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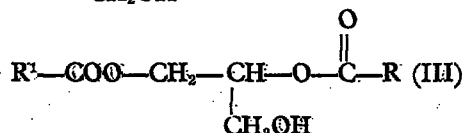
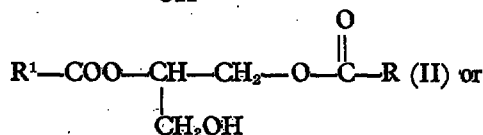
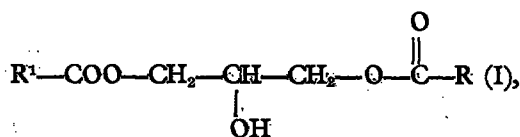


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(54) QUICK DRYING SYNTHETIC RESIN COATING COMPOSITIONS

- (71) We, NIPPON PAINT CO., LTD., a corporation organised under the laws of Japan, of 1—1, Oyodomachi-Kita-2-chome, Oyodo-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 The present invention relates to quick-drying coating compositions comprising a copolymer and an alkyd resin as the principal vehicle. Quick drying synthetic resin coating compositions which comprise as the principal
- 15 vehicle a copolymer obtained by copolymerizing an acrylate, a methacrylate or styrene are usually called acrylic resin paints or vinyl resin paints.
- 20 Although the dried films of these acrylic or vinyl resin paints have excellent durability, and gloss-holding properties, the paints themselves can be difficult to use and often have poor spray workabilities, and high build. These defects result from the fact that copolymers, one of the principal vehicle components, are typical high molecular weight materials and that the resin solids content of the paint composition is extremely low when diluted with a solvent to a viscosity suitable for the spray-coating. Although these defects can be
- 30 remedied considerably by reducing the molecular weight of the copolymer, other properties of the films obtained such as durability, weather-resistance and crack-resistance are impaired. Similarly, although the addition of plasticizers such as butyl benzyl phthalate or dibutyl phthalate to the copolymers improves considerably their spray workability or high build, the film obtained has a high temperature-sensitivity, and the weather-resistance and gasoline-resistance thereof are often impaired. Methods of remedying these defects by addition of a condensation resin, particularly an alkyd resin, instead of the plasticizer, have not been generally employed because the copolymer and a conventional alkyd resin are generally not compatible with each other.
- It is known that the presence of a tertiary aliphatic hydrocarbon group in the copolymer employed in quick drying synthetic resin coating compositions has a large effect on weather-resistance and gloss. We have already succeeded in not only increasing the compatibility between the copolymer and an alkyd resin, but also in obtaining a quick drying coating composition excellent in weather-resistance and gloss by introducing a tertiary aliphatic hydrocarbon group into both the vehicle components. Thus, our British Patent Specification No. 10863/73 (Serial No. 1337142) (divided out hereof) discloses and claims a quick drying synthetic resin coating composition comprising an organic solvent and a resin composition consisting of (A) 100 parts by weight of a copolymer of (1) 5 to 50% by weight of at least one polymerizable monomer represented by the formula:



5 wherein R stands for a monovalent tertiary aliphatic hydrocarbon group having in total 4 to 26 carbon atoms; R¹ stands for a monovalent α,β-ethylenically unsaturated hydrocarbon group having 2 to 3 carbon atoms which may be substituted with one group of the formula COOR², wherein R² is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, (2) 50 to 95% by weight of methyl methacrylate and (3) 0 to 45% by weight of at least one other monomer copolymerizable with said polymerizable monomer (1); and (B) 5 to 100 parts by weight of an alkyd resin containing 10 to 60% by weight of units derived from a tertiary aliphatic carboxylic acid represented by the formula:



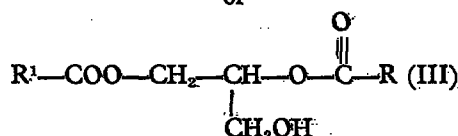
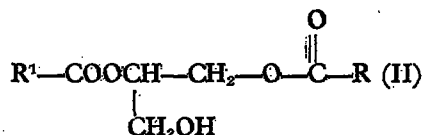
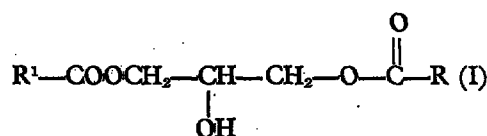
wherein R has the same meaning as defined above.

25 The present invention represents an improvement in or a modification of the invention disclosed in our British Patent Specification No. 10863/73 (Serial No. 1337142).

We have now found that quick-drying synthetic resin coating compositions can be obtained by extending the ranges of the components of the coating composition disclosed in Specification No. 10863/73 (Serial No. 1337142). In particular, the alkyd resin which constitutes component (B) of the coating composition can be used in increased quantities of up to 600 parts by weight per 100 parts of component (A), and the units derived from the tertiary aliphatic carboxylic acid of the formula RCOOH can constitute from 1 to 70% by weight of the alkyd resin. Additionally, the quantity of the monomer of the formula (I), (II) or (III) used in the preparation of copolymer A can be increased up to 70% by weight, and whereas it was thought essential that the copolymer A be made up of at least 50% by weight of methyl methacrylate, any monomer or combination of monomers copolymerizable with a monomer of the form-

ula (I), (II) or (III) can be used in the range 30 to 95% by weight.

