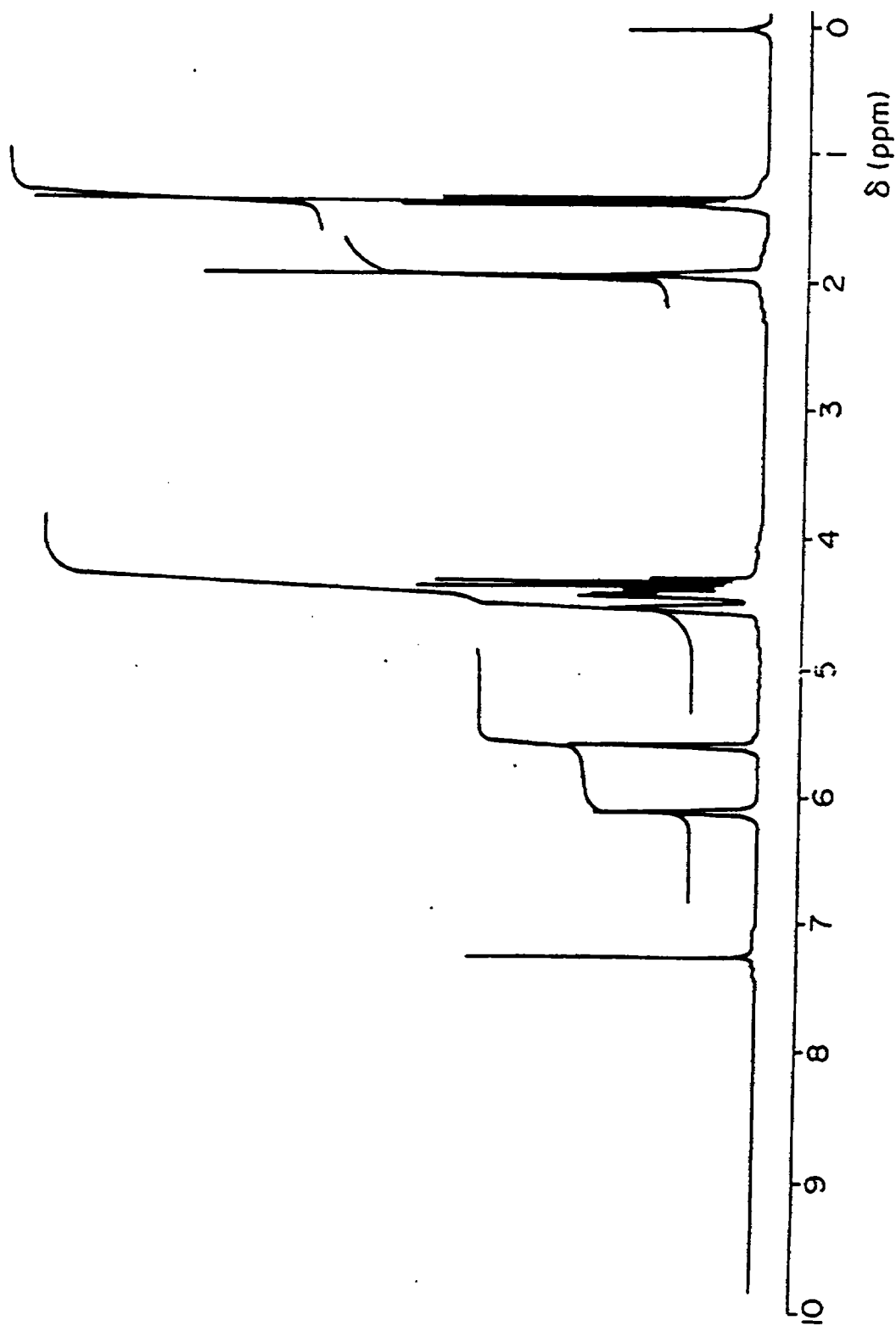
FIG. 8



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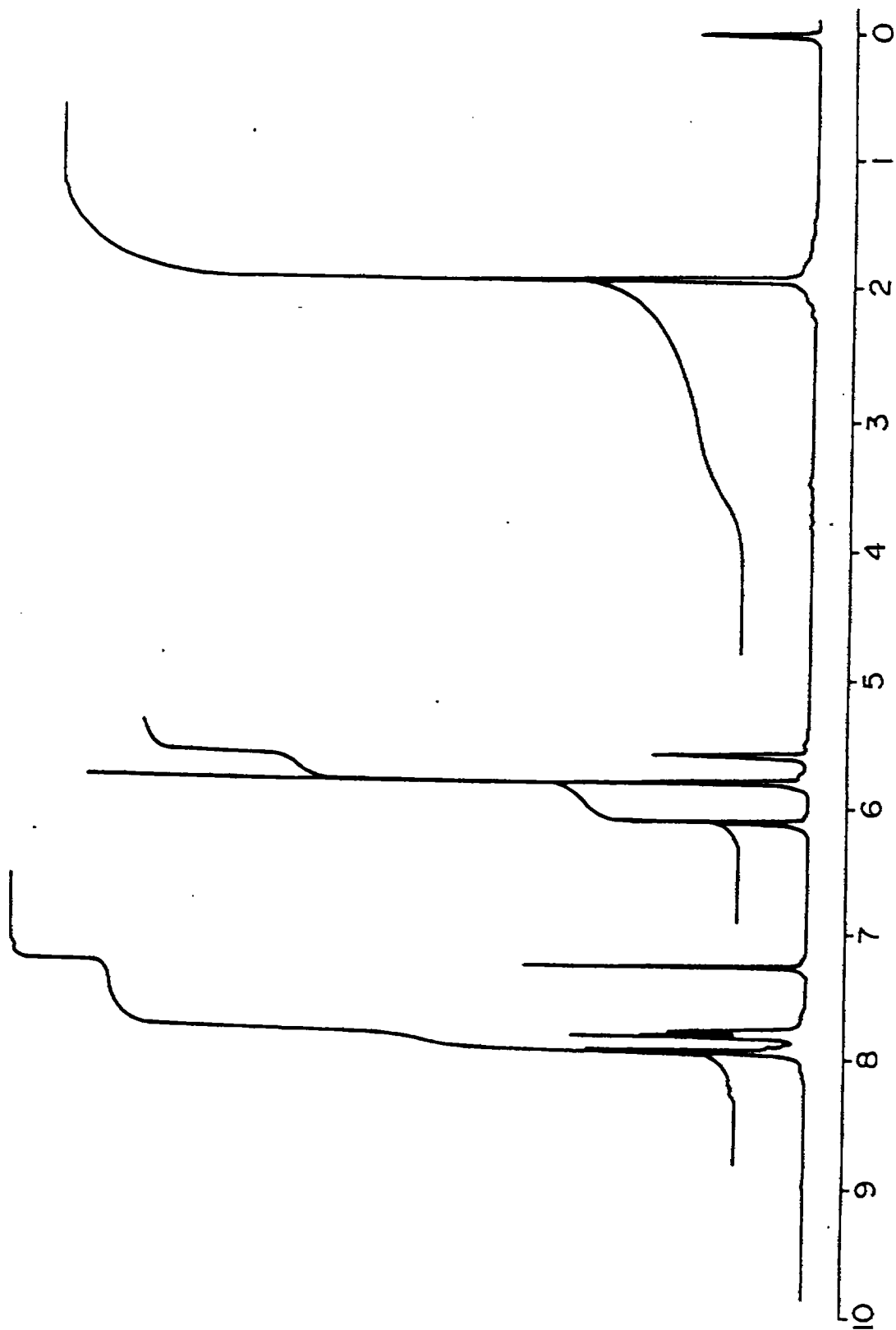
FIG. 9



