

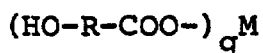
HYDROLYSABLE POLYESTER RESINS

This invention relates to a process for preparing hydrolysable polyester resins. Such resins, derived from polycarboxylic acids and polyhydric alcohols, have been widely used in coating compositions, owing to the excellent properties, including toughness, of the films which can be obtained therefrom. One reason for these properties is believed to be the resistance of the ester bond to hydrolysis, irrespective of the degree of polymerisation.

Recently, hydrolysable resins have been investigated, in view of the possibility of obtaining flat coatings, on hydrolysis in use, following the application of relatively rough coatings, e.g. on a ship's bottom. However, it has been difficult to reconcile the requirement of stability with decomposition in sea water, for hydrolysable polyester resins.

Polyesters are relatively soluble in water, owing to the presence of polar carboxyl groups. Having regard to the desire for resins which can hydrolyse in, for example, sea water, it would be desirable to produce a polyester which is relatively stable in water, but is gradually decomposed or hydrolysed, e.g. into low molecular fragments, under sailing conditions.

According to the present invention, a process for preparing a hydrolysable polyester resin comprises reacting a polycarboxylic acid with a hydroxycarboxylic acid salt of the formula



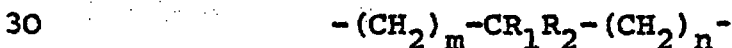
wherein R is an organic linking group and M is a metal of valency q , q being from 1 to 4, of any of the Periodic Table Groups Ia, Ib, IIa, IIb, IVb, VIIa and VIII, and, if q is 1, with a polyhydric alcohol.

A hydrolysable polyester resin of the invention can be hydrolysis-resistant under neutral conditions, but gradually decomposed or hydrolysed under weak alkaline conditions, i.e. the conditions found in sea water.

The polycarboxylic acid may be, for example, a straight-chain dicarboxylic acid such as oxalic acid, succinic acid, succinic anhydride, adipic acid, azelaic acid or sebacic acid; an aromatic acid such as phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic acid, hexahydrophthalic anhydride, tetrabromophthalic anhydride, trimellitic acid, trimellitic anhydride, pyromellitic acid or pyromellitic anhydride; or an unsaturated dicarboxylic acid such as maleic acid, maleic anhydride, fumaric acid or itaconic acid. If desired, a monocarboxylic acid such as benzoic acid, *p*-*t*-butylbenzoic acid, and various fatty acids of animal and vegetable fats and oils, may be added as molecular regulator.

The polycarboxylic acid may be reacted with a hydroxycarboxylic acid salt as defined alone or together with a polyhydric alcohol. In the hydroxycarboxylic acid salt, the R group may be a hydrocarbon residue optionally interspersed with COO or O groups. R may be saturated or unsaturated, straight or branched, aliphatic or aromatic.

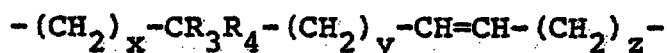
A preference for R is that it is C₁₋₃₈ alkylene. More preferably, R has the formula



wherein R₁ and R₂ are independently selected from hydrogen, C₁₋₁₀ alkyl and C₂₋₁₀ alkenyl, and m and n are each from 0 to 16. Preferably, R₁ and R₂ are

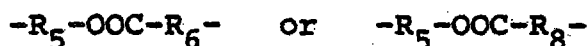
independently selected from hydrogen and C_{1-8} alkyl, and m and n are each from 0 to 10. A particularly preferred hydroxycarboxylic acid of this type is lactic, hydracrylic, 12-hydroxystearic or glycolic acid. These four acids are most preferred in the invention.

Again, R may be C_{2-38} alkenylene. For example, R may have the formula



wherein R_3 and R_4 are independently selected from hydrogen, C_{1-10} alkyl and C_{2-10} alkenyl, and x , y and z are each from 0 to 10. Preferably, R_3 and R_4 are independently selected from hydrogen and C_{1-8} alkyl, x is from 0 to 4 and y is from 0 to 6. A particularly preferred hydroxycarboxylic acid of this type is ricinoleic or ricinoelaidic acid.

Alternatively, R may be a residue of a half-ester of an aliphatic dicarboxylic acid. For example, R may have the formula



wherein R_5 is C_{1-8} alkylene or C_{4-8} alkylene interspersed with ether oxygen atoms, R_6 is optionally unsaturated C_{2-4} alkylene, and R_8 is a C_{6-7} saturated, unsaturated or aromatic cyclic hydrocarbon radical. Examples of hydroxycarboxylic acids of these types are half-esters of aliphatic dicarboxylic acids such as maleic anhydride, succinic anhydride, dimethyl maleic anhydride or dimethylsuccinic anhydride, and of aromatic dicarboxylic acids such as phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride or himic anhydride, with polyols such as ethylene glycol, propylene glycol, 1,3-butylenediol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, neopentyl glycol or triethylene glycol.

Many hydroxycarboxylic acid salts for use in the invention are known. If necessary, they can easily be prepared by reaction of the acid with the oxide, hydroxide or carbonate of the metal M.