Accordingly the quick drying synthetic resin coating compositions, as extended by the present invention, comprise an organic solvent and a resin composition consisting of (A) 100 parts by weight of a copolymer of (1) 5 to 70% by weight of at least one polymerizable monomer represented by the formula:



wherein R stands for a monovalent tertiary aliphatic hydrocarbon group having in total 4 to 26 carbon atoms; R¹ stands for a monovalent α,β-ethylenically unsaturated hydrocarbon group having 2 to 3 carbon atoms which may be substituted with one COOR² group wherein R² is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and (2) 30 to 95% by weight of at least one monomer copolymerizable with said polymerizable monomer (1); and (B) 5 to 600 parts by weight of an alkyd resin containing 1 to 70% by weight of units derived from a tertiary aliphatic carboxylic acid represented by the formula:



i) The addition-reaction of the carboxyl group of an α,β -ethylenically unsaturated carboxylic acid with the epoxy group of a glycidyl ester of a tertiary aliphatic carboxylic acid.

i) The addition-reaction of the carboxyl group of an α,β -ethylenically unsaturated carboxylic acid with the epoxy group of a glycidyl ester of a tertiary aliphatic carboxylic acid.



of a glycidyl ester of an α,β -ethylenically unsaturated carboxylic acid with the carboxyl group of a tertiary aliphatic carboxylic acid.

of a glycidyl ester of an α,β -ethylenically unsaturated carboxylic acid with the carboxyl group of a tertiary aliphatic carboxylic acid.

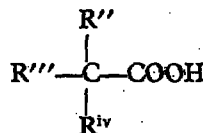


wherein R' is a monovalent saturated C₃ to C₁₁ tertiary aliphatic branched chain hydrocarbon radical).

Examples of glycidyl esters of α/β -ethylenically unsaturated carboxylic acids employed for the addition reaction ii) include glycidyl acrylate, glycidyl methacrylate, glycidyl crotonate, monoglycidyl itaconate, monoglycidyl maleate, monoglycidyl fumarate, glycidyl esters of monoalkyl (C_1-C_4) itaconate, glycidyl esters of monoalkyl (C_1-C_4) fumarate and glycidyl esters of monoalkyl (C_1-C_4) maleate. These compounds may also be used alone or in combinations of two or more. Examples of a suitable tertiary carboxylic acid are "Versatic Acid 911" (a trade mark of Shell Chemical Company for a mixture of compounds having the formula,

wherein, R'', R''' and R^{iv} are monovalent aliphatic groups having 8 to 10 carbon atoms in total), neopentanoic acid, neoheptanoic acid, neodecanoic acid and neotridecanoic acid. These acids may be used alone or in combinations of two or more.

The addition reactions i) and ii) proceed smoothly without side reactions at temperatures of from 80° to 180°C, preferably from

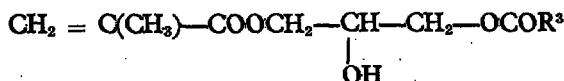


140° to 170°C. In the addition reaction, a Lewis base catalyst, such as a tertiary amine, may be employed if desired.

- 5 The proportion of the monomer component (1) in the copolymer (A) ranges from 5 to 70 % by weight and below this range it cannot impart to the copolymer A a sufficient compatibility with the alkyd resin (B). A particularly preferred proportion is from 6 to 40 % by weight.

- 10 Examples of the copolymerizable monomer (2) in the copolymer (A) are those having 2 to 30 carbon atoms and including esters of acrylic acid or methacrylic acid with alkanols having 1 to 16 carbon atoms, for example, methyl acrylate, propyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate; butyl acrylate, and butyl methacrylate; a vinyl ester of a saturated aliphatic carboxylic acid such as vinyl acetate and vinyl propionate; mono- and di-

olefinic hydrocarbons such as styrene, vinyl toluene, α -methylstyrene, ethylene and butadiene; unsaturated amides such as acrylamide and methacrylamide; unsaturated nitriles such as acrylonitrile and methacrylonitrile; methylolated unsaturated amides such as N-methylol acrylamide and N-methylol methacrylamide; alkylethers of methylolated unsaturated amides such as N-methylol methacrylamide alkyl ethers, and N-methylol acrylamide alkyl ethers, hydroxyalkyl acrylates or methacrylates such as hydroxymethyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxybutyl methacrylate; polymerizable monomers having a non-drying oil fatty acid residue, a semidrying oil fatty acid residue or a drying oil fatty acid residue, for example, addition-reaction products represented by the formula:



- 45 wherein R^3 stands for a non-drying, semi-drying or drying oil fatty acid residue e.g., coconut oil fatty acid residue, castor oil fatty acid residue, peanut oil fatty acid residue, rice bran oil fatty acid residue, cotton-seed oil fatty acid residue, soybean oil fatty acid residue, sunflower oil fatty acid residue, tung oil fatty acid residue, perilla oil fatty acid residue, linseed oil fatty acid residue, and hempseed oil fatty acid residue.

- 50 For the preparation of the copolymer (A) a conventional method of polymerization can be employed, for example the method used in the polymerization of methyl methacrylate or styrene. The polymerization reaction is preferably carried out in a solvent at a temperature of from 70° to 160°C in the presence of a polymerization initiator such as a peroxide or an azo compound.