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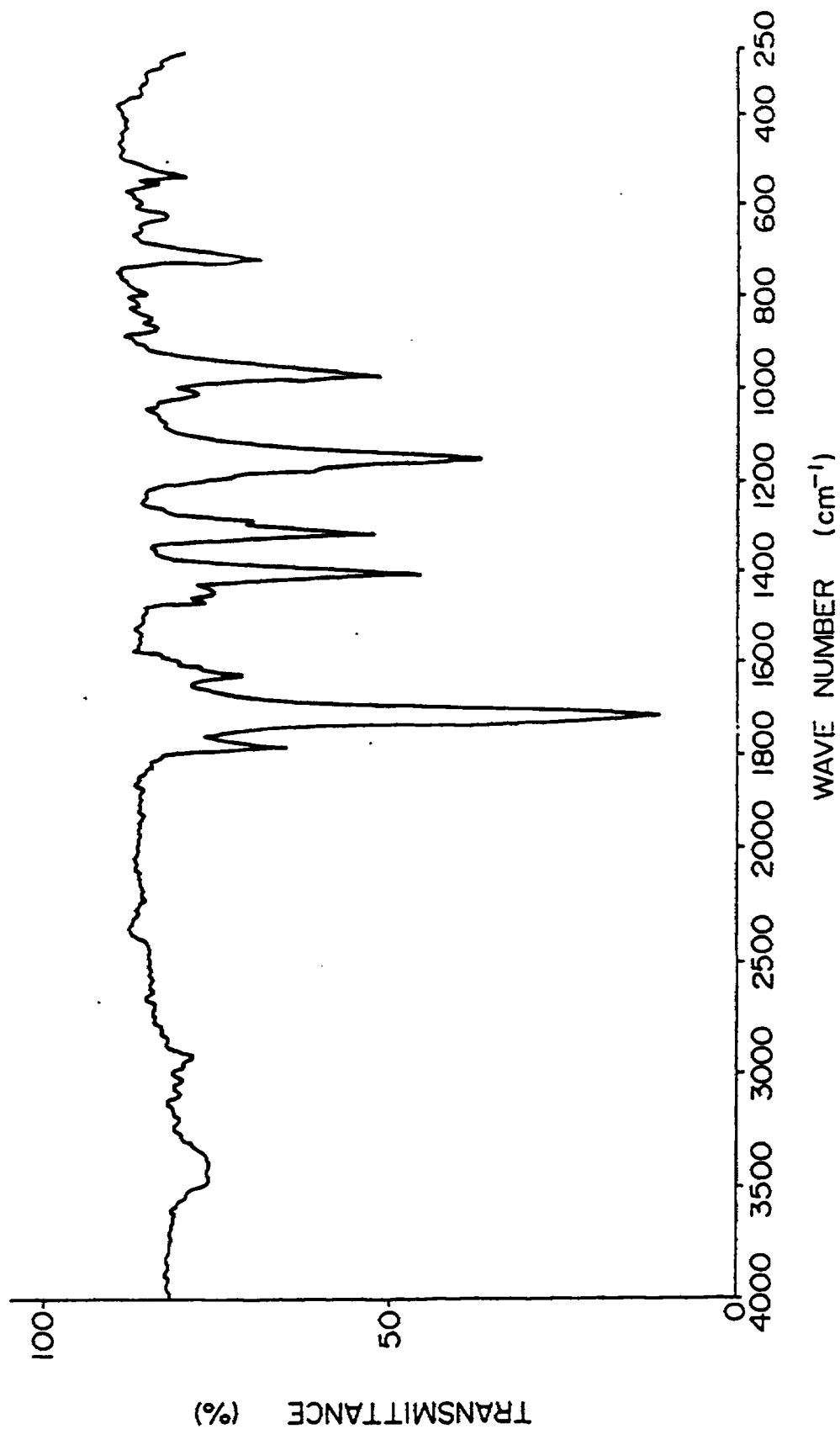
FIG: 10