5 The Periodic Table to which reference is made herein is, for example, that shown in Partington's "General and Inorganic Chemistry", 3rd edition. The metal may be of any of Groups Ia (e.g. Li, K, Na), Ib (e.g. Cu, Ag), IIa (e.g. Mg, Ca, Ba), IIb (e.g. Zn, Cd, 10 Hg), IVb (e.g. Sn, Pb), VIIa (e.g. Mn) and VIII (e.g. Fe, Co, Ni). The metal is preferably K, Na, Cu, Ag, Mg, Zn, Sn, Pb, Fe, Co and Ni, and particular preference is given to Na, Cu, Mg, Zn and Ni. When q , the valency of M, is 1, the polycondensation reaction must involve 15 a polyhydric alcohol in addition to the salt. When a polyhydric alcohol is used, it may be any of those generally used for the preparation of polyester resins, including glycols such as ethylene glycol, propylene glycol, 1,3-butylenediol, 1,6-hexanediol, diethylene 20 glycol, neopentyl glycol, dipropylene glycol or triethylene glycol, hydrogenated bisphenol A, bisphenol dihydroxypropyl ether, glycerol, trimethylolethane, trimethylolpropane and pentaerythritol.

 The polycondensation reaction involved in the 25 process of the invention is suitably conducted in an inert solvent, with or without a catalyst, at an elevated temperature, while removing water of reaction. The salt will usually be insoluble in ketones and other aromatic solvents, and it is therefore usually 30 preferred to add the salt to the polycarboxylic acid and to heat the mixture while removing the water of reaction. When an acid anhydride is used, the mixture may be merely heated and fused together. In order to avoid excessive local heating, an aromatic solvent 35 such as toluene or xylene may be used, the reaction

mixture being heated at around the melting point of the polycarboxylic acid. Next, a catalyst customarily used for the preparation of polyesters such as, for example, dibutyltin oxide or lithium naphthenate, is added, optionally with polyol or a solvent, and esterification is effected at an elevated temperature. At too high a temperature, the metal salt may decompose; therefore, the reaction should be carried out at a temperature lower than the decomposition temperature of the salt. Most of the given salts, with the exception of alkali metal salts, decompose at around 200°C or above; the reaction is preferably carried out at 160 to 180°C. The decomposition temperature can be considerably lower, as for Pb and Mn salts, and, therefore, the actual temperature should be selected in an optimum range depending on the type of metal salt used.

In an alternative procedure, a certain degree of polycondensation between polycarboxylic acid and polyhydric alcohol may be achieved before the desired amount of metal salt is added and esterification continued. As in conventional procedures for preparing polyester resins, modifications with fatty acids or resinous materials may be made.

The progress of polycondensation may be traced by checking the amount of water generated, and the acid value of the product produced. In order to obtain a polymer product for coating use, polymerisation is preferably stopped at a relatively early stage, thereby producing a lower molecular weight, solvent-soluble-type product. The degree of polycondensation, optimum molecular weight of the polymer, and control of the reaction are, however, obvious to those skilled in the art. After completion of the reaction, the mixture may be diluted with an organic solvent such as an aromatic hydrocarbon (e.g. toluene or xylene), a ketone (e.g. methyl ethyl ketone or methyl isobutyl

ketone), an ester (e.g. ethylene glycol monoethyl ether acetate, butyl acetate or ethyl acetate), an alcohol (e.g. n-butyl alcohol, isobutyl alcohol or sec-butyl alcohol), or an ether (e.g. 1,4-dioxan or tetrahydrofuran), or a mixture thereof, to the desired solids content; the product may be used as a resinous vehicle or varnish as it is,

According to the method of this invention, it is also possible to prepare a hydrolysable polyester having a higher molecular weight, which is likewise useful for coating purposes. Therefore, the term "polyester resin", as used herein, should be taken as including products with comparatively low molecular weight, e.g. a number-average molecular weight of about 500 to 10,000 (most preferably from 800 to 6000) which is particularly useful in coating compositions, and products with a far higher molecular weight.

The polyester resin produced according to the present invention is, regardless of its degree of polymerisation, characterised by having in the backbone a number of metal-ester bonds of the formula $-(COO)_M$. The resin can be inert to water under neutral condition but liable to hydrolysis, at the site of the metal-ester bonds, under weak alkaline conditions as in the soil and sea water, thereby liberating the metal ions and giving lower molecular, water-soluble polymer segments with carboxylic groups. This hydrolysis rate or, in other words, solubilisation rate, may vary with the nature of, and be directly proportional to the amount of, the metal salt, and with the acid and hydroxyl values of the polyester resin. It is also closely connected with the type of metal selected. For example, at an equivalent concentration, the hydrolysis rates may vary with the metals as follows:

Cu>Ni>Co>Zn>Mn>Mg>Ba>Ca

It seems that the hydrolysis rate is inversely proportional to the ionisation potential of the metal.

The polyester resins obtained in the invention can be used as a resin component in varnishes and coating compositions. With a number-average weight of the order of 500 to 10,000, the resin is usually soluble in common organic solvents such as toluene, xylene, tetrahydrofuran, methyl isobutyl ketone and butyl acetate, and is compatible with various other resinous solutions. The film-forming property of the polymer can be advantageously utilised in varnish and coating compositions. However, even if the polymer is insoluble in the given organic solvents because it has a higher molecular weight, the polymer can be dispersed or mixed with solvents or other film-forming resinous materials. In either case, the polyester per se can be very stable in neutral conditions, but gradually hydrolysed and decomposed under weak alkaline conditions.