- 55 The above-mentioned alkyd resin, the (B) component, may be prepared by reacting either a tertiary aliphatic carboxylic acid of the formula RCOOH , wherein R is as defined previously, or a glycidyl ester thereof with a polybasic acid having from 3 to 30 carbon atoms (or an anhydride thereof), a polyhydric alcohol having from 2 to 30 carbon atoms and, optionally, a vegetable oil or a fatty acid by a conventional method for the preparation of an alkyd resin (cf. T. C. Patton, "Alkyd Resin Technology, Formulating Techniques and Allied Calculations", Interscience Publishers, 1962 New York). Examples of suitable polybasic acids are phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, tetrahydrophthalic anhydride, trimellitic acid, trimellitic anhydride, maleic acid, maleic anhydride, fumaric acid, succinic acid, adipic

acid and sebacic acid. Examples of the polyhydric alcohol include ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, glycerin, trimethylol ethane, trimethylol propane, pentaerythritol and sorbitol. Each of the reactants may be employed alone or in combinations of two or more. Examples of suitable vegetable oils are tung oil, tall oil, linseed oil, dehydrated castor oil, soybean oil, cottonseed oil, olive oil, castor oil and coconut oil and fatty acids derived therefrom, and these compounds can also be used alone or in combinations of two or more.

95 The compatibility of the aforesaid copolymer with said alkyd resin depends upon the polybasic acids and polyhydric alcohols employed in the alkyd resin, and it is greatly improved when said alkyd resin contains 1 to 70 % by weight of the tertiary aliphatic carboxylic acid component. This is perhaps due to a high chemical affinity between the pendent tertiary aliphatic hydrocarbon groups in the copolymer and the tertiary aliphatic hydrocarbon groups in the alkyd resin.

100 The proportion of the copolymer (A) to the alkyd resin (B) may be varied over a wide range depending upon the performance required of the coating in use. For vehicles, suitable proportions are 100:5—100 parts by weight, for vessels and buildings, 100:100—600 parts by weight, and for general appliances, 100:50—200 parts. Satisfactory coatings are not obtained by using compositions outside these ranges.

115 Examples of solvents and diluents which are useful in the preparation of the copolymer and alkyd resin or the quick drying synthetic resin coating composition of the present invention, or in the application thereof, include

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aliphatic, cycloaliphatic and aromatic hydrocarbons, ethers, esters, ketones and alcohols and they may be employed either alone or in combinations of two or more. Ethyl acetate, butyl acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, ethylene glycol monoethyl ether acetate and butanol are particularly useful.

The amount of the solvent used is preferably from 20 to 95 % by weight based on the total weight of the composition.

Plasticizers and pigments conventionally employed in paints, and additives added in the preparation of paints and in the application thereof, such as silicone resins or surface active agents, may be employed in conventional amounts.

The amount of pigments employed in the quick drying synthetic resin paint of the present invention varies largely depending upon the kind of pigments employed, and it is preferably from 1 to 280 % by weight based upon the resin solids (i.e. the total weight of copolymer A and resin B).

The volume of solvents and diluents used for the application of the paints varies depending upon the coating method employed. However the weight ratio of resin solids to solvents or diluents in the paint at the time of coating is preferably from 60:40 to 10:90.

In the quick drying synthetic resin coating composition of the present invention, cellulosic derivatives such as nitrocellulose and cellulose acetate butyrate or other polymeric materials such as melamine-formaldehyde resins, benzoguanamine-formaldehyde resins, or urea-formaldehyde resins can be added if desired in conventional quantities, that is to say, such that the ratio of the combined weight of the copolymer and alkyd resin to the weight of these cellulosic derivatives or amino resin solids is from 100:0 to 70:30. Further, metallic salt dryers such as cobalt, manganese, lead and zirconium salts may also be added in conventional quantities if desired.

The quick drying synthetic resin coating composition of the present invention can be applied to a substrate by any suitable technique, for example by spray-coating, brush-coating, immersion-coating or roller-coating. The film obtained from the present coating composition can be cured by allowing it to stand at room temperature and also by heating to a temperature below 300°C.

Suitable substrates for coating with the composition of the present invention are metals, wood, rubber, glass, fibers and a variety of plastic moldings.

The present invention is illustrated by the following examples, in which all parts are by weight unless otherwise specified.

Example 1.

1—a) Preparation of component (1) of copolymer (A).

"Cardura E"	875.00 parts	65
Methacrylic acid	344.00 parts	
Xylene	305.00 parts	
Hydroquinone	0.18 parts	

These reactants were charged into a reaction vessel and heated to 140°C with stirring. The addition reaction of the epoxy-group in "Cardura E" with the carboxyl group of methacrylic acid was traced while quantitatively determining the remaining carboxyl group in the system.

The addition reaction was a considerably exothermic and xylene was added to prevent a sudden over-heating of the system. Hydroquinone was added to prevent polymerization at this stage. The addition reaction was completed in about 40 minutes. Consequently, a polymerizable addition reaction product solution was obtained. This polymerizable addition reaction product may, of course, be isolated from the system and purified; however, in the present invention, there is no necessity of isolation and purification of the product and the xylene solution containing a total amount of 80% by weight of the addition reaction product obtained in said reaction and a trace amount of methacrylic acid remaining owing to the addition in a slight excess (the acid number of said solution being 18) was used as such.

1—b) Preparation of copolymer (A)

Addition reaction product solution obtained in 1—a)	80.0 parts	95
Methyl methacrylate	336.0 parts	
Xylene	268.0 parts	100
Toluene	160.0 parts	

These reactants were charged into a reaction vessel and heated to reflux with stirring. While maintaining the reflux, a polymerization initiator solution obtained by dissolving 4.0 parts of azobisisobutyronitrile in 160.0 parts of ethyl acetate was added over a period of two hours to effect the polymerization reaction. After the completion of the addition, the reactants were heated under reflux for a further 2 hours with stirring. The thus obtained copolymer resin solution contained 40 % of non-volatile matters.

