

RADIATION-CURABLE RESIN COMPOSITION

This invention relates generally to a resin composition hardenable by irradiation of high energy radiation and, more specifically to a resin composition suitable for plugging through-holes of a metal-plated board in manufacturing printed wiring boards.

Recent developments in the electronics industry demand printed wiring boards having a high circuit density. Thus, printed wiring boards provided with wiring patterns on both sides thereof are now increasingly used. One well known method for the production of such both-sides wiring boards includes the steps of: drilling or punching a board to form a multiplicity of through-holes, plating copper on both sides of the board and on inside walls of the through-holes, plugging the through-holes with an alkali-soluble resin, curing or hardening the resin within the through-holes, abrading or sanding both surfaces of the metal-plated board to remove deposits of the resin thereon, screen printing positive patterns with an alkali-soluble resist, curing the resist patterns, etching the exposed metal layer with an acidic etching liquid, and removing the resist patterns and the plugged resin using a 2-3% aqueous sodium hydroxide solution.

The plugging of the through-holes is generally performed as follows. A curable or hardenable resin is first applied to the board by means of, for example, a roll coater to plug the through-holes. Excess resin on the surface of the board is then removed by a squeegee and the resin plugged in the through-holes is heat-treated or UV-treated for effecting curing or hardening. The resulting board is then sanded or abraded by means of a buff roll or a belt sander to remove the hardened resin which has not been removed during the treatment with the squeegee and to clean the surface of the metal-plated board.

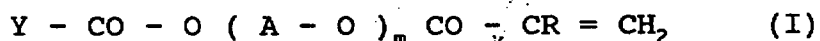
As resin for plugging through-holes of the board, there has been used a heat-curable or a photo-curable resin. Since a photo-curable resin can be hardened within a shorter period of time as compared with
 5 a heat-curable resin and since the former resin is substantially free of change of volume upon hardening, the recent trend is toward the use of the photo-curable resin. Such resin, however, poses problems because only a surface portion of the resin within the through-holes
 10 is hardened when irradiated by UV rays and also because the hardened resin is not easily dissolved in an alkali solution.

More particularly, with the known UV-hardenable resin the hardening occurs only to a depth of about 1/3
 15 from both surfaces of the through-hole and the intermediate 1/3 portion remains still unhardened. As a result, the resin which has not yet been hardened is often exposed on the surface during the abrading steps to cause various problems in the succeeding steps. In the
 20 step of removing the hardened resin by spraying an aqueous alkaline solution, such as a 3% aqueous sodium hydroxide solution, which is to be carried out after the formation of wiring pattern by etching, about 10 minutes are required for completely dissolving the hardened resin
 25 in the solution even when this treatment is performed at about 45°C.

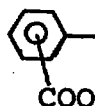
With a view toward overcoming the above problems, there has been proposed in Japanese Published Unexamined Patent Application No. 62-59606 an improved
 30 resin composition containing the following ingredients:

(a) a resin selected from the group consisting of rosins and modified rosins and having an acid value of at least 150 and a Gardner color scale of not greater than 15;

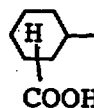
35 (b) a compound of the general formula (I):



wherein Y represents



or



, A

represents an alkylene having 1-4 carbon atoms, R represents hydrogen or methyl and m is an integer of 1-4; and

- 5 (c) a hydroxyl group-containing compound having only one acrylic or methacrylic group and at least one hydroxyl group.

While the hardening of this composition proceeds satisfactorily not only in surface portions but
 10 also in the middle portion of the through-holes, and the period of time required for removing the hardened resin by contact with an alkaline liquid is about a half of that required in the case of using the above-mentioned conventional resin composition, this composition still
 15 has a problem in that the impact strength of the hardened resin is not high. Thus, during the abrasion step for removing excess hardened resins on the surface of the board, cracks tend to be formed in the hardened resin bodies within the through-holes, which also causes
 20 breakage of the plugging resin bodies. When such cracking or breakage occurs, the plated layer inside of the through-holes are attacked by etching solution in the succeeding stage, causing electrical disconnection between the wiring patterns on both sides of the board.

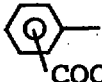
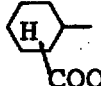
25 It is, therefore, an object of the present invention to provide an improved resin composition which is hardenable by irradiation with high energy radiation, especially UV radiation or electron beams, and which is suitable for use in plugging through-holes of metal
 30 plated boards.