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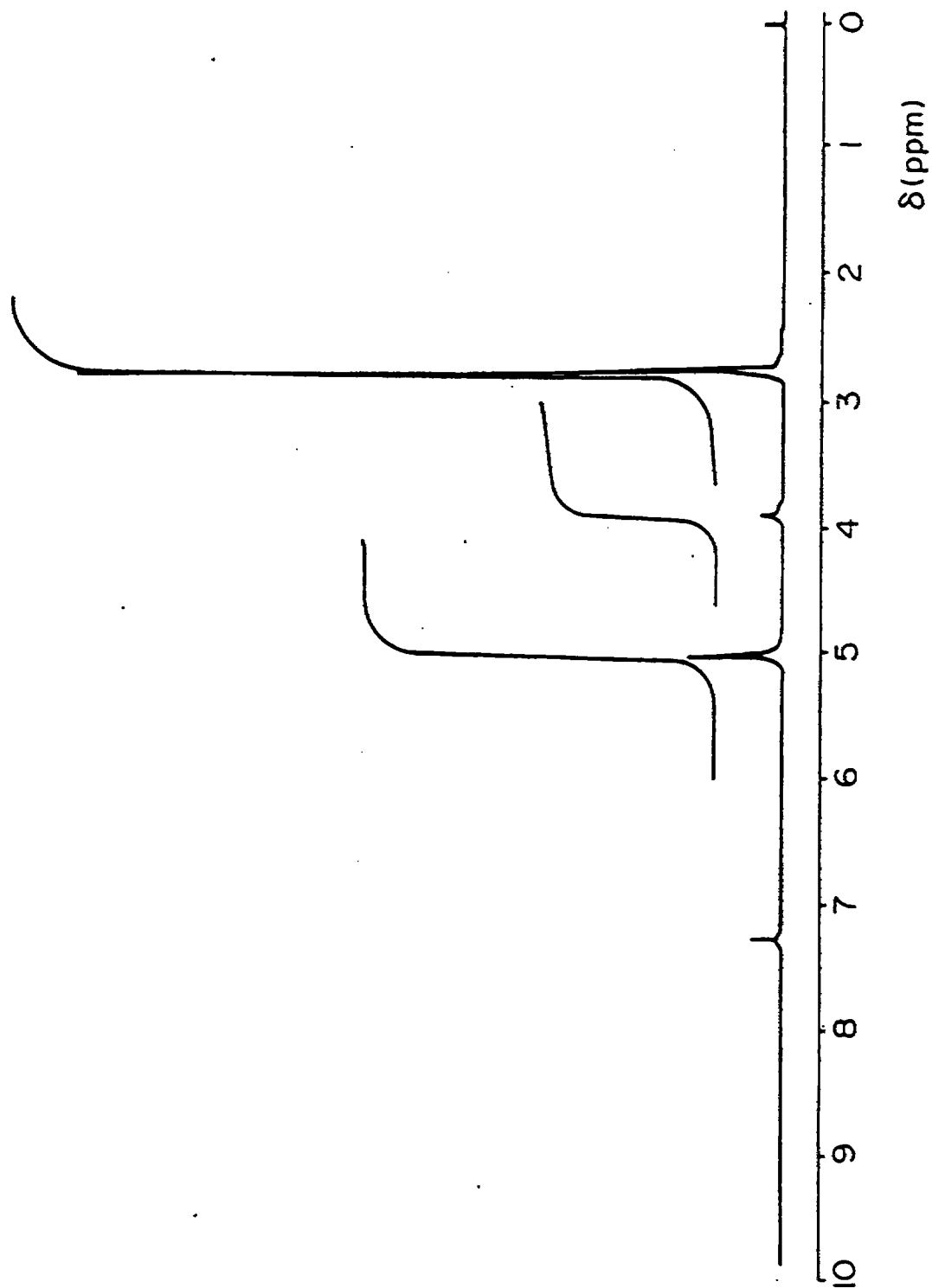
FIG. II



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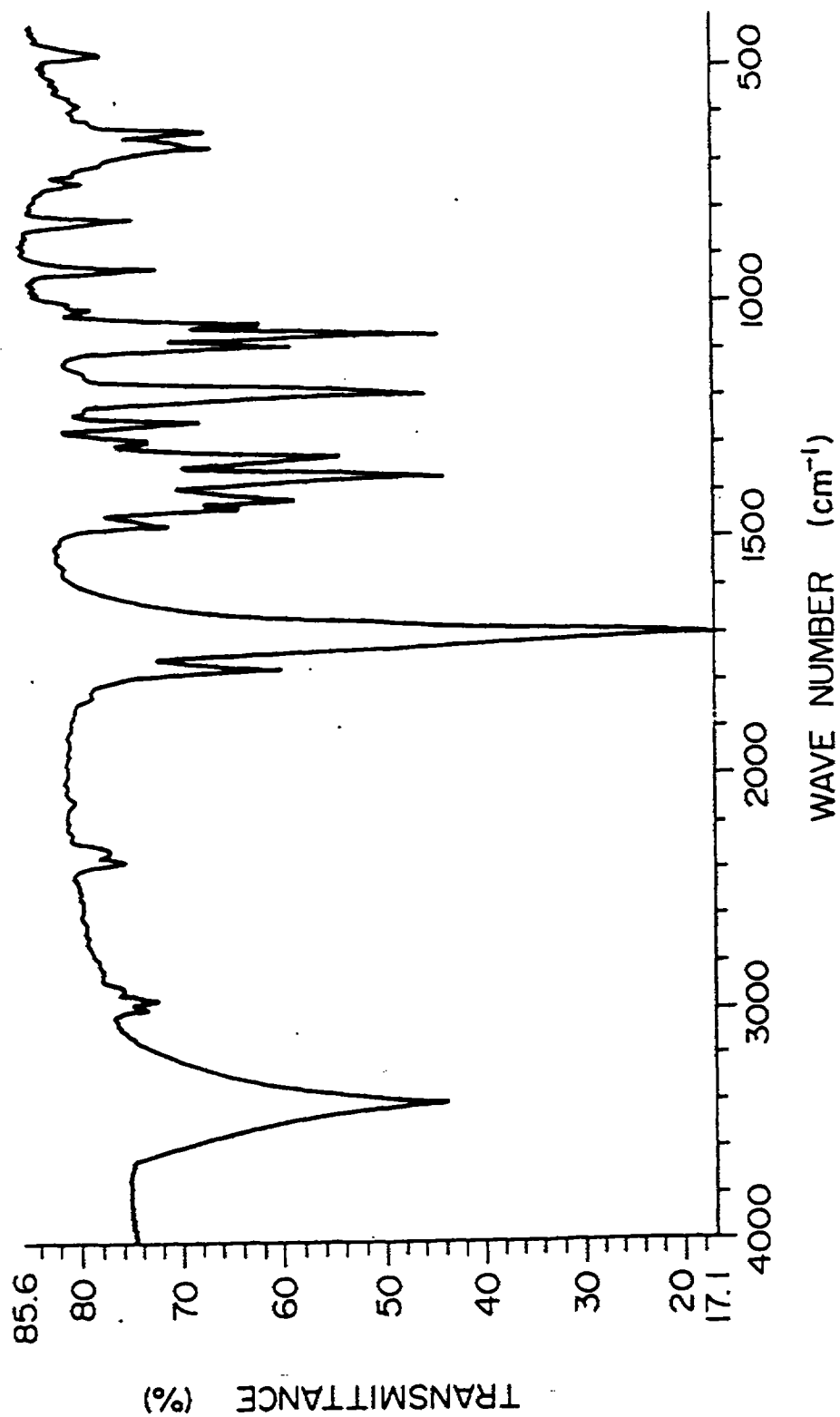
FIG. 12