1—c) Preparation of resin (B)

Phthalic anhydride	444.0 parts	115
Glycerin	135.0 parts	
"Cardura E"	375.0 parts	
Xylene	70.0 parts	

The reactants were charged into a reaction vessel and subjected to an esterification reaction at reflux temperature while removing water out of the system in the form of an azeotropic mixture with xylene. The esterification was continued until the acid number reached 2, when the mixture was cooled to 120°C. A mixture of 148.0 parts of phthalic anhydride and 250.0 parts of "Cardura E" was added and the reaction was continued at 150°C until the acid number reached 7. The mixture was then diluted with xylene to give a resin solution containing 70 % of non-volatile matter.

- 15 1—d) Preparation of coating composition
 Copolymer resin solution obtained in 1—b) 150.0 parts
 Alkyd resin solution obtained in 1—c) 12.0 parts
 20 These ingredients were mixed together to give a paint.

Example 2.

- 2—a) Preparation of copolymer (A)
 Addition reaction product solution obtained in Example 1—a) 100.0 parts
 Methyl methacrylate 200.0 parts
 n-Butyl acrylate 120.0 parts
 Xylene 264.0 parts
 30 Toluene 160.0 parts

These reactants were charged into a reaction vessel and a copolymerization reaction was carried out in the same manner as in Example 1—b) using an initiator comprising 4.0 parts of azobisisobutyronitrile and 160.0 parts of ethyl acetate. The thus obtained resin solution contained 40 % of non-volatile matter.

- 2—b) Preparation of resin (B)
 40 Phthalic anhydride 214.0 parts
 Glycerin 96.0 parts
 Soybean oil fatty acid 575.0 parts
 "Cardura E" 240.0 parts
 Xylene 57.0 parts

45 These reactants were charged into a reaction vessel and heated, and an esterification reaction was carried out at the reflux temperature. The condensed water was removed from the system in the form of an azeotropic mixture with xylene. The reaction was continued until the acid number reached 4, when the reaction mixture was cooled and diluted with xylene to give a resin solution containing 70 % of non-volatile matter.

- 55 2—c) Preparation of coating composition
 Copolymer synthetic resin solution obtained in 2—a) 35.0 parts
 Alkyd resin solution obtained in 2—b) 100.0 parts

- Solution of cobalt naphthenate in xylene (Co content: 6 %) 1.0 part
 Rutile type titanium oxide "R-820" (a product of Ishihara Sangyo Co.) 50.0 parts 65

These ingredients were mixed and dispersed to obtain a paint.

Example 3.

- 3—a) Preparation of copolymer (A)
 Addition reaction product solution obtained in Example 1—a) 150.0 parts
 Styrene 150.0 parts
 Ethyl acrylate 30.0 parts
 n-Butyl acrylate 30.0 parts 75
 2-Hydroxyethyl methacrylate 40.0 parts
 Xylene 254.0 parts
 Toluene 160.0 parts

These reactants were charged into a reaction vessel and a copolymerization reaction was carried out in the same manner as in Example 1—b) using an initiator solution comprising 4.0 parts of azobisisobutyronitrile and 160.0 parts of ethyl acetate. The thus obtained resin solution contained 40 % of non-volatile matter and viscosity thereof was T (as measured on a Gardner-Holdt viscometer).

- 3—b) Preparation of resin (B)
 Neopentyl glycol 130.0 parts 90
 Trimellitic anhydride 303.0 parts
 Xylene 20.0 parts

These reactants were charged into a reaction vessel, heated to reflux, an esterification reaction was effected for 3 hours while removing water out of the system and the reactants were then cooled to 150°C. 500.0 parts of "Cardura E" was added and the reaction was continued at 150°C for a further 30 minutes. The reaction mixture was diluted with xylene to give a resin solution containing 60 % of non-volatile matters.

- 3—c) Preparation of coating composition
 Copolymer resin solution obtained in 3—a) 85.0 parts 105
 Alkyd resin solution obtained in 3—b) 110.0 parts
 Benzoguanamine - formaldehyde resin solution ("Nikalack BL-60" a trade mark of Nippon Carbide Co. Ltd. for an amino resin containing 60 % of non-volatile matter) 40.0 parts
 Aluminium pigment "Alpaste 1109 MA" (a trade mark of Toyo Aluminium Co. Ltd.) 3.3 parts 115

Colored pigment "Microlith
4 GT Blue" (a trade mark
of Ciba Corp.) 2.5 parts

5 These ingredients were mixed and dis-
persed to obtain a paint.

Example 4.

4—a) Preparation of copolymer (A)

Addition reaction product
solution obtained in Ex-
ample 1—a) 125.0 parts
10 Methyl methacrylate 180.0 parts
Styrene 100.0 parts
n-Butyl methacrylate 20.0 parts
Xylene 260.0 parts
15 Toluene 160.0 parts

20 These reactants were charged into a re-
action vessel and subjected to polymerization
reaction in the same manner as in Example
1—b) using an initiator solution comprising
40 parts of azobisisobutyronitrile and 160.0
parts of ethyl acetate. The thus obtained resin
solution contained 40 % of non-volatile mat-
ters.

4—b) Preparation of resin (B)

25 Phthalic anhydride, 74.0 parts
Glycerin 91.0 parts
Coconut oil fatty acid 220.0 parts
Xylene 25.0 parts

30 These reactants were charged into a re-
action vessel and subjected to an esterification
reaction at 240°C while refluxing xylene until
the acid number reached 1.2. The reaction
mixture was cooled to 100°C. 222.0 parts of
phthalic anhydride and 376.0 parts of "Car-
dura E" were added thereto, and the esterifi-
cation reaction was further continued at 250°C
35 until the acid number reached 7. The reaction
product was cooled and diluted with xylene
so that the non-volatile matter content was
40 75 %.