More particularly, the present invention provides a resin composition hardenable by irradiation with a high energy radiation, comprising the following ingredients (a) through (d):

(a) a resin selected from the group consisting of rosins and modified rosins and having an acid value of at least 150 and a Gardner color scale of not greater than 15;

5 (b) a compound of the general formula (I):



wherein Y represents  or , A

represents an alkylene having 1-4 carbon atoms, R represents hydrogen or methyl and m is an integer of 1-4;

10 (c) a hydroxyl group-containing compound having only one acrylic or methacrylic group and at least one hydroxyl group; and

(d) a polyol compound having at least two hydroxyl groups;

15 the amounts of said ingredients (a) through (d) being as follows:

ingredient (a):	15-60%
ingredient (b):	10-60%
ingredient (c):	10-50%
20 ingredient (d):	1-30%

based on the total weight of ingredients (a) through (d), with the proportion of ingredient (b) being 30-85% based on the total weight of ingredients (b) and (c).

The term "acid number" used in the present
 25 specification in connection with rosins or modified rosins is defined as the amount (mg) of potassium hydroxide required for neutralizing 1g of the sample. The acid number is measured in accordance with JIS K5400 by titration of a solution of the sample in toluene,
 30 methyl ethyl ketone or the like solvent using a 0.1 N aqueous potassium hydroxide solution and phenolphthalein as an indicator.

The term "Gardner color scale" used in the present specification in connection with rosins or
 35 modified rosins is defined as a scale of the Gardner

color standard whose color corresponds to the color of a 50% by weight solution of a sample in methyl ethyl ketone and is measured in accordance with JIS K5400.

As already mentioned, the resin composition according to the present invention contains ingredients (a)-(d) as main ingredients.

Ingredient (a) is a resin which is a rosin or a modified rosin and which has an acid value of at least 150 and a Gardner color scale of not greater than 15.

10 An acid value of the rosin or modified rosin of at least 150 is necessary in order to obtain suitable solubility of the hardened resin composition in an alkaline solution. When the Gardner color scale of the rosin or modified rosin exceeds 15, the hardening of a layer or
15 body of the resulting composition with which through-holes are plugged fails to proceed sufficiently in the interior thereof.

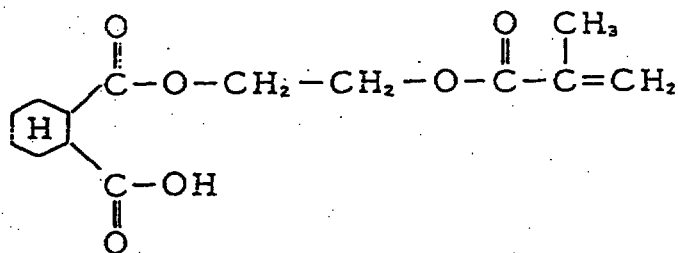
The modified rosin is preferably one which is modified by reaction _____

with an acid or an alcohol. Illustrative of suitable acids for the modification of rosin are maleic acid, maleic anhydride, fumaric acid, fumaric anhydride, phthalic acid and phthalic anhydride. Illustrative of suitable alcohols are

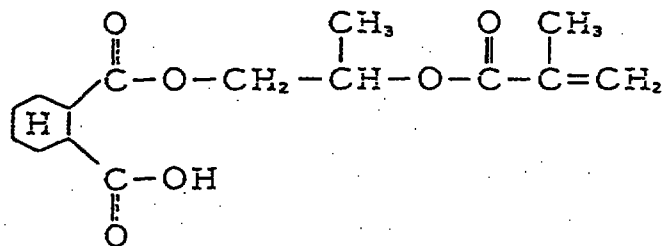
- 5 pentaerythritol and glycerin. If desired, the rosin or modified rosin may be used in conjunction with a small amount of a resin such as a carboxyl group-containing polymer (such as SMR Resin manufactured by ARCO Chemical Company, U.S.A. or OXYLAC manufactured by Nihon Shokubai Kagaku Kogyo K. K.), a phenol
- 10 novolak resin or a cresol novolak resin.

