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"Coating composition and method"

This invention relates to a photosensitive resin composition. More particularly, it relates to a photosensitive resin composition for forming a protective coating film having excellent characteristics which may be used either alone to provide a photosensitive tacky coat or combined with a variety of other types of ingredients such as a crosslinker to increase crosslinking density, a resin to remove tackiness, or another photosensitive ingredient to increase sensitivity to light. The uses of the instant photosensitive coating material include photoresist applications such, for example, as plating resist, etch resist and solder mask.

Soldering masks are used to produce printed wiring boards. The solder mask's function is basically to prevent soldering bridges, to keep electric insulation between conductors thus preventing conduction between solder areas and to prevent the corrosion of a naked copper conductor. It is also desirable to have photo-imagable solder masks which are able to retain an image which may be used as a blueprint on which the solder is placed. Because of the desirability of increasing wiring density, a solder mask having precise resolution and extremely good electrical insulation properties is required. The instant photosensitive composition can provide these advantages.

Solder masks are described in U.S. Patent No. 4,499,163 which discloses a photosensitive resin

composition containing urethane diacrylate or dimeth-
acrylate, a linear polymeric compound having a glass
transition temperature between about 40° and 150° C.,
and a sensitizer which generates free radicals in actinic
5 light. The linear polymeric compounds described include
the vinyl series linear polymers or copolymers such as,
for example, polymers from vinyl monomers including,
for example, methyl methacrylate, butyl methacrylate,
methyl styrene, and vinyl toluene. Sensitizers include,
10 for example, substituted and unsubstituted polynuclear
quinones.

Another photocurable urethane acrylate resin
composition suitable for permanent resists is described
in U.S. Patent No. 4,587,201. The composition therein
15 described uses a urethane-acrylate resin based on a
butadiene polymer. This resin is combined with a photo-
polymerization initiator to form the permanent resist
material.

Most photoimable solder masks, however, lack
20 the ability of being developed in an aqueous solution.
This necessitates the use of organic solvent developing
solutions. The use of such organic solvents has become
undesirable because of the environmental regulations for
controlling solvent emission.

25 Another disadvantage found with solder masks that
use organic solvent developing solutions is the continued
sensitivity of the final product to organic solvents such,

for example, as methylene chloride. In certain product applications, such susceptibility is undesirable.

It is therefore desirable to provide photoimagable solder mask coating compositions which may be developed in aqueous solutions, and which are resistant to organic solvents such as methylene chloride. It is an object of the instant invention to provide such a coating composition. It is also an object of the instant invention to provide a solder mask coating composition which may be stripped with commercial alkaline strippers. The photosensitive resin compositions described herein have good resolution, flexibility, adherence to metal, solvent resistance, high temperature resistance and electrical insulation properties.

The present invention provides a photoimagable coating composition comprising: a polymer selected from carboxylated urethane polymethacrylates and carboxylated urethane polyacrylates; said polymer being made by condensing a reaction mixture comprising component (a) a diisocyanate having from 6 to 18 carbon atoms, component (b) a carboxylic acid polyol having the formula $[HO]_x-R_6-COOH$; wherein x represents an integer from 2 to 5, and wherein R_6 is a cyclic, linear or branched, saturated or unsaturated aliphatic, or aromatic, hydrocarbon moiety having from 2 to 29 carbon atoms, and component (c) selected from hydroxyalkyl acrylates and hydroxyalkyl methacrylates, wherein each alkyl has from 2

5

to 28 carbon atoms; provided that component (a) is present in an amount of from 30 to 80% by weight of the total amount of the reaction mixture; component (b) is present in an amount of from 5 to 45% by weight of the total amount of the reaction mixture, there being at least 0.8 milliequivalents of acid per gram of the total amount of the reaction mixture, and component (c) is present in an amount of from 5 to 50% by weight of the total amount of the reaction mixture, there being at least 0.5 milliequivalents of (meth)acrylate per gram of the total amount of the reaction mixture, the composition also comprising a binder.

The present invention further provides a method for the preparation of a UV sensitive polymeric composition comprising conducting a condensation reaction with a reaction mixture comprising: component (a) a diisocyanate having from 6 to 18 carbon atoms, component (b) a carboxylic acid polyol having the formula $[\text{OH}]_x\text{-R}_6\text{-COOH}$; wherein x represents an integer from 2 to 5, and wherein R_6 is a cyclic, linear or branched, saturated or unsaturated aliphatic or aromatic, hydrocarbon moiety having from 2 to 29 carbon atoms, and component (c) a hydroxyalkyl acrylate or a hydroxyalkyl methacrylate wherein each alkyl has from 2 to 28 carbon atoms; provided that component (a) is present in an amount of from 30 to 80% by weight of the total amount of the reaction mixture; component (b) is present in an

amount of from 5 to 45% by weight of the total amount of the reaction mixture, there being at least 0.8 milliequivalents of acid per gram of the total amount of the reaction mixture, and component (c) is present in an amount of from 5 to 50% by weight of the total amount of the reaction mixture, there being at least 0.5 milliequivalents of (meth)acrylate per gram of the total amount of the reaction mixture, and mixing the condensation product with a binder.