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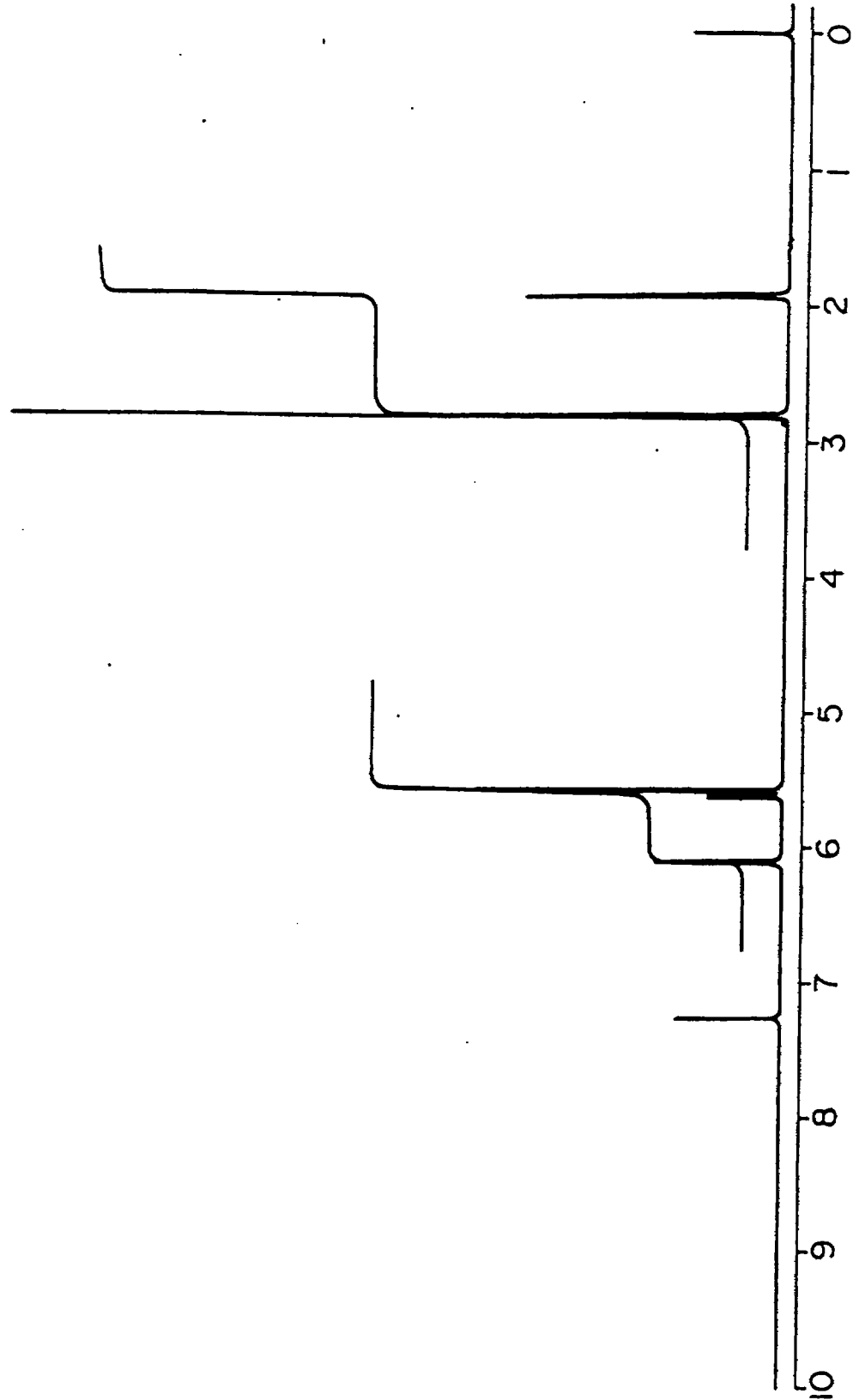
FIG. 13



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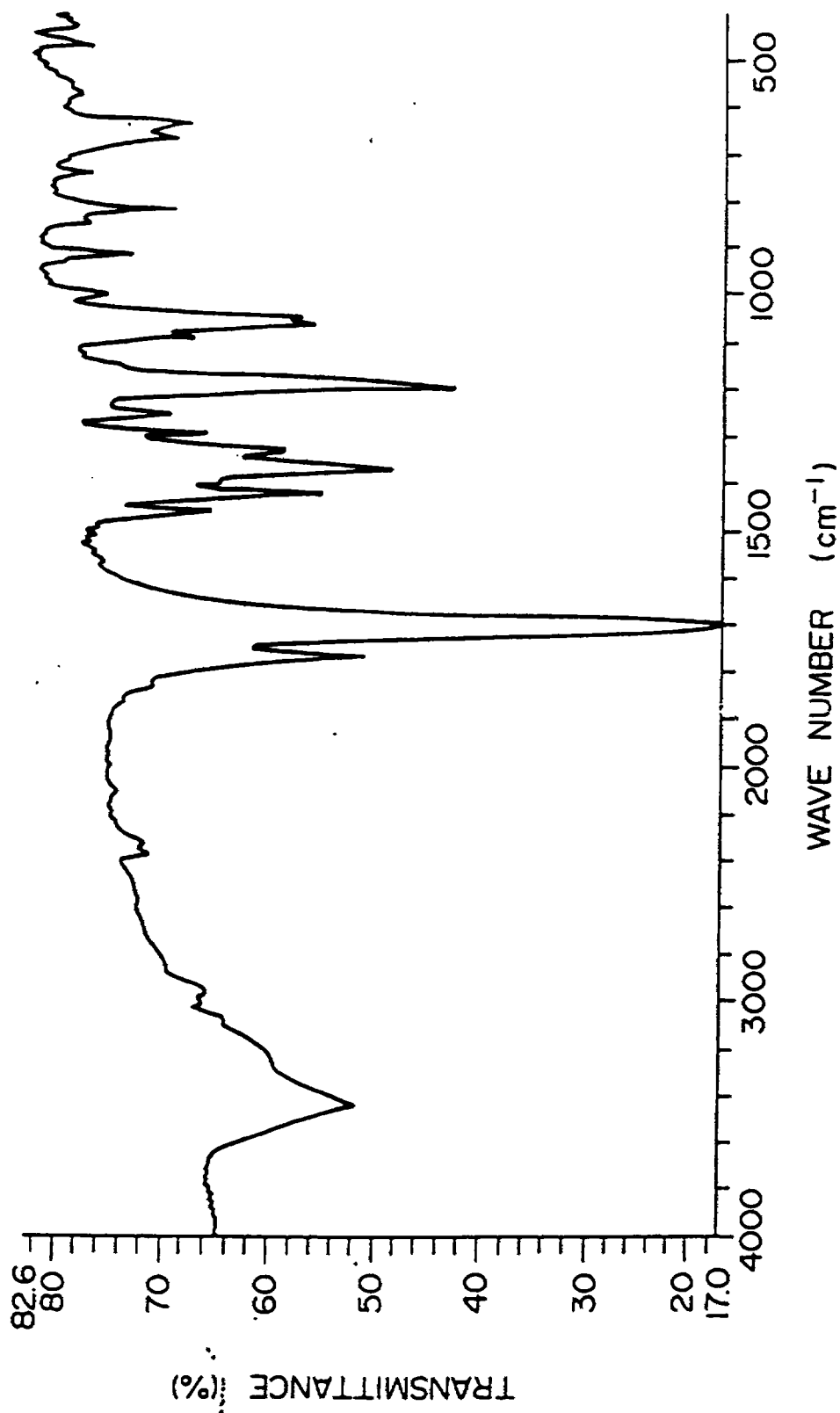
FIG. 14