Ingredient (b) is a compound the above general formula (I). Examples of suitable compounds are as follows:

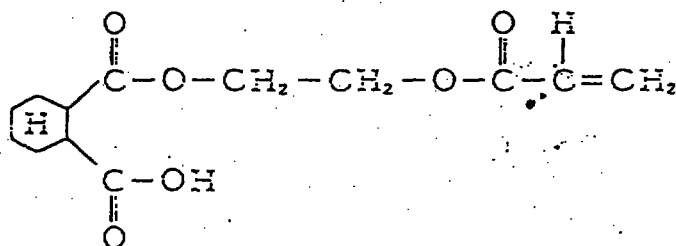
- (1) Monomethacryloylethyl hexahydrophthalate



- (2) Monomethacryloyloxy-1-isopropyl hexahydrophthalate

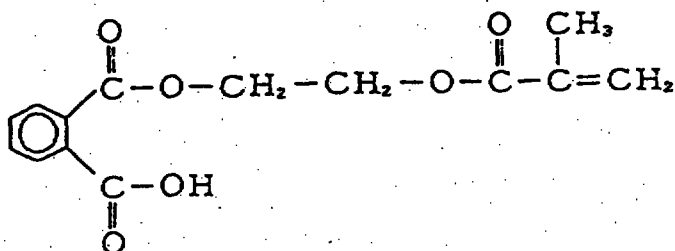


- (3) Monoacryloyloxyethyl hexahydrophthalate



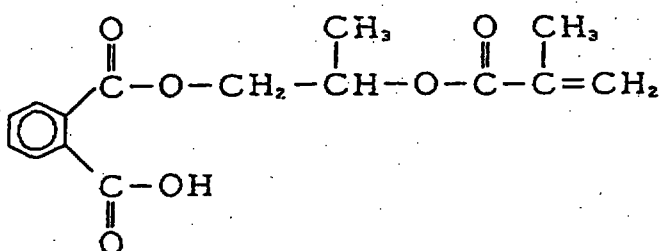
(4) Monomethacryloyloxyethyl phthalate

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(5) Monomethacryloyloxy-1-isopropyl phthalate

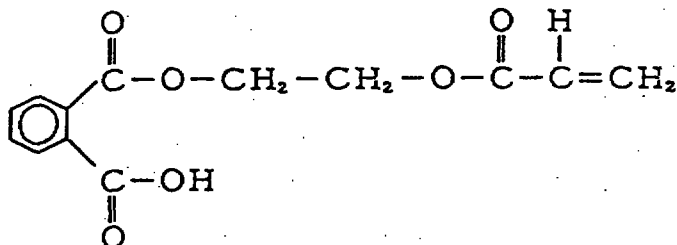
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(6) Monoacryloyloxyethyl phthalate

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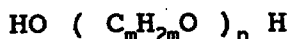
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Ingredient (c) is a hydroxyl group-containing compound having only one acrylic or methacrylic group and at least one hydroxyl group and, preferably, is liquid at room temperature. Examples of such compounds include 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate. The hydroxyl group-containing compound serves to improve removability of the hardened resin composition by dissolution into an alkali solution.

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Ingredient (d) is a polyol having at least two hydroxyl groups and is preferably glycerin or a diol which is liquid at room temperature. The diol may include, for example, compounds having the following general formula:



wherein m stands for an integer of 2 or more, and n stands for an integer of 1 or more. Illustrative of suitable diols are ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol and a polyalkylene glycol having both oxyethylene and oxypropylene groups. The use of a polyethylene glycol which is liquid at room temperature is especially preferred. The polyol serves to improve the impact strength of a hardened body of the resin composition.

The amounts of ingredients (a) through (d) which are used according to the invention are as follows:

	ingredient (a):	15-60%
	ingredient (b):	10-60%
15	ingredient (c):	10-50%
	ingredient (d):	1-30%

based on the total weight of ingredients (a) through (d), wherein the proportion of ingredient (b) is 30-85% based on the total weight of ingredients (b) and (c).

Preferred ranges are as follows:

20	ingredient (a):	25-50%
	ingredient (b):	15-50%
	ingredient (c):	15-50%
	ingredient (d):	1-25%

based on the total weight of ingredients (a) through (d), wherein the proportion of ingredient (b) is at least 35% based on the total weight of ingredients (b) and (c).