In addition to the utility described above, where rough coatings including a resin of the invention are formed on a ship's bottom, and become smooth in use, thereby removing protruding portions and improving fuel economy and sailing speed, products of the invention can be used for other purposes. If a toxic substance can be liberated from a hull coating, it can be used to control marine organisms such as acorn shell. In the agricultural field, an active ingredient encapsulated in a capsule of the resin can be released slowly. On resin hydrolysis, metal is released as metal ion; for relatively toxic metals such as Cu, Pb, Zn or Sn, it can be used for controlling marine organisms while, if the metal is, say, Mg, Mn, Zn, Cu, Mo or Fe, it can be used as a plant growth promoter.

In general, a resin composition according to the invention, for use as a varnish or coating

composition, comprises an organic solvent and a hydrolyzable polyester resin prepared by the process of the invention. In formulating a resin composition of the invention, any conventional technique may be used. The solvent may be any of those exemplified above. However, since the solvent need not completely dissolve the resinous material, various other solvents employed in the coating area may be satisfactorily used. If desired, the solvent can be a monomer or other resinous varnish. It is of course possible to add conventional colouring matter, coating additives or the like to the composition of this invention. The resin composition can be formulated as a hull paint and, especially, an antifouling paint. For the economy of fuel consumption and maintenance of sailing speed, the paint may be formulated only with the ~~new~~ resin. However, for antifouling purposes, it is often desired or preferred to add an antifouling agent. Such agent may be of any type customarily used for the intended purpose; suitable examples are metallic copper, copper compounds (e.g. cupric hydroxide, cuprous oxide, cuprous thiocyanate), tributyltin compounds (e.g. bistrityltin oxide, tributyltin fluoride, tributyltin α, α' -dibromosuccinate), triphenyltin compounds (e.g. triphenyltin hydroxide, triphenyltin fluoride, triphenyltin chloride, triphenyltin α, α' -dibromosuccinate), and sulfur compounds (e.g. tetramethylthiuram disulfide, zinc dimethyldithiocarbamate, manganese ethylenebisdithiocarbamate, zinc ethylenebisdithiocarbamate). Of course, any conventional dissolving aid such as, for example, rosin, may be freely added thereto.

The amounts of the components in a resin composition of the invention may be chosen as desired, without affecting the film-forming properties of the resin. In contrast to known antifouling paints, the antifouling agent in a composition of the invention has

its effectiveness maintained as a result of the gradual hydrolysis.

The following Examples illustrate the invention, by comparison with Comparative Examples. Unless otherwise stated, all parts and percentages are by weight.

Example 1

Into a four-necked flask equipped with reflux condenser, decanter and stirrer, were placed 100 parts of copper 12-hydroxy stearate (abbreviated as CuHS), 245.5 parts of phthalic anhydride and 25 parts of toluene, and the mixture was heated to 100°C. Next, 191 parts of 1,6-hexanediol and 1 part of dibutyltin oxide (catalyst) were added, the mixture was heated under nitrogen stream to 160°C and the polycondensation reaction was continued, while removing the formed water, for 8 hours. With the progress of the reaction, the temperature of the system increased; the final temperature was 180°C. Thereafter, the reaction mixture was allowed to cool to 110°C and diluted with 263 parts of methyl isobutyl ketone to obtain a dark-green varnish whose properties are given in Table 1 (the acid value was determined by titration with 0.5N KOH/methanol, using Methyl Red as indicator). The solvent was removed from the varnish to obtain a solid polyester resin, whose properties are tabulated below (Tg was measured by using TMA-30 manufactured by Shimazu Seisakusho).

Example 2

Using the same procedure as in Example 1, 100 parts of CuHS and 41 parts of phthalic anhydride were reacted at 160°C in 10 parts of xylene in the presence of 0.2 parts of dibutyltin oxide under a nitrogen stream. Thereafter, the reaction mixture was diluted with 50 parts of tetrahydrofuran to obtain a dark-green varnish.

Example 3

The procedure of Example 1 was repeated, but

using 101 parts of zinc 12-hydroxy stearate, 246 parts of phthalic anhydride, 166.4 parts of neopentyl glycol, 25 parts of toluene, 1 part of dibutyltin oxide and 236 parts of methyl isobutyl ketone (as diluent) to obtain a clear varnish.

Example 4

The procedure of Example 1 was repeated, but using 38 parts of copper lactate, 245.5 parts of phthalic anhydride, 215 parts of dipropylene glycol, 25 parts of toluene, 1 part of dibutyltin oxide and 189 parts of methyl isobutyl ketone, to obtain a dark-green varnish.

Example 5

The procedure of Example 1 was repeated, but using 46 parts of zinc lactate, 148 parts of phthalic anhydride, 95 parts of adipic acid, 36 parts of trimethylolethane, 128 parts of 1,3-butylenediol, 25 parts of toluene, 1 part of dibutyltin oxide and 205 parts of methyl isobutyl ketone (diluent), to obtain a clear varnish.

Example 6

The procedure of Example 1 was repeated, but using 253 parts of phthalic anhydride, 24 parts of copper lactate, 50.4 parts of pentaerythritol, 105.4 parts of neopentyl glycol, 1 part of dibutyltin oxide and 370 parts of methyl isobutyl ketone, to obtain a dark-green varnish.

Example 7

The procedure of Example 1 was repeated, but using 263.3 parts of hexahydrophthalic anhydride, 28 parts of magnesium lactate, 4.5 parts of sodium lactate, 50.4 parts of pentaerythritol, 105.4 parts of neopentyl glycol, 1 part of dibutyltin oxide and 200 parts of methyl isobutyl ketone, to obtain a clear varnish.