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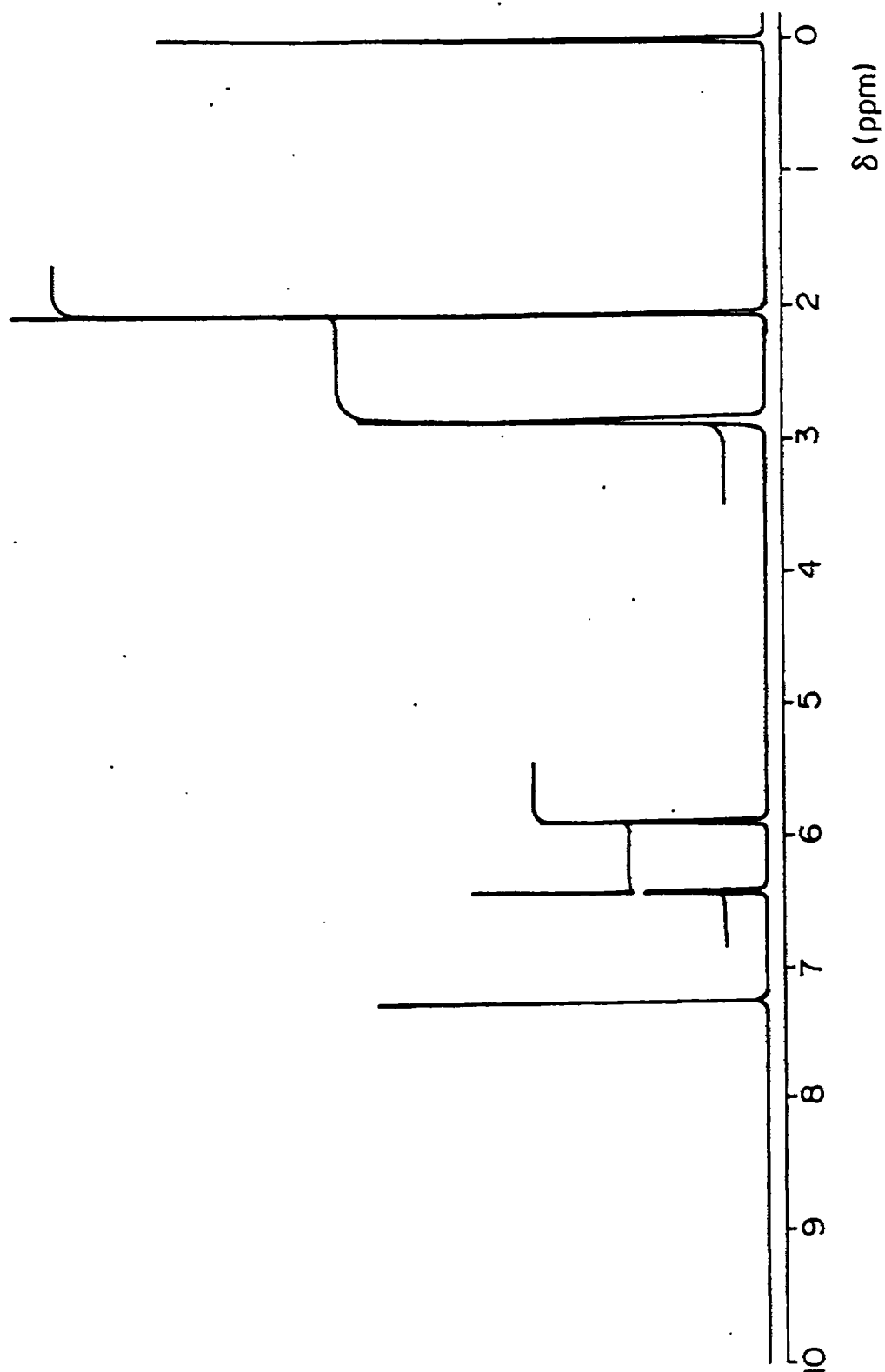
FIG. 15