An amount of ingredient (a) below 15% by weight is undesirable because the viscosity of the resulting resin composition becomes too low to properly plug through-holes of a board and, additionally, because it becomes difficult to remove the hardened resin by dissolution into an alkali solution. When the amount of ingredient (a) exceeds 60% by weight, the resulting resin composition becomes so viscous that it becomes difficult to plug through-holes therewith.

An amount of ingredient (b) below 10% by weight causes difficulties in removing the hardened resin by

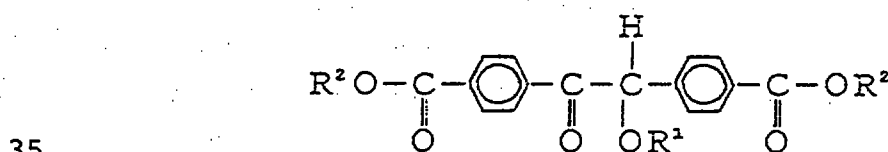
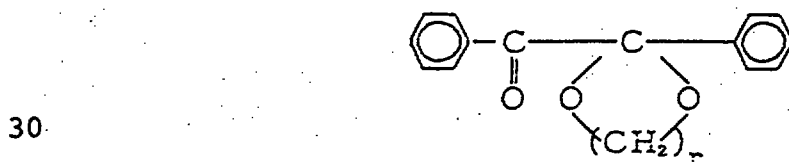
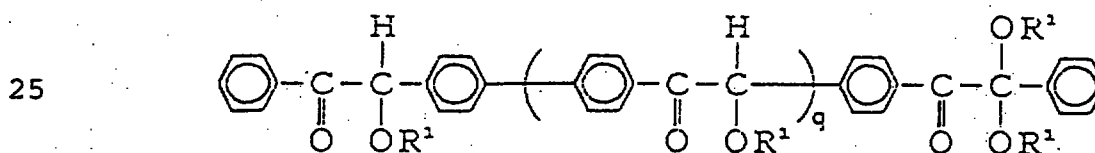
dissolution into an alkali solution. Too large an amount of ingredient (b) in excess of 60 % by weight is undesirable because the resulting resin composition becomes very viscous.

5 An amount of ingredient (c) below 10 % by weight is insufficient to provide a hardened resin having good removability. On the other hand, too large an amount of ingredient (c) in excess of 50 % by weight is undesirable because the viscosity of the resin composition becomes excessively low.

10 An amount of ingredient (d) below 1 % by weight is insufficient to improve the impact strength of a hardened body of the resin composition. On the other hand, when the amount of ingredient (d) exceeds 30 % by weight, the hardened body becomes soft and sticky.

15 The hardenable resin composition according to the present invention may further contain one or more additives such as a photopolymerization photosensitizer, a filler, a thermal polymerization inhibitor and anti-foaming agents.

20 Illustrative of suitable photosensitizers are benzoin, phenyl ketone compounds such as 1-hydroxycyclohexyl phenyl ketone) and ether derivatives of benzoin compounds such as shown below:



wherein R^1 and R^2 represent independently from each other an alkyl group having 1-18 carbons, a cycloalkyl group or a phenyl group and q and r are integers of 1-6. The photosensitizer may be used in an amount of 2-20 % by weight, preferably 4-15 % by weight based on the weight of the resin composition.

Illustrative of suitable fillers are silicon dioxide, aluminum silicate, magnesium silicate and aluminum hydroxide. The filler preferably has an average particle size of 10 μ m or less and is used in an amount of 20 % by weight or less based on the weight of the resin composition. The filler serves to adjust the viscosity of the resin composition to a suitable range.

Illustrative of suitable thermal polymerization inhibitors are hydroquinone, 4-methoxyphenol, 2,6-di-tert-butyl-4-cresol, 2,2-methylenebis(4-ethyl-6-tert-butylphenol), tert-butylcatechol, pyrogallol, 2-naphthylamine, 4-toluquinone, triphenylphosphite, a salt or a chelate (Al, Cu or Zn) of N-nitrosophenylhydroxylamine and ethylenediamine tetraacetic acid or a salt thereof. The inhibitor is generally used in an amount of 0.005-3 % by weight based on the weight of the composition.

As the anti-foaming agent, there may be used silicone compounds generally used in screen printing inks. The amount of the agent is generally 0.005-1 % by weight based on the resin composition.