Example 8

The procedure of Example 1 was repeated, but using 253 parts of phthalic anhydride, 83 parts of the

magnesium salt of mono(hydroxyhexyl)phthalate, 50.4 parts of pentaerythritol, 105.4 parts of neopentyl glycol, 1 part of dibutyltin oxide and 345 parts of methyl isobutyl ketone, to obtain a clear varnish.

5 Example 9

The procedure of Example 8 was repeated, but using, in place of 83 parts of the magnesium salt, 90 parts of the corresponding zinc salt, to obtain a clear varnish.

10 Comparative Examples 1 and 2

According to the procedures of Example 1, two comparative varnishes were prepared by using (1) 58.1 parts of phthalic anhydride, 12.1 parts of neopentyl glycol, 9.6 parts of 1,6-hexanediol and 20.5 parts of
15 trimethylolethane; and (2) 54.9 parts of phthalic anhydride and 50.1 parts of 1,6-hexanediol.

Comparative Example 3

Into a solution of 50 parts of methyl methacrylate and 50 parts of tributyltin methacrylate in 100
20 parts of toluene, was added dropwise an initiator solution containing 0.8 parts of benzoyl peroxide at 90°C over 3 hours. The resultant varnish is not of the polyester type, but is a conventional hydrolysable acrylic resin.

25 Onto a glass plate (60 mm x 50 mm), the varnish of each of the preceding Examples was applied to give 100 μ dry thickness and heated at 105°C for 3 hours. The total (initial) weight was measured. Thereafter, the glass plate was dipped into 350 cc of an aqueous
30 alkaline solution (pH 10) and maintained therein at 40°C for 18 hours. The glass plate was taken out of the bath, washed with water, dried and weighed again. The hydrolysis rate was calculated as the ratio of the loss in weight to the initial weight. The test results
35 are shown in Table 1.

Example 10

Using the same apparatus as in Example 1, a mixture of 30 parts of xylene, 112 parts of CuHS, 48 parts of phthalic anhydride and 70.5 parts of azelaic acid was heated to 100 to 110°C and maintained at the same temperature for 30 minutes. Thereafter, 56.5 parts of neopentyl glycol, 13 parts of trimethylpropane and 0.6 parts of dibutyltin oxide were added, and the dehydration reaction was carried out under the same conditions as in Example 1. After completion of the reaction, the mixture was allowed to cool to 110°C. A mixture of xylene/n-butanol (9/1) was added, to obtain a varnish.

Example 11

Using the same apparatus as in Example 1, a mixture of 30 parts of xylene, 90 parts of CuHS, 120.5 parts of adipic acid, and 0.6 parts of dibutyltin oxide was heated to 160°C. The dehydration was carried out for 2 hours and the mixture was allowed to cool to 120°C. Thereafter, 44 parts of diethylene glycol, 39 parts of neopentyl glycol and 6.5 parts of trimethylolethane were added and the mixture was heated to 160°C and the dehydration was carried out for 10 hours. The reaction temperature was maintained at 160 to 180°C. After completion of the reaction, the mixture was allowed to cool to 100°C. Xylene was added to obtain a varnish.

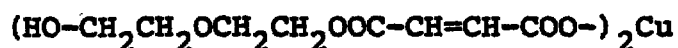
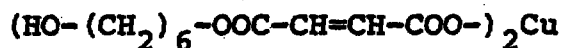
Table 1

Example	Solids Content (%)	Gardner Viscosity	Acid Value of solids	Tg (°C)	Number av. m. wt.	Hydrolysis rate
1	62.7	G	9.7	-5	1400	0.32
2	68.8	P	9.5	25	1200	0.30
3	65.4	J	9.6	10	1400	0.28
4	69.8	N	9.9	15	1300	0.30
5	65.3	V	10.0	35	2900	0.25
6	50.3	T	9.6	50	3500	0.24
7	65.3	S	9.7	55	2300	0.20
8	55.4	U	9.4	65	3600	0.22
9	54.8	U	9.6	70	3500	0.23
10	50.4	N		12	4200	
11	59.8	P		10	2600	
C1	50.4	P	9.7			0.00
C2	65.3	J	9.7			0.00
C3	50.4	N				0.16

Examples 12 to 49

Using the procedure of Example 1, 8, 10 or 11, with the materials shown in Table 2, various varnishes (V-12 to 49) were prepared. Their hydrolysis rates were determined and shown in Table 2. In these examples, a mixture of xylene and n-butanol (8/2) was used as a dilution solvent to adjust the percentage solids, as shown in the Table.

For Examples 40 to 49, Cu mono(hydroxyhexyl)-maleate, Cu mono(hydroxydiethyl ether) maleate and Cu mono(hydroxydiethyl ether) succinate are:



15
Table 2

Example No.	12	13	14	15	16	17
Raw materials used						
Cu 12-HO stearate	23.1	29.1	37.2	42.8	42.8	30.5
Zn 12-HO stearate						
Na 12-HO stearate						
phthalic anhydride	46.5	43.6	39.7	36.9	18.4	46.0
succinic anhydride						
maleic anhydride						
hexahydro phth.anhyd.						
adipic acid					18.3	
azelaic acid						
trimethylolethane						4.3
trimethylolpropane	5.2	4.9	4.4	4.1	4.1	
ethylene glycol						6.3
neopentyl glycol	25.2	22.4	18.7	16.2		12.9
diethylene glycol					16.4	
benzoic acid						
dibutyl tin oxide	0.2	0.2	0.2	0.2	0.2	0.2
method of Example	1	1	1	1	10	1
varnish No.	V-12	V-13	V-14	V-15	V-16	V-17
molecular weight	4400	3800	4200	4600	5000	3200
T _g	15°C	10°C	18°C	20°C	20°C	-5°C
viscosity/solid %	P/55.4	S/60.5	R/61.2	Q/49.8	O/51.3	T/58.8
hydrolysis rate	0.08	0.11	0.18	0.22	0.24	0.12

Table 2
(continued)

Example No.	18	19	20	21	22	23
Raw materials used						
Cu 12-HO stearate	28.9	33.1	34.5	45.2	39.4	
Zn 12-HO stearate						37.7
Na 12-HO stearate						
phthalic anhydride						
succinic anhydride	5.3	5.0	31.4	27.4		18.9
maleic anhydride						
hexahydro phth.anhyd.					36.7	
adipic acid	37.2	35.5				13.8
azelaic acid						
trimethylolethane	2.1	2.0	2.5	2.2	1.9	2.2
trimethylolpropane						
ethylene glycol						
neopentyl glycol						7.4
diethylene glycol	26.5	24.4	31.6	25.2	22.0	20.0
benzoic acid						
dibutyl tin oxide	0.2	0.2	0.2	0.2	0.2	0.2
method of Example	10	10	1	1	1	10
varnish No.	V-18	V-19	V-20	V-21	V-22	V-23
molecular weight	2800	4400	4200	4200	4100	3800
T _g	10°C	15°C	15°C	25°C	20°C	10°C
viscosity/solid %	S/59.2	R/54.8	L/51.3	N/50.5	N/51.0	M/49.3
hydrolysis rate	0.14	0.18	0.18	0.25	0.20	0.18

Table 2

(continued)

Example No.	24	25	26	27	28	29
Raw materials used						
Cu 12-HO stearate			41.5	28.1	23.7	32.4
Zn 12-HO stearate	30.1	30.0				
Na 12-HO stearate						
phthalic anhydride	20.4	18.4				
succinic anhydride			26.2		38.1	34.6
maleic anhydride			5.0			
hexahydro phth.anhyd.						
adipic acid	19.9	18.0		12.4		
azelaic acid				31.9		
trimethylolethane	2.1	1.9	2.5	2.0		
trimethylolpropane						
ethylene glycol			8.1			
neopentyl glycol		28.1		12.0		
diethylene glycol	27.5		16.7	13.5	38.2	33.0
benzoic acid		3.6				
dibutyl tin oxide	0.2	0.2	0.2	0.2	0.2	0.2
method of Example	10	10	1	11	1	1
varnish No.	V-24	V-25	V-26	V-27	V-28	V-29
molecular weight	3200	1300	5000	2800	1300	1600
Tg	5°C	5°C	25°C	12°C	0°C	5°C
viscosity/solid %	L/52.3	L/60.8	R/49.2	N/61.1	G/60.4	L/61.5
hydrolysis rate	0.16	0.28	0.18	0.10	0.29	0.31

18
Table 2
(continued)

Example No.	30	31	32	33	34
Raw materials used					
Cu 12-HO stearate	31.4		19.4	39.6	35.2
Ni 12-HO stearate		20.4			
Na 12-HO stearate			5.7		
phthalic anhydride		47.0	44.0		40.2
succinic anhydride	27.3			31.7	
maleic anhydride					
hexahydro phth.anhyd.					
adipic acid	9.3				
azelaic acid					
trimethylolethane					
trimethylolpropane					
ethylene glycol					
neopentyl glycol					24.6
diethylene glycol	32.0	32.6	30.9	28.7	
benzoic acid					
dibutyl tin oxide	0.2	0.2	0.2	0.2	0.2
method of Example	10	1	1	1	1
varnish No.	V-30	V-31	V-32	V-33	V-34
molecular weight	1100	1100	880	1200	1600
Tg	-5°C	5°C	-5°C	8°C	5°C
viscosity/solid %	G/60.1	J/58.4	C/61.2	H/60.2	J/59.3
hydrolysis rate	0.32	0.21	0.28	0.30	0.28

Table 2

(continued)

Example No.	35	36	37	38	39
Raw materials used					
Cu.mono(hydroxyhexyl) maleate					
Cu.mono(hydroxydiethyl ether) maleate					
Cu.mono(hydroxydiethyl ether) succinate					
Cu ricinoleate		31.3	34.2	33.8	41.1
Zn ricinoleate	20.3				
adipic acid		9.3			
phthalic anhydride	47.1				9.2
succinic anhydride		27.4	31.7	34.2	25.0
trimethylol ethane			2.5		4.7
trimethylol propane				5.7	
neopentyl glycol				15.3	15.7
diethylene glycol	32.6	32.0	31.6	11.0	4.3
dibutyl tin oxide	0.2	0.2	0.2	0.2	0.2
method of Example	1	10	1	1	1
varnish No.	V-35	V-36	V-37	V-38	V-39
molecular weight	1100	1200	4400	4200	2800
Tg	2°C	-7°C	8°C	5°C	0°C
viscosity/solid %	H/61.3	F/58.6	K/50.2	L/49.8	O/56.3
hydrolysis rate	0.17	0.28	0.15	0.14	0.28