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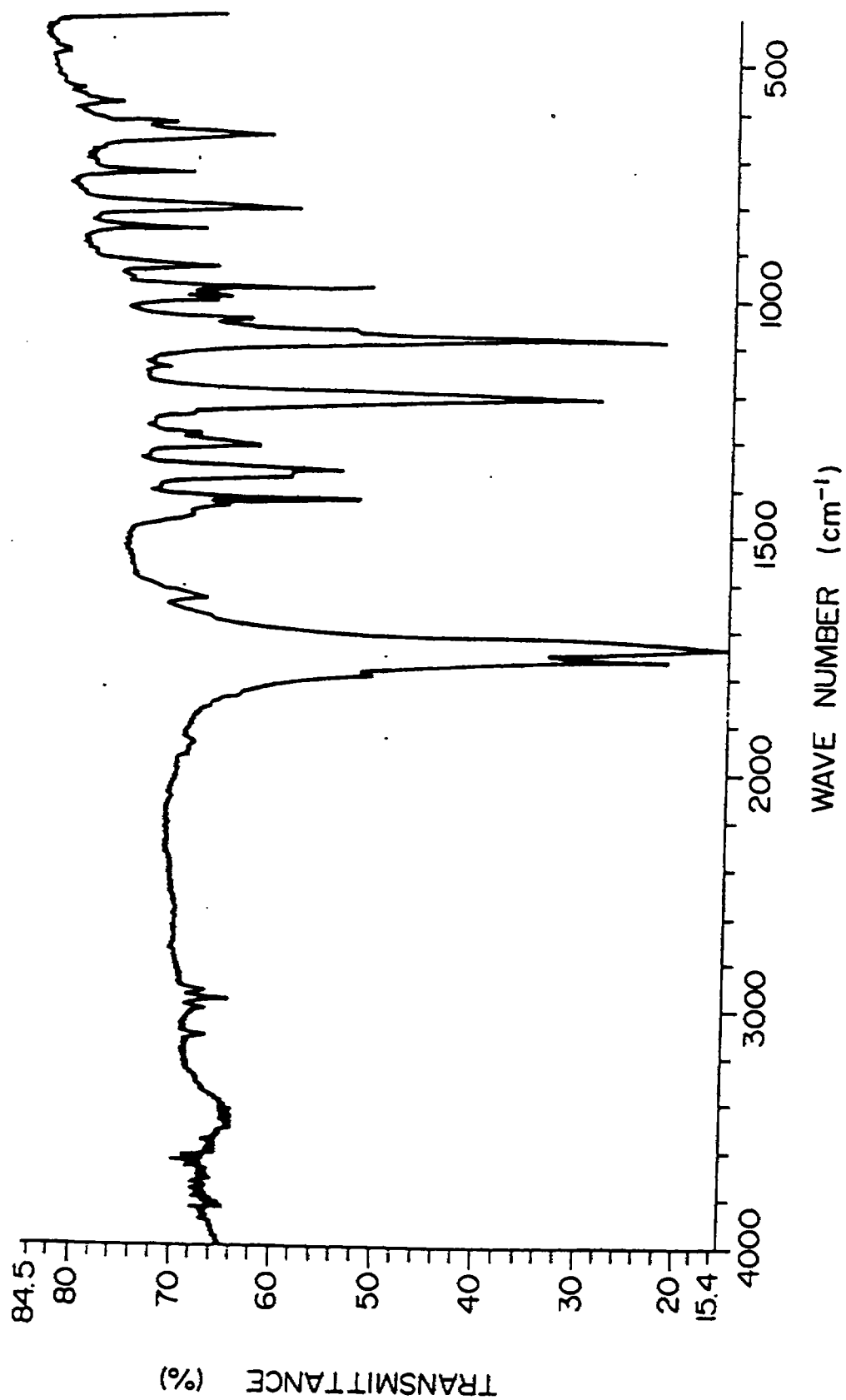
FIG. 16