The hardenable resin composition of the present invention may be suitably prepared in the following manner. Ingredients (b), (c) and (d) and, if necessary, a thermal polymerization inhibitor are mixed and heated at 40-100 °C to obtain a homogeneous solution, to which is then added ingredient (a) with stirring for dissolution. The resulting solution is further blended with a photosensitizer and/or a filler, if desired, and the blend is homogeneously mixed using a roll mill or the like mixer. The hardenable resin when irradiated by UV rays, electron beams or other high energy radiation is hardened as a result of polymerization.

The following examples will further illustrate the present invention. In the examples, "part" is by weight.

Example 1

A resin composition composed of the following ingredients was prepared:

	Ingredient (a)	
5	Modified rosin *1:	40 parts
	Ingredient (b)	
	Acrylic ester *2:	35 parts
	Ingredient (c)	
	2-Hydroxyethyl methacrylate:	15 parts
10	Ingredient (d)	
	Polyethylene glycol *3:	10 parts
	Benzoin isopropyl ether:	8 parts
	Silica *4:	2 parts
	N-Nitrosophenylhydroxylamine	
15	ammonium salt *5:	0.05 part

*1: Rosin modified with maleic anhydride and pentaerythritol. Acid value: 305, Gardner scale: 8

*2: Monomethacryloyloxyethyl hexahydrophthalate

20 *3: Average molecular weight: 2000

*4: TOKUSEAL U manufactured by Tokuyama Soda Inc.

*5: CUPHERRON Q-1300 manufactured by Wako Junyaku Inc.

25 The thus obtained resin composition was tested for its hardenability and for removability and crack-resistance of its hardened product. The test results are summarized in Table 1. The test methods are as follows:

Hardenability Test:

30 A plate-like jig having a rectangular groove is provided. The bottom of the groove is sloped such that the depth of the groove increases continuously gradually from 0 to 1.5 mm in a direction from one end thereof to the other opposite end. After placing a polyester film (thickness: 100 μ m) on the
35 bottom of the groove, the groove is filled with a test sample to form a resin layer whose top surface is rendered flat. The

thickness of the resin layer thus gradually increases from one end to the other end thereof inconformity with the shape of the groove. The jig is then passed at a conveying speed of 1.5 m/minute beneath a high pressure mercury lamp (80 W/cm) with a distance therebetween of 15 cm, thereby to harden the resin layer. The UV-treated resin layer is removed from the groove together with the polyester film and the thickness of the resin layer at a position where the resin has been completely hardened throughout its thickness and where the thickness becomes maximum is measured. The maximum thickness (excluding the thickness of the polyester film) represents the hardenability of the sample resin. The greater the thickness, the better is the hardenability.

15 Removability Test:

A test sample is applied to a copper clad laminate (thickness: 1.6 mm) having a copper-plated through-holes having a diameter of 3 mm using a roll coater so as to plug the through-hole. The laminate is then passed, at a conveying speed of 2 m/minutes, through a pair of high pressure mercury lamps (80 W/cm) with a distance between the laminate and each lamp being 15 cm so that the plug resin in the through-hole is irradiated by UV rays from both sides thereof. An aqueous sodium hydroxide solution (3 % by weight) at 40 °C is then continuously poured at a constant flow rate on the plugged through-hole. The period of time from the start of the pouring till the solution has passed through the through-hole represents the removability of the sample resin. The shorter this period the better is the removability.

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Cracking Test:

A test sample is applied onto a copper clad laminate (thickness: 1.6 mm) to form a resin layer having a thickness of 320 μ m. The laminate is then passed at a conveying speed of 2.0 m/minute beneath a high pressure mercury lamp (80 W/cm) with a distance therebetween of 15 cm, thereby to harden the resin layer. A metal ball weighing 5.4 g is dropped on the hardened

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layer to check whether or not crack is formed in the resin layer. This procedure is repeated while gradually increasing the height of the ball from which it is dropped. The maximum height above which crack is caused represents crack-resistance.

5 The greater the height, the better is the resistance to crack (impact strength).

Comparative Example 1

10 A resin composition was prepared in the same manner as that in Example 1 except that no polyethylene glycol was used and that the amount of hydroxyethyl methacrylate was increased to 25 parts. The composition was then tested for its hardenability and for removability and crack-resistance of its hardened product. The test results are summarized in Table 1.