20
Table 2
(continued)

Example No.	40	41	42	43	44	45
Raw materials used						
Cu.mono(hydroxyhexyl) maleate	24.3	21.2				
Cu.mono(hydroxydiethyl ether) maleate			30.3	30.8		
Cu.mono(hydroxydiethyl ether) succinate					23.0	21.1
Cu ricinoleate						
Zn ricinoleate						
adipic acid						
phthalic anhydride	43.7					
succinic anhydride		36.8	33.0	34.8	36.5	40.3
trimethylol ethane			2.6		2.9	6.1
trimethylol propane	2.5	3.2				
neopentyl glycol	15.4	19.2	22.4	23.9	24.7	16.7
diethylene glycol	14.1	19.6	11.7	10.5	12.9	15.8
dibutyl tin oxide	0.2	0.2	0.2	0.2		
method of Example	8	8	8	8	8	8
varnish No.	V-40	V-41	V-42	V-43	V-44	V-45
molecular weight	3200	3400	3700	920	3800	5200
Tg	5°C	7°C	5°C	-10°C	10°C	12°C
viscosity/solid %	M/54.3	L/55.8	L/54.2	L/60.3	N/56.3	R/50.3
hydrolysis rate	0.25	0.22	0.14	0.24	0.10	0.07

33

21
Table 2
(continued)

Example No.	46	47	48	49
Raw materials used				
Cu.mono(hydroxyhexyl) maleate				
Cu.mono(hydroxydiethyl ether) maleate			8.4	
Cu.mono(hydroxydiethyl ether) succinate	18.3	24.5	16.8	21.6
Cu ricinoleate				7.5
Zn ricinoleate				
adipic acid				
phthalic anhydride		13.3		
succinic anhydride	41.0	27.6	37.6	34.3
trimethylol ethane				2.7
trimethylol propane				
neopentyl glycol	16.1	12.6	14.7	33.9
diethylene glycol	24.6	22.0	22.5	
dibutyl tin oxide				
method of Example	8	8	8	8
varnish No.	V-46	V-47	V-48	V-49
molecular weight	1000	980	1200	3600
Tg	-5°C	-10°C	0°C	5°C
viscosity/solid %	N/61.2	H/58.3	I/60.3	S/60.4
hydrolysis rate	0.12	0.19	0.20	0.17

Examples 50 to 54 and Comparative Examples 4 and 5

Using the resinous varnishes obtained in Examples 1 to 5, and following the prescriptions given in the following Table 3, antifouling paints 1 to 5 of the present invention were prepared. For comparison, a commercialised, insoluble matrix-type antifouling paint (Comparative Example 4) and an antifouling paint based on Comparative Example 3 (Comparative Example 5) were prepared, as shown in the same Table. Onto a sand-blasted steel plate previously coated with an anti-corrosive paint, the respective paint was applied twice, by brushing, to give a coating of 100 μ dry thickness each time. The following tests were carried out with these plates.

15 Antifouling test and result

The test plates were immersed in sea water for a defined period of time and antifouling effects were determined. This test was conducted at Aioi Bay, Hyogo Prefecture, Japan. The results in Table 4 show the percentage of adherent marine organisms.

Erosive dissolution test and result

Test plate having a defined thickness of coating was attached to Discrotor, immersed in sea water (18 to 23°C) and rotated at a constant speed (peripheral speed 65 km/hr) for 60 days and nights. Use-up rate of the coating was determined microscopically, from the ratio of the decrease in film thickness to the initial film thickness. The results are shown in Table 5.

Table 3

	Example					Compara. Exam.	
	50	51	52	53	54	4	5
resinous varnish V-1	45						
V-2		40					
V-3			60				
V-4				45			
V-5					40		
compara. varnish 3							50
WV rosin						7	
vinyl chloride resin VVHH						7	
dioctyl phthalate						2	
cuprous oxide	35	40		30	40	35	35
triphenyl tin hydroxide	5		5			5	
triphenyl tin chloride				5			
tributyl tin fluoride			10			3	
colcothar	5	5		5	5	10	5
zinc white			20				
methyl isobutyl ketone	5	5	5	5	5	15	
xylene	5	10		10	10	16	10
total	100	100	100	100	100	100	100

Table 4

immersed months	3	6	9	12	18	24	30
Example 50	0	0	0	0	0	0	0
Example 51	0	0	0	0	0	0	0
Example 52	0	0	0	0	0	0	0
Example 53	0	0	0	0	0	0	0
Example 54	0	0	0	0	0	0	0
Comp. Exam. 4	0	0	0	5	80	100	100
Comp. Exam. 5	0	0	0	0	5	20	60

Table 5

	initial film thickness	film thickness after test	Use-up rate
Exam. 50	210 μ	145 μ	0.31
Exam. 51	220	135	0.39
Exam. 52	200	155	0.22
Exam. 53	190	145	0.24
Exam. 54	200	160	0.20
Comp. Ex. 4	200	200	0.0
Comp. Ex. 5	190	150	0.21

Examples 55 to 101

Using the resinous varnishes V-10 to V-49 obtained in Examples 10 to 49, and following the prescriptions given in Table 6, antifouling paints were prepared. The antifouling tests and erosive dissolution tests used in Examples 50 to 54 were repeated with these paints, and results are shown in Table 7. In the antifouling tests for 36 months, attached organisms were observed for Examples 61, 65 and 97 (5% surface area) and Examples 64 and 96 (5% after 24 months, 10% after 36 months) only.