4—c) Preparation of coating composition

Copolymer resin solution ob-
tained in 4—a) 110.0 parts
45 Alkyd resin solution obtained
in 4—b) 48.0 parts
20% Solution of 1/2" nitro-
cellulose (in a mixed sol-
vent comprising toluene,
butyl acetate and butanol
50 in a ratio of 50:30:20) 100.0 parts
Carbon black 2.0 parts

These ingredients were mixed and dis-
persed to obtain a paint.

4—d) Preparation of coating composition

Copolymer resin solution ob-
tained in 4—a) 70.0 parts 55
Alkyd resin solution ob-
tained in 4—b) 76.0 parts
20 % Solution of 1/2" nitro-
cellulose 75.0 parts 60
Titanium white 50.0 parts

These ingredients were mixed and dis-
persed to obtain a paint.

Example 5.

5—a) Preparation of component (1) of co- polymer (A).

Glycidyl methacrylate 142.0 parts
Castor oil fatty acid 330.0 parts
N,N' - Diethylaminoethyl
methacrylate 0.14 part 70
Hydroquinone 0.28 part

These reactants were charged into a re-
action vessel and heated with stirring in a
nitrogen gas atmosphere. The reaction was
continued for 5 hours at 120°C. The addi-
tion reaction was completed with an ap-
proximately 100 % yield. 75

5—b) Preparation of copolymer (A)

Addition reaction product
solution obtained in 1—a) 100.0 parts 80
Addition reaction product ob-
tained in 5—a) 80.0 parts
Methyl methacrylate 140.0 parts
Styrene 80.0 parts
n-Butylacrylate 20.0 parts 85
Xylene 264.0 parts
Toluene 160.0 parts

These reactants were charged into a re-
action vessel and the polymerization reaction
was effected in the same manner as in Ex-
ample 1—b) using an initiator solution com-
prising 4.0 parts of azobisisobutyronitrile and
160 parts of ethyl acetate. The thus obtained
resin solution contained 40 % of non-volatile
matter. 90

5—c) Preparation of coating composition

Copolymer resin solution ob-
tained in 5—b) 145.0 parts
Alkyd resin solution obtained
in 3—b) 70.0 parts 100
Butylated melamine resin
solution "Super Beckamin
G821" [non-volatile mat-
ter: 50%; solvent:
xylene/butanol (a product
of Nihon Reichhold Co.
Ltd.)] 30.0 parts
Titanium white 50.0 parts
Said components were mixed and dispersed
to obtain a paint. 110

- 5—d) Preparation of coating composition—
 Copolymer resin solution obtained in 5—b) 150.0 parts
 Alkyd resin solution obtained in 4—b) 32.0 parts
 20 % Solution of 1/2" nitrocellulose 80.0 parts
 Microlith 4GT Blue 3.5 parts
- 10 These ingredients were mixed and dispersed to obtain a paint.

Example 6.

- 6—a) Preparation of copolymer (A).
 Addition reaction product solution obtained in
 15 1—a) 260.0 parts
 Methyl methacrylate 142.0 parts
 n-Butyl acrylate 50.0 parts
 Xylene 230.0 parts
 Toluene 160.0 parts
- 20 These reactants were charged into a reaction vessel and the polymerization reaction was carried out in the same manner as in Example 1—b) using an initiator solution comprising 4.0 parts of azobisisobutyronitrile and
 25 160.0 parts of ethyl acetate. The thus obtained resin solution contained 40 % of non-volatile matter.
- 6—b) Preparation of resin (B)
 30 Phthalic anhydride 74.0 parts
 Glycerin 74.0 parts
 Fatty acid of dehydrated castor oil 280.0 parts
 Xylene 25.0 parts
- 35 Said reactants were charged into a reaction vessel and subjected to esterification reaction at 240°C while refluxing xylene until the acid number reached 1.6. The reaction mixture was then cooled to 100°C. Subsequently 281.0 parts of phthalic anhydride and 600.0 parts of "Cardura E" were added thereto and the esterification reaction was further continued
 40 at 250°C until the acid number reached 10. The reaction mixture was cooled and diluted with xylene so that the non-volatile matter
 45 content was 70 %.

- 6—c) Preparation of coating composition
 Copolymer solution obtained in 6—a) 70.0 parts
 Alkyd resin solution obtained in 6—b) 100.0 parts
 Titanium white 100.0 parts
 Xylene solution of cobalt naphthenate (cobalt content: 6—) 1.0 part
- 50

These ingredients were mixed and dispersed to obtain a paint. 55

The following is a description of the properties of coating films obtained from the paints prepared in Examples 1—d), 2—c), 4—c), 4—d), 5—d), and 6—c). 60

The paints of Examples 1—d), 4—c), 4—d), and 5—d) were diluted with a solvent comprising 15 parts of ethyl acetate, 45 parts of toluene, 20 parts of xylene, 10 parts of isobutanol and 10 parts of ethylene glycol monoethyl ether acetate until they had the viscosity of 15 to 25 seconds as measured with a Ford-cup No. 4 at 20°C. This was applied by an air-spray onto a steel-panel having a thickness of 0.8 mm on which an epoxy-resin modified acrylic primer had been applied and it was dried at room temperature for seven days. The thickness of the primer coating was about 40 microns and that of the quick drying synthetic resin paint was from 40 to 50 microns. 65