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Table 1

	Example 1	Comparative Example 1
20 Hardenability (μm)	840	830
Removability (second)	80	85
Crack-Resistance (cm)	40	5

Example 2

25 Example 1 was repeated in the same manner as described except that a polyethylene glycol having an average molecular weight of 1000 was used as ingredient (d). The crack-resistance of the hardened product of the resin composition was found to be 46 cm.

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Example 3

35 Example 1 was repeated in the same manner as described except that a polyethylene glycol having an average molecular weight of 6000 was used as ingredient (d). The crack-resistance of the hardened product of the resin composition was 42 cm.

Example 4

Example 1 was repeated in the same manner as described except that 2-hydroxyethyl methacrylate was used in an amount of 20 parts and that 5 parts of glycerin were used in place of 10 parts of the polyethylene glycol. The crack-resistance of the hardened product of the resin composition was 30 cm.

Example 5

Example 1 was repeated in the same manner as described except that 2-hydroxyethyl methacrylate was used in an amount of 20 parts and that 5 parts of propylene glycol were used in place of 10 parts of the polyethylene glycol. The crack-resistance of the hardened product of the resin composition was 42 cm.



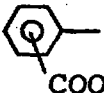
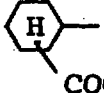
CLAIMS:

1. A resin composition hardenable by irradiation with high energy radiation, comprising the following ingredients (a) through (d):

(a) a resin selected from the group consisting of rosins and modified rosins and having an acid value of at least 150 and a Gardner color scale of not greater than 15;

(b) a compound of the general formula (I):



wherein Y represents  or , A

represents an alkylene having 1-4 carbon atoms, R represents hydrogen or methyl and m is an integer of 1-4;

(c) a hydroxyl group-containing compound having only one acrylic or methacrylic group and at least one hydroxyl group; and

(d) a polyol compound having at least two hydroxyl groups;

the amounts of said ingredients (a) through (d) being as follows:

ingredient (a):	15-60%
ingredient (b):	10-60%
ingredient (c):	10-50%
ingredient (d):	1-30%

based on the total weight of ingredients (a) through (d), with the proportion of ingredient (b) being 30-85% based on the total weight of ingredients (b) and (c).

2. A composition as set forth in Claim 1, wherein said modified rosins are rosins modified by reaction with an acid or an alcohol.

3. A composition as set forth in Claim 2, wherein said acid is selected from the group consisting



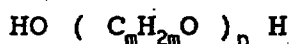
of maleic acid, maleic anhydride, fumaric acid, fumaric anhydride, phthalic acid and phthalic anhydride, and said alcohol is selected from the group consisting of pentaerythritol and glycerin.

4. A composition as set forth in any preceding claim, wherein said compound of the formula (I) is selected from the group consisting of monomethacryloyloxyethyl hexahydrophthalate, monomethacryloyloxy-1-isopropyl hexahydrophthalate, monoacryloyloxyethyl hexahydrophthalate, monomethacryloyloxyethyl-1-isopropyl phthalate and monoacryloyloxyethyl phthalate.

5. A composition as set forth in any preceding claim, wherein said hydroxyl group-containing compound is a compound selected from the group consisting of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate.

6. A composition as set forth in any preceding claim, wherein said polyol is glycerin or a diol which is liquid at room temperature.

7. A composition as set forth in Claim 6, wherein said diol is a compound having the general formula:



wherein m is an integer of 2 or more and n is an integer of 1 or more.

8. A composition as set forth in Claim 7, wherein said diol is selected from ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol and a polyalkylene glycol having both oxyethylene and oxypropylene groups.



9. A composition as set forth in any preceding claim, wherein the amounts of ingredients (a) through (d) are as follows:

ingredient (a):	25-50%
ingredient (b):	15-50%
ingredient (c):	15-50%
ingredient (d):	1-25%

based on the total weight of ingredients (a) through (d), with the proportion of ingredient (b) being at least 35% based on the total weight of ingredients (b) and (c).

10. A composition as set forth in any preceding claim, further comprising at least one additive selected from the group consisting of photopolymerization photosensitizers, fillers, thermal polymerization inhibitors and anti-foaming agents.

11. A resin composition, as set forth in Claim 1 and substantially as described in any one of the Examples herein.