In Table 6, ZDMC stands for zinc dimethyldithiocarbamate, TMT for tetramethylthiuram disulfide, MANEB for manganese ethylenebisdithiocarbamate, and ZINEB for zinc ethylenebisdithiocarbamate.

Table 6

	Example						
	55	56	57	58	59	60	61
resinous varnish V-10	40						
V-11		35					
V-12			40	40			
V-13					35	40	
V-14							35
cuprous thiocyanate				20			
cuprous oxide	25	10	35		35		40
ZDMC							
TMT							
MANEB			5				
ZINEB		8	5			5	
triphenyl tin hydroxide		10		5	10	5	
triphenyl tin chloride							
tributyl tin fluoride				5		10	
colcothar	5	5	5		5		
zinc white	20	20		15		25	10
xylene	10	12		15	15	15	15
white spirit			10				
total	100	100	100	100	100	100	100

Table 6

(continued)

	Example						
	62	63	64	65	66	67	68
V-15	40						
V-16		40					
V-17			35				
V-18				35			
V-19					40		
V-20						40	40
cuprous thiocyanate		15				15	
cuprous oxide	35			35	35		20
ZDMC							
TMT			10				
MANEB	5						
ZINEB		10	10			10	
triphenyl tin hydroxide		5		10	10	5	
triphenyl tin chloride			5				5
tributyl tin fluoride		5				5	
colcothar				5	5		
zinc white	10	15	20			15	20
xylene	10	10	20	15		10	15
white spirit					10		
total	100	100	100	100	100	100	100

Table 6

(continued)

	Example						
	69	70	71	72	73	74	75
resinous varnish V-20							
V-21	40	45					
V-22			60				
V-23				40			
V-24					40		
V-25						50	
V-26							40
cuprous thiocyanate		10					
cuprous oxide	35			35	50	35	35
ZDMC							
TMT							
MANEB	5						
ZINEB		10					5
triphenyl tin hydroxide			5	5			
triphenyl tin chloride				5			
tributyl tin fluoride			10	5			
colcothar	5				5	5	5
zinc white		25	20				
xylene	15	10	5	10	5	10	15
white spirit							
total	100	100	100	100	100	100	100

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Table 6

(continued)

	Example						
	76	77	78	79	80	81	82
V-27	50						
V-28		40	40				
V-29				35	40		
V-30						35	50
cuprous thiocyanate				20			
cuprous oxide		35				10	
ZDMC			15	5			
TMT					15		
MANEB	5				5		5
ZINEB	5				5	8	5
triphenyl tin hydroxide	5	5	5	5	5	10	5
triphenyl tin chloride				5			
tributyl tin fluoride	10		5	5	5		10
colcothar		5				5	
zinc white	10	5	20	15	15	20	10
xylene	15	10	15	10	10	12	15
white spirit							
total	100	100	100	100	100	100	100

Table 6

(continued)

	Example						
	83	84	85	86	87	88	89
V-31	45						
V-32		45					
V-33			45				
V-34				45			
V-35					35		
V-36						35	
V-37							40
cuprous thiocyanate							
cuprous oxide		25		25	40		35
ZDMC	10		10				
TMT	5		5			10	
MANEB							5
ZINEB						10	
triphenyl tin hydroxide	5		5				
triphenyl tin chloride						5	
tributyl tin fluoride	10	5	10	5			
colcothar							5
zinc white	15	15	15	15	10	20	
xylene	10	10	10	10	15	20	15
white spirit							
total	100	100	100	100	100	100	100

Table 6
(continued)

	Example					
	90	91	92	93	94	95
V-38	35					
V-39		40				
V-40			40			
V-41				40		
V-42					40	
V-43						35
cuprous thiocyanate		15			20	
cuprous oxide	10			10		
ZDMC					5	
TMT		10	10			10
MANEB				5		
ZINEB	8			10		10
triphenyl tin hydroxide	10	5	5		5	
triphenyl tin chloride			5		5	5
tributyl tin fluoride			5		5	
colcothar	5				5	
zinc white	10	20	20	25		20
xylene	22	10	15	10	15	20
white spirit						
total	100	100	100	100	100	100

Table 6

(continued)

	Example					
	96	97	98	99	100	101
V-44	40					
V-45		50				
V-46			30			
V-47				30		
V-48					30	
V-49						30
cuprous thiocyanate		10				
cuprous oxide	10		40	40	40	40
ZDMC		10				
TMT	5					
MANEB						
ZINEB		5				
triphenyl tin hydroxide			5	5	5	5
triphenyl tin chloride						
tributyl tin fluoride	5					
colcothar		5				
zinc white	25					
xylene	15	20	25	25	25	25
white spirit						
total	100	100	100	100	100	100

Table 7

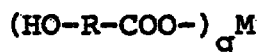
	initial film thickness	film thickness after test	Use-up rate
Example 55	220 μ	165 μ	0.25
Example 56	200	170	0.15
Example 57	210	190	0.10
Example 58	210	180	0.13
Example 59	180	145	0.19
Example 60	180	140	0.22
Example 61	210	165	0.21
Example 62	200	160	0.20
Example 63	210	155	0.26
Example 64	200	170	0.15
Example 65	190	155	0.18
Example 66	210	180	0.14
Example 67	190	150	0.21
Example 68	220	165	0.25
Example 69	220	170	0.23
Example 70	200	160	0.20
Example 71	230	185	0.20
Example 72	210	185	0.12
Example 73	180	155	0.14
Example 74	210	145	0.31
Example 75	200	170	0.15
Example 76	190	170	0.11
Example 77	190	120	0.37
Example 78	200	130	0.35