The gloss of the resulting film was measured by means of a Murakami's glossmeter at an angle of 60°. The surface hardness of the coated film was examined by a pencil scratching hardness. The impact strength was measured by a DuPont type impact tester on a stand having a diameter of 1/2 inch using a weight of 500 g. The adhesiveness was measured by making 100 squares having 2 mm width on the coated film with a recording needle, sticking an adhesive tape thereon, and stripping off the tape forcibly. The test was considered "passed" when none of the squares were stripped off. Water-resistance was tested by soaking the film in tap-water at room temperature for 240 hours. Gasoline-resistance was determined by spotting a high octane gasoline on the coated film, evaporating the gasoline at room temperature and observing any abnormal conditions of the film. The results of the above tests are shown in Table 1. 70 75 80 85 90 95

As is apparent from Table 1, the condition and workability of the films were excellent.

TABLE 1

Testings \ Paints	Example 1—d)	Example 4—c)	Example 4—d)	Example 5—d)
Gloss	94	96	91	93
Pencil hardness	F	H	F	H
Impact strength (cm)	20	20	30	20
Adhesiveness	Passed	Passed	Passed	Passed
Water-resistance	Not abnormal	Not abnormal	Not abnormal	Not abnormal
Gasoline-resistance	Not abnormal	Not abnormal	Not abnormal	Not abnormal

The paints of Examples 2—c) and 6—c) were diluted with a diluent comprising 30 parts of toluene and 80 parts of xylene, so that the viscosity of each paint was about 50 at 20°C, expressed as a Stormer viscosity. These paints were applied with a brush to a steel plate to which an epoxy resin anti-corrosive primer had been applied and dried at room temperature for 14 days.

After exposure of the resulting film to natural weathering for a year, each film proved to be excellent, and no abnormality was found except for a slight reduction of the gloss.

Still more, these paints are suitable for various coating methods such as spray-coating, airless spray coating and curtain-wall coating.

The paints of Examples 3—c) and 5—c) are plate-curing type paints. The paints obtained in Examples 3—c) and 5—c) diluted with a diluent comprising toluene/xylene/butanol in a proportion of 4/4/2 were applied by spray-coating to a steel plate having a thickness of 0.8 mm treated with a zinc phosphate type surface treating agent and were plated, cured and dried at 140°C for 32 minutes. The thickness of the dried film was so controlled as to be 25 to 35 μ at the spray-coating.

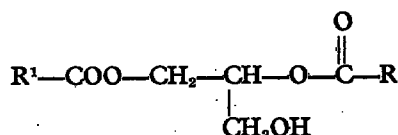
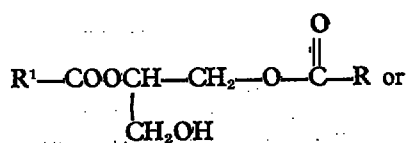
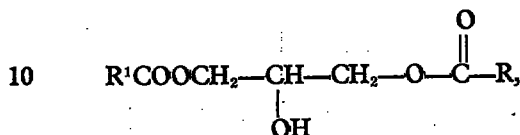
The properties of the resulting coated film were examined according to the methods described in the case of Example 1—d) and the results are shown in Table 2.

TABLE 2

	Example 3—c)	Example 5—c)
Gloss	94	88
Pencil hardness	H	H
Impact strength (cm)	40	30
Adhesiveness	Passed	Passed
Water-resistance	Not abnormal	Not abnormal
Gasoline-resistance	Not abnormal	Not abnormal

The subject matter claimed in Claim 1 of our British Patent Specification No. 10863/73 (Serial No. 1337142), namely:—

- 5 A quick drying synthetic resin coating composition comprising an organic solvent and a resin composition consisting of (A) 100 parts by weight of a copolymer of (1) 5 to 50 % by weight of at least one polymerizable monomer represented by the formula:



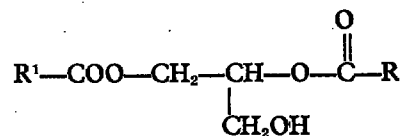
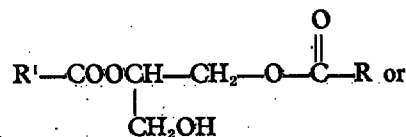
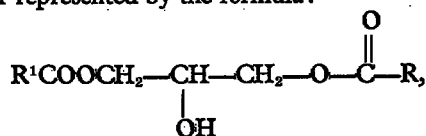
- wherein R stands for a monovalent tertiary aliphatic hydrocarbon group having in total 4 to 26 carbon atoms; R¹ stands for a monovalent α,β -ethylenically unsaturated hydrocarbon group having 2 to 3 carbon atoms which may be substituted with one group of the formula COOR², wherein R² is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, (2) 50 to 95 % by weight of methyl methacrylate and (3) 0 to 45 % by weight of at least one other monomer copolymerisable with said polymerisable monomer (1); and (B) 5 to 100 parts by weight of an alkyd resin containing 10 to 60 % by weight of units derived from a tertiary aliphatic carboxylic acid represented by the formula:



- 30 wherein R has the same meaning as defined above, is specifically disclaimed from the following claims.

Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—

- 35 1. A quick drying synthetic resin coating composition comprising an organic solvent and a resin composition consisting of (A) 100 parts by weight of a copolymer of (1) 5 to 70 % by weight of at least one polymerizable monomer represented by the formula:



wherein R stands for a monovalent tertiary aliphatic hydrocarbon group having in total 4 to 26 carbon atoms; R¹ stands for a monovalent α,β -ethylenically unsaturated hydrocarbon group having 2 to 3 carbon atoms which may be substituted with one group of the formula COOR², wherein R² is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and (2) 30 to 95 % by weight of at least one other monomer copolymerizable with said polymerizable monomer (1); and (B) 5 to 600 parts by weight of an alkyd resin containing 1 to 70 % by weight of units derived from a tertiary aliphatic carboxylic acid represented by the formula:

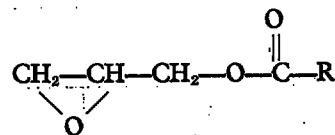


wherein R has the same meaning as defined above.

2. A composition according to Claim 1 wherein the monomer component (1) is an addition reaction product of an α,β -ethylenically unsaturated carboxylic acid represented by the formula:



wherein R¹ has the same meaning as in Claim 1 with a glycidyl ester of a tertiary aliphatic carboxylic acid represented by the formula:



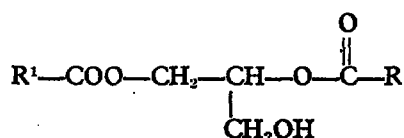
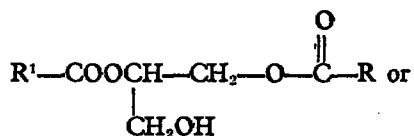
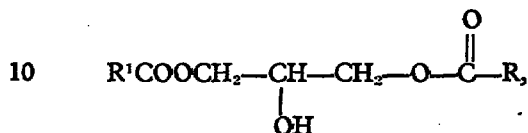
wherein R has the same meaning as in Claim 1.

3. A composition according to Claim 2, wherein the α,β -ethylenically unsaturated carboxylic acid is an unsaturated monocarboxylic acid having 3 or 4 carbon atoms, an unsaturated dicarboxylic acid having 4 or 5 carbon atoms, or a monoester of said dicarboxylic acid with an alkanol having 1 to 4 carbon atoms.

4. A composition according to Claim 3, wherein the unsaturated monocarboxylic acid is acrylic acid, methacrylic acid or crotonic acid.

The subject matter claimed in Claim 1 of our British Patent Specification No. 10863/73 (Serial No. 1337142), namely:—

- 5 A quick drying synthetic resin coating composition comprising an organic solvent and a resin composition consisting of (A) 100 parts by weight of a copolymer of (1) 5 to 50 % by weight of at least one polymerizable monomer represented by the formula:



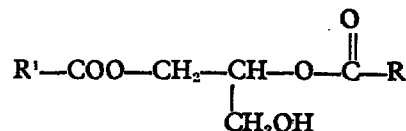
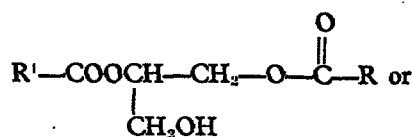
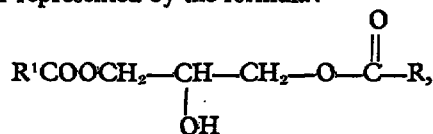
- wherein R stands for a monovalent tertiary aliphatic hydrocarbon group having in total 4 to 26 carbon atoms; R¹ stands for a monovalent α,β -ethylenically unsaturated hydrocarbon group having 2 to 3 carbon atoms which may be substituted with one group of the formula COOR², wherein R² is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, (2) 50 to 95 % by weight of methyl methacrylate and (3) 0 to 45 % by weight of at least one other monomer copolymerisable with said polymerisable monomer (1); and (B) 5 to 100 parts by weight of an alkyd resin containing 10 to 60 % by weight of units derived from a tertiary aliphatic carboxylic acid represented by the formula:



- 30 wherein R has the same meaning as defined above, is specifically disclaimed from the following claims.

Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—

- 35 1. A quick drying synthetic resin coating composition comprising an organic solvent and a resin composition consisting of (A) 100 parts by weight of a copolymer of (1) 5 to 70 % by weight of at least one polymerizable monomer represented by the formula:



wherein R stands for a monovalent tertiary aliphatic hydrocarbon group having in total 4 to 26 carbon atoms; R¹ stands for a monovalent α,β -ethylenically unsaturated hydrocarbon group having 2 to 3 carbon atoms which may be substituted with one group of the formula COOR², wherein R² is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and (2) 30 to 95 % by weight of at least one other monomer copolymerizable with said polymerizable monomer (1); and (B) 5 to 600 parts by weight of an alkyd resin containing 1 to 70 % by weight of units derived from a tertiary aliphatic carboxylic acid represented by the formula:

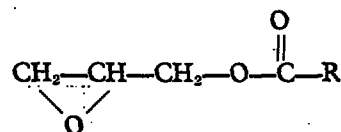


wherein R has the same meaning as defined above.

2. A composition according to Claim 1 wherein the monomer component (1) is an addition reaction product of an α,β -ethylenically unsaturated carboxylic acid represented by the formula:



wherein R¹ has the same meaning as in Claim 1 with a glycidyl ester of a tertiary aliphatic carboxylic acid represented by the formula:



wherein R has the same meaning as in Claim 1.

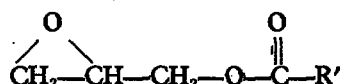
3. A composition according to Claim 2, wherein the α,β -ethylenically unsaturated carboxylic acid is an unsaturated monocarboxylic acid having 3 or 4 carbon atoms, an unsaturated dicarboxylic acid having 4 or 5 carbon atoms, or a monoester of said dicarboxylic acid with an alkanol having 1 to 4 carbon atoms.