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FIG. 17



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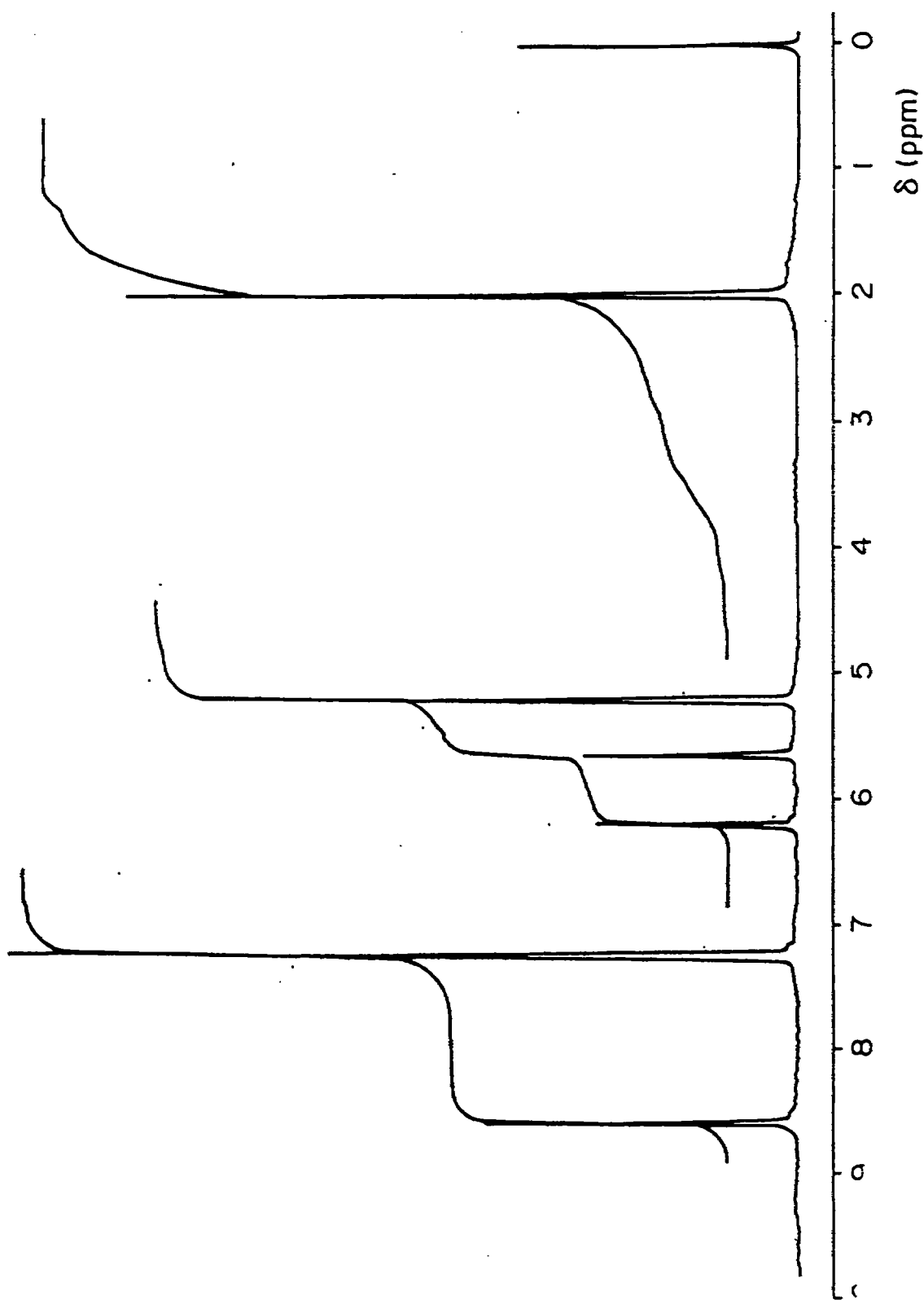
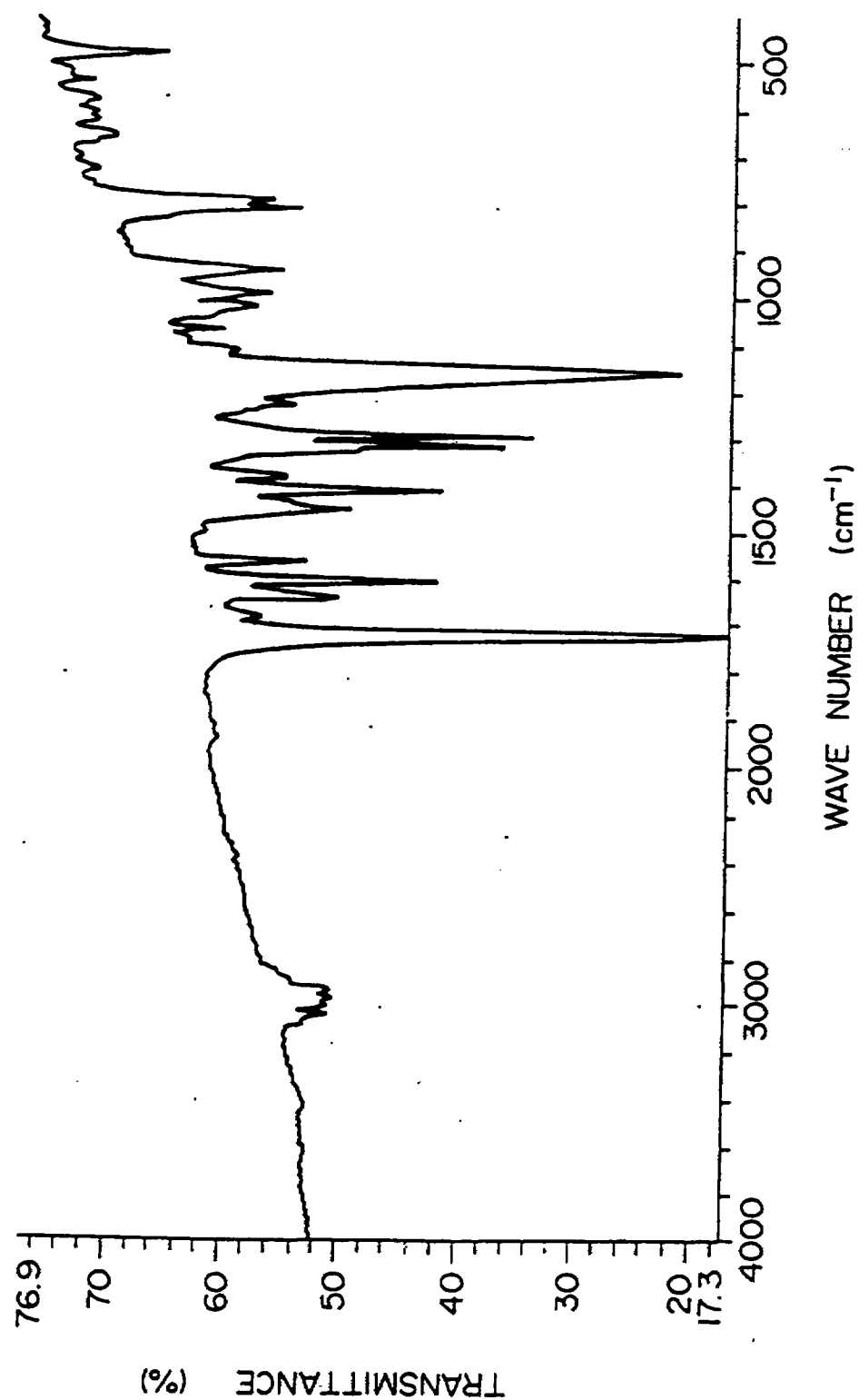