Table 7
(continued)

	initial film thickness	film thickness after test	Use-up rate
Example 79	210 μ	125 μ	0.40
Example 80	220	145	0.34
Example 81	190	110	0.42
Example 82	220	140	0.36
Example 83	200	165	0.18
Example 84	210	145	0.31
Example 85	230	145	0.37
Example 86	190	125	0.34
Example 87	180	155	0.14
Example 88	180	135	0.25
Example 89	220	190	0.14
Example 90	210	180	0.14
Example 91	200	155	0.23
Example 92	200	155	0.23
Example 93	190	150	0.21
Example 94	210	185	0.12
Example 95	180	135	0.25
Example 96	180	165	0.08
Example 97	200	185	0.08
Example 98	200	175	0.13
Example 99	210	165	0.21
Example 100	200	160	0.20
Example 101	210	180	0.14

CLAIMS

1. A process for preparing a hydrolysable polyester resin, which comprises reacting a polycarboxylic acid with a hydroxycarboxylic acid salt of the formula

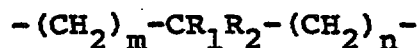


5 wherein R is an organic linking group and M is a metal of valency q , q being from 1 to 4, of any of the Periodic Table Groups Ia, Ib, IIa, IIb, IVb, VIIa and VIII, and, if q is 1, with a polyhydric alcohol.

2. A process according to claim 1, wherein R is

10 C_{1-38} alkylene.

3. A process according to claim 2, wherein R has the formula



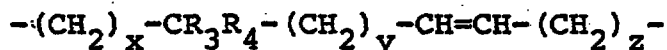
wherein R_1 and R_2 are independently selected from
15 hydrogen, C_{1-10} alkyl and C_{2-10} alkenyl, and m and n are each from 0 to 16.

4. A process according to claim 3, wherein R_1 and R_2 are independently selected from hydrogen and C_{1-8} alkyl, and m and n are each from 0 to 10.

20 5. A process according to claim 1, wherein the hydroxycarboxylic acid is lactic, hydracrylic, 12-hydroxystearic or glycolic acid.

6. A process according to claim 1, wherein R is C_{2-38} alkenylene.

25 7. A process according to claim 6, wherein R has the formula



wherein R_3 and R_4 are independently selected from
hydrogen, C_{1-10} alkyl and C_{2-10} alkenyl, and x , y and
30 z are each from 0 to 10.



8. A process according to claim 7, wherein R_3 and R_4 are independently selected from hydrogen and C_{1-8} alkyl, x is from 0 to 4 and y is from 0 to 6.

9. A process according to claim 1, wherein the
5 hydroxycarboxylic acid is ricinoleic or ricinoelaidic acid.

10. A process according to claim 1, wherein R has the formula



10 wherein R_5 is C_{1-8} alkylene or C_{4-8} alkylene interspersed with ether oxygen atoms, and R_6 is optionally unsaturated C_{2-4} alkylene.

11. A process according to claim 1, wherein the hydroxycarboxylic acid is a half ester of an aliphatic
15 dicarboxylic acid selected from maleic anhydride, succinic anhydride, dimethylmaleic anhydride and dimethylsuccinic anhydride, with a polyol selected from ethylene glycol, propylene glycol, 1,3-butylenediol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, neopentyl
20 glycol and triethylene glycol.

12. A process according to claim 1, wherein R has the formula



wherein R_5 is as defined in claim 10, and R_8 is a C_{6-7}
25 saturated, unsaturated or aromatic cyclic hydrocarbon radical.

13. A process according to claim 1, wherein the hydroxycarboxylic acid is a half ester of an aromatic dicarboxylic acid selected from phthalic anhydride,
30 tetrahydrophthalic anhydride, hexahydrophthalic anhydride and himic anhydride, with a polyol as defined in claim 11.

14. A process according to any preceding claim, wherein M is selected from Li, K, Na, Cu, Ag, Mg, Ca,
35 Ba, Zn, Cd, Hg, Sn, Pb, Mn, Fe, Co and Ni.



15. A process according to claim 14, wherein M is selected from K, Na, Cu, Ag, Mg, Zn, Sn, Pb, Fe, Co and Ni.
16. A process according to claim 15, wherein M is selected from Na, Cu, Mg, Zn and Ni.
17. A process for preparing a hydrolysable polyester resin, which comprises reacting a polycarboxylic acid with a polyhydric alcohol and a hydroxycarboxylic acid salt as defined in any preceding claim.
18. A process according to claim 1, substantially as described in any of the Examples.
19. A resin composition which comprises an organic solvent and a hydrolysable polyester resin prepared by a process according to any preceding claim.
20. An antifouling paint composition which comprises a resin composition according to claim 19 and an antifouling agent.
21. An antifouling paint composition according to claim 20, wherein the antifouling agent is selected from metallic copper, cupric hydroxide, cuprous oxide, cuprous thiocyanate, bis-tributyltin oxide, tributyltin fluoride, chloride or α, α' -dibromosuccinate, tetramethylthiuram disulfide, zinc dimethyldithiocarbamate and manganese or zinc ethylenebisdithiocarbamate.
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