4. A composition according to Claim 3, wherein the unsaturated monocarboxylic acid is acrylic acid, methacrylic acid or crotonic acid.



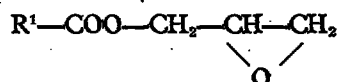
5. A composition according to Claim 3, wherein the unsaturated dicarboxylic acid is itaconic acid, maleic acid, or fumaric acid.

6. A composition according to any one of Claims 2 to 5, wherein the glycidyl ester of a tertiary aliphatic carboxylic acid is a mixture of compounds having the formula,



- wherein R' is a monovalent saturated C₈ to C₁₁ tertiary aliphatic branched chain hydrocarbon radical.

7. A composition according to Claim 1, wherein the monomer component (1) is an addition reaction product of a glycidyl ester of an α,β -ethylenically unsaturated carboxylic acid represented by the formula:



- wherein R¹ has the same meaning as in Claim 1, with a tertiary aliphatic carboxylic acid represented by the formula:

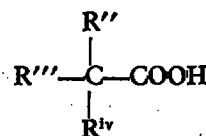


wherein R has the same meaning as in Claim 1.

8. A composition according to Claim 7 wherein the glycidyl ester of an α,β -ethylenically unsaturated carboxylic acid is glycidyl acrylate, glycidyl methacrylate, glycidyl crotonate, monoglycidyl itaconate, monoglycidyl maleate, or monoglycidyl fumarate.

9. A composition according to Claim 7 or Claim 8, wherein the tertiary aliphatic carb-

oxylic acid is neopentanoic acid, neoheptanoic acid, neodecanoic acid, neotridecanoic acid or a mixture of compounds having the formula,

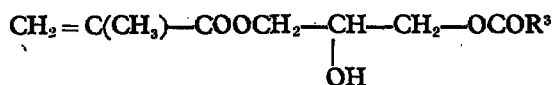


wherein R'', R''' and R^{iv} are monovalent aliphatic groups having 8 to 10 carbon atoms in total.

10. A composition according to any one of Claims 1 to 9, wherein the monomer component (2) is an ester of an alkanol having 1 to 16 carbon atoms with acrylic acid or methacrylic acid; a vinyl ester of a saturated aliphatic carboxylic acid; a mono- or diolefinic hydrocarbon; an unsaturated nitrile; an unsaturated amide, a methylolated unsaturated amide, a methylolated unsaturated amide alkyl ether; or a hydroxy alkyl acrylate or methacrylate.

11. A composition according to any one of Claims 1 to 9, wherein the component (2) is methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, vinyl acetate, vinyl propionate, styrene, vinyl toluene, α -methylstyrene, ethylene, butadiene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate or hydroxybutyl methacrylate.

12. A composition according to any one of claims 1 to 9, wherein the monomer component (2) is a polymerizable monomer represented by the formula:



- wherein R³ stands for a non-drying oil fatty acid residue, semi-drying oil fatty acid residue, or a drying oil fatty acid residue.

13. A composition according to any one of the preceding claims, wherein the component (B) is a reaction product of a tertiary aliphatic carboxylic acid represented by the formula:



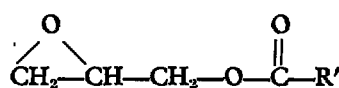
- wherein R has the same meaning as in Claim 1 or glycidyl ester thereof, with a polybasic acid having 3 to 30 carbon atoms or an anhydride thereof, a polyhydric alcohol having 2 to 30 carbon atoms and, optionally, a vegetable oil or fatty acid.

14. A composition according to Claim 13, wherein the polybasic acid or anhydride is

phthalic anhydride, trimellitic anhydride, or adipic acid.

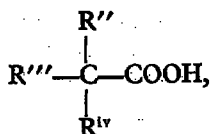
15. A composition according to Claim 13 or Claim 14, wherein the polyhydric alcohol is glycerin or neopentyl glycol.

16. A composition according to any one of Claims 13 to 15, wherein the tertiary aliphatic carboxylic acid or glycidyl ester thereof is a compound having the formula,



wherein R' is a monovalent saturated C₈ to C₁₁ tertiary aliphatic branched chain hydrocarbon radical, a mixture of compounds having the formula,





wherein R'', R''' and R^{iv} are monovalent aliphatic groups having 8 to 10 carbon atoms in total, neopentanoic acid, neoheptanoic acid, neodecanoic acid or neotridecanoic acid.

17. A composition according to any one of Claims 13 to 16 wherein the fatty acid is soybean oil fatty acid, coconut oil fatty acid, castor oil fatty acid, or dehydrated castor oil fatty acid.

18. A composition according to any one of Claims 1 to 17, which further contains 1 to 280% by weight of pigment based upon the copolymer and alkyd resin solids.

19. A composition according to any one of Claims 1 to 18, which further contains up to 30% by weight of a cellulosic derivative, a melamine-formaldehyde resin, a benzoguanamine-formaldehyde resin, or a urea-formaldehyde resin, based upon the total weight of the copolymer, alkyd resin, and cellulosic derivative or amino-formaldehyde resin.

20. A composition according to Claim 19, wherein the cellulosic derivative is nitrocellulose or cellulose acetate butyrate.

21. A composition according to any one of Claims 1 to 20, wherein the organic solvent is ethyl acetate, butyl acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, ethylene glycol monoethyl ether acetate, or butanol.

22. A composition according to any one of Claims 1 to 21, wherein the amount of the solvent is 20 to 95% by weight based on the total weight of the composition.

23. A quick-drying synthetic resin coating composition substantially as hereinbefore described in any one of the examples.

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