The present invention also provides a photosensitive coating composition comprising a binder and a carboxylated urethane poly(meth)acrylate, said poly(meth)acrylate being obtainable by, and preferably obtained by, the reaction of

- (a) a diisocyanate
- (b) a carboxylic acid polyol, and
- (c) a hydroxyaliphatic (meth)acrylate

the proportion of acid groups being at least 0.8, and the proportion of (meth)acrylate groups optionally being at least 0.5, milliequivalents per gram of carboxylated urethane poly(meth)acrylate.

Specific embodiments of the instant composition provide a highly viscous photosensitive material which is useful as an additive for compositions that require both thickening and the addition of a photosensitive coating

material. In this way, the instant photosensitive materials fulfil a dual role, both as a thickener and as a photosensitive, photocurable additive. Such embodiments of the instant compositions are thus useful photosensitive, photocurable thickening agents for materials such, for example, as paints and inks.

In a preferred embodiment of the invention, the photocurable coating composition comprises a UV sensitive compound selected from: carboxylated urethane diacrylate,

carboxylated urethane triacrylate, carboxylated urethane dimethacrylate and carboxylated urethane trimethacrylate. This group is hereinafter referred to as carboxylated urethane di (and/or) tri(meth)acrylate. In this
5 specification "(meth)acrylate" includes acrylate and/or methacrylate. Higher poly(meth)acrylates are also provided.

These carboxylated urethane di and/or tri(meth)-acrylates are prepared from acidified moieties which provide the carboxyl group. These compositions are prepared by condensing a diisocyanate, a carboxylic acid
10 polyol, and a hydroxyaliphatic (meth)acrylate. The aliphatic radical in the last-mentioned component may be acyclic (linear or branched) or cyclic, may be saturated or unsaturated, and may be interrupted once or more by
15 an oxygen atom. However, in most embodiments it is an alkyl radical, and the component will be referred to for simplicity as a hydroxyalkyl (meth)acrylate. The carboxylic acid polyol should be present in an amount sufficient to provide at least 0.8 milliequivalents of acid per gram
20 of the combined amount of the total amount of reactants, abbreviated herein as meq/g of TR (total reactants usually are the diisocyanate, carboxylic acid polyol, and hydroxy alkyl (meth)acrylate). In order to obtain a suitable level of photosensitivity in the product, the
25 hydroxy alkyl (meth)acrylate is desirably used in a proportion of at least 0.5 milliequivalents per gram of the combined amount of the diisocyanate, carboxylic acid polyol

and hydroxy alkyl (meth)acrylate.

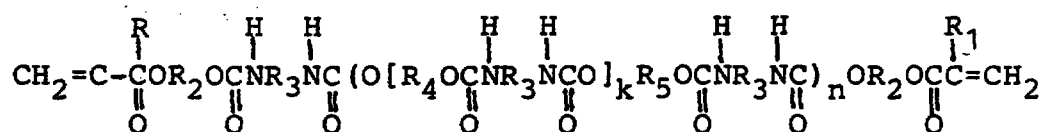
The invention provides a variety of embodiments, achieved by combining the above coating composition with other specifically selected ingredients.

- 5 Such ingredients, selected in order to provide or enhance a specific quality or characteristic, include:
a crosslinking agent, dyes, pigments, thermopolymerization inhibitors, and additives designed to improve coating properties.

- 10 The instant photocurable coating composition contains the carboxyl moiety, which alters the organophilic nature of the urethane (meth)acrylate polymer. As a result, the instant coating compositions become more organophobic, and thus are resistant to organic solvents
15 such as methylene chloride. Further, these carboxylated photosensitive polymers may be mixed in large amounts with other hydrophilic binders and crosslinkers. In addition to this, the introduction of the carboxyl moiety makes the instant coating compositions soluble or
20 swellable in aqueous alkali solutions (pH in excess of 7.5) until exposure to UV light. Advantageously, when the instant compositions are used to provide a photocurable coating, or solder mask, the development step may be done in aqueous alkali solutions. It will be noted that
25 although the incorporation of the carboxyl moiety changes the nature of the urethane (meth)acrylate, making it soluble in aqueous alkali, the sensitivity of the compound

to UV light is retained. The carboxylation, moreover, improves adherence to metals. Thus, an improved solder mask is provided by the combination of a binder, a crosslinker, and a carboxylated urethane di (and/or) tri-
 5 (meth)acrylate. A preferred combination uses a copolymer of styrene/maleic anhydride as the binder (also providing carboxyl groups). Preferred crosslinkers are the (meth)-acrylate, and polyfunctional (meth)acrylate, monomers.