FIG. 18

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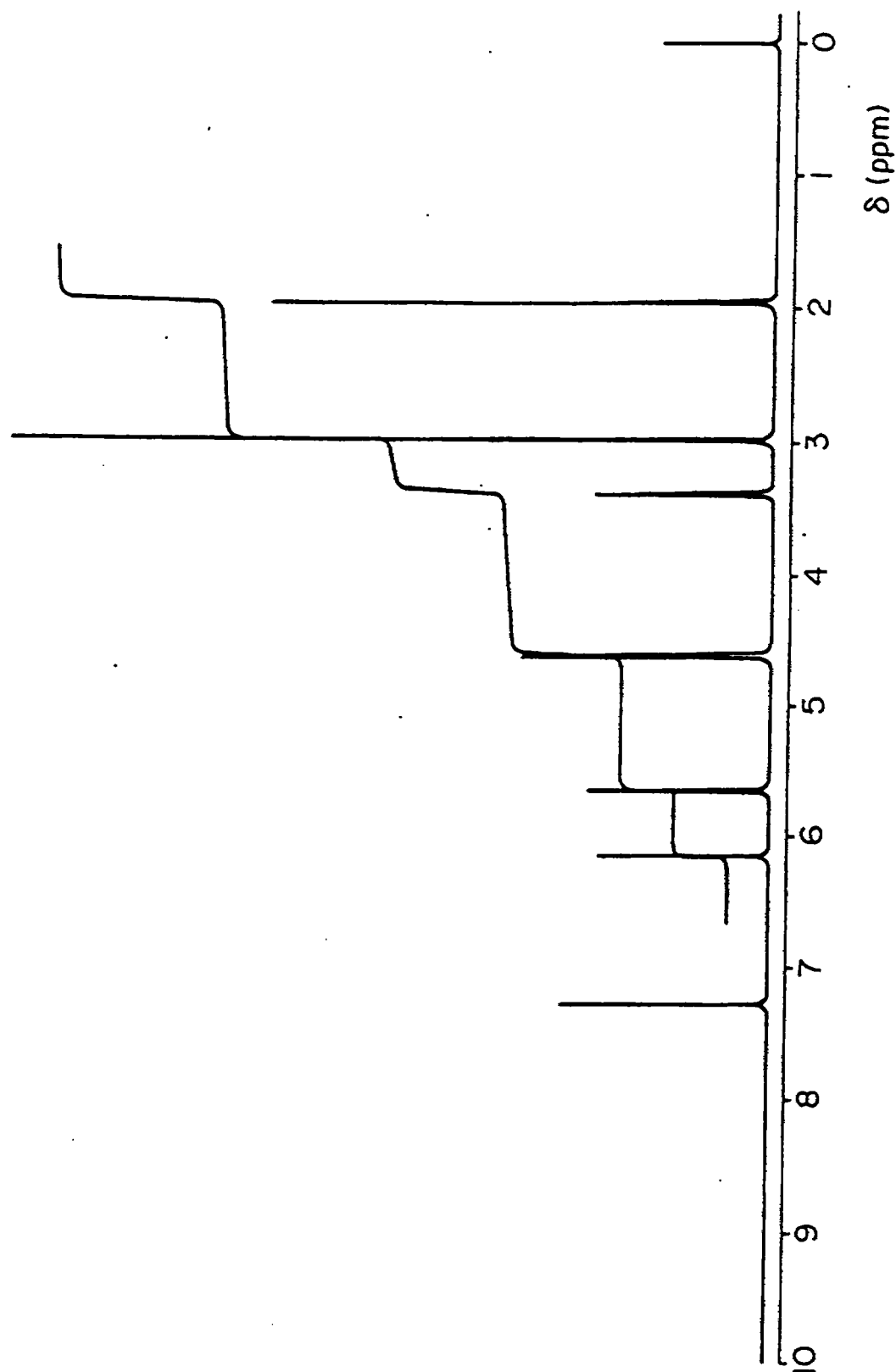
FIG. 19



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Date: 31 MAY 1999

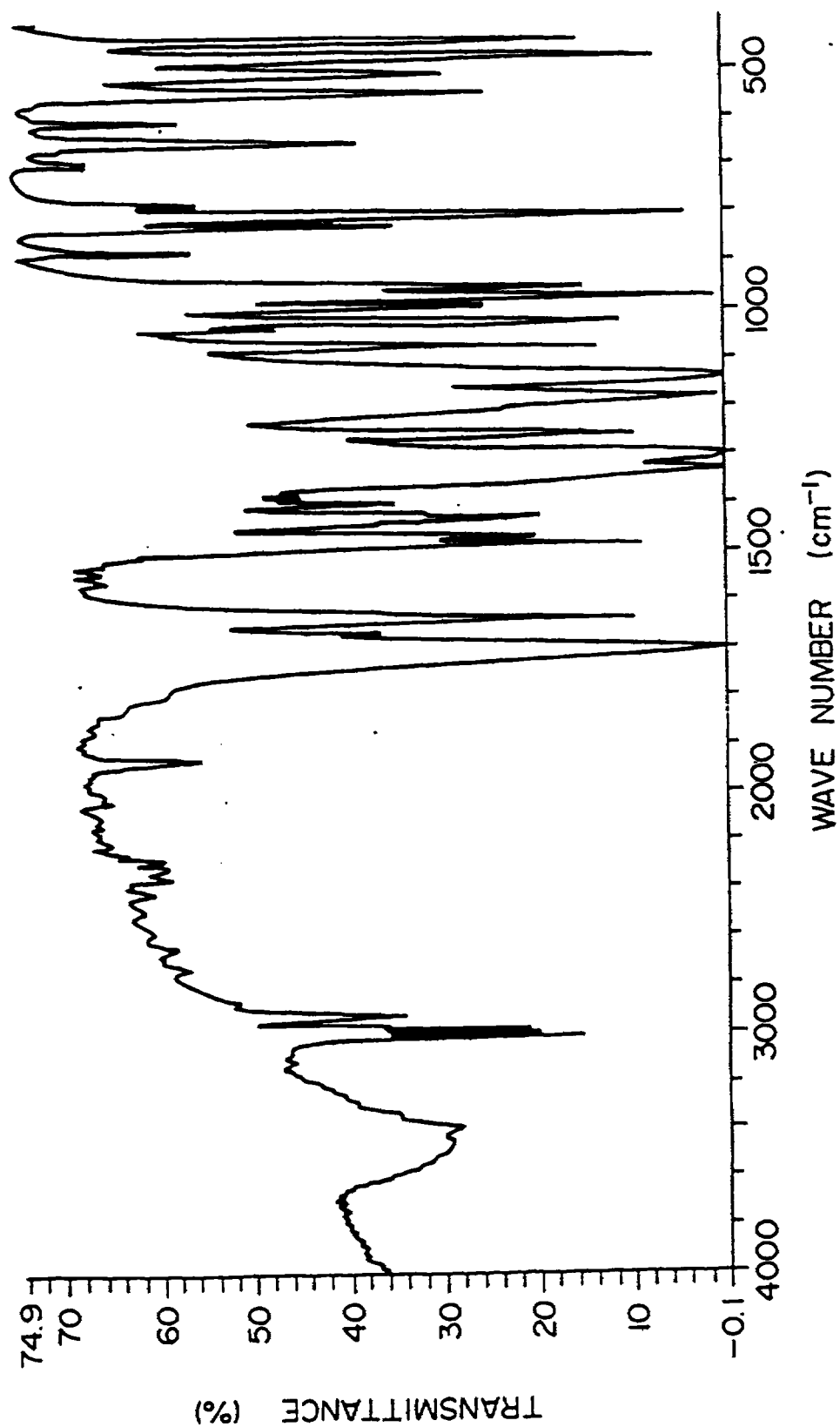
FIG. 20



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FIG. 21



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