Preferred carboxylated urethane di, tri, and higher poly-
 10 (meth)acrylates of the instant invention may be represented by Formula 1 :



15 Formula 1

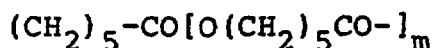
In Formula 1, n is an integer from 1 to 4; k may be 0 or 1; and R₁, derived from the (meth)acrylate reaction component represents a hydrogen atom or a methyl group; R₂, also derived from the (meth)acrylate reaction component
 20 represents a linear or branched saturated aliphatic moiety having from 2 to 28 carbon atoms optionally interrupted by one or more oxygen atoms and R₃, derived from the diisocyanate portion of the reaction mixture, represents a branched, linear or cyclic, saturated or unsaturated
 25 aliphatic or an aromatic hydrocarbon moiety. R₃ may advantageously have from 4 to 20 carbon atoms and

preferably has from 6 to 18 carbon atoms. For preferred embodiments R_3 is derived from the diisocyanate reactant selected from trimethylhexamethylene, hexamethylene, isophorone, tolylene, 4,4-methylbis(cyclohexyl) methylene-
5 diphenyl, and tetramethylxylene diisocyanates. R_4 represents a linear, cyclic or branched, saturated or unsaturated aliphatic or an aromatic hydrocarbon advantageously having from 2 to 28 carbon atoms. R_4 may optionally also contain a hydroxyl moiety (remaining from
10 the polyol used in the preparation of the composition). R_5 is derived from a reaction mixture including (a) the carboxylic acid polyol of Formula 2 below or (b) the carboxylic acid polyol of Formula 2 and from the hydroxydicarboxylic acid of Formula 3 below. Thus, R_5 will
15 always have at least one COOH moiety and a minimum of 3 carbon atoms. When R_5 is derived from (a) (from Formula 2 compounds only) it will have only one COOH group with a branched or linear saturated or unsaturated aliphatic or an aromatic radical, advantageously having
20 a total of from 3 to 30 carbon atoms including the carboxyl carbon atom. When R_5 is derived from (b) the overall composition will have R_5 moieties derived from the carboxylic acid polyol of Formula 2 and also R_5 moieties derived from the hydroxyl dicarboxylic acids of
25 Formula 3. The R_5 moieties derived from the Formula 3 hydroxydicarboxylic acid compounds will have two COOH groups and also may have from 3 to 30 carbon atoms,

including the two carboxyl carbons. The discussion below of the Formula 2 and Formula 3 compounds will provide more information regarding the preferred concentrations and structures of these R_5 moieties. It will be understood that a mixture of components of any particular category may be employed. For example, both acrylate and methacrylate may be used, in which case some of the R_1 's will represent hydrogen and others methyl.

It should be realized that the exact location of each R_5 moiety within the polymer molecule will depend upon the number of reactive hydroxyl groups of the Formula 2 or Formula 3 compound, and upon the somewhat random condensation reaction. For example, when R_5 is derived from (b) and when y of Formula 3 is one, R_5 will be a terminal group having two COOH moieties; simultaneously other R_5 moieties from the same reaction mixture (derived from the Formula 2 carboxylic acid polyol) will be randomly located within the backbone of the polymeric molecular structure as indicated above in Formula 1.

In Formula 1, R_2 preferably has from 2 to 16 carbon atoms, and more preferably, is a moiety selected from the group consisting of: ethyl, propyl, butyl, and:



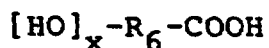
where $m = 1$ or 2 .

R_4 is derived from the optional polyol which may

be added to the reaction mixture. R_4 will, therefore, have from 2 to 28 carbon atoms and from 2 to 5 oxygen atoms. The oxygen atoms may possibly be in an unreacted hydroxyl moiety. When R_4 is present, it advantageously has from 2 to 28 carbon atoms or preferably from 2 to 16 carbon atoms optionally also having a hydroxyl moiety. Other preferred embodiments allow R_4 to be a saturated or unsaturated hydrocarbon moiety having from 2 to 10 carbon atoms and from 2 to 5 oxygen atoms possibly as an unreacted hydroxyl group. In specific examples of such preferred embodiments, R_4 is a moiety selected from: ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl and having from 2 to 5 oxygen atoms from the previous hydroxyl moieties. R_4 may also be derived from glyceryl or 2-ethyl-2-(hydroxymethyl)-1,3-propylene.

The carboxylated urethane di (and/or) tri(meth)acrylates of the instant invention may be obtained by condensing a diisocyanate with a carboxylic polyol (see Formula 2) and a hydroxyalkyl(meth)acrylate in a one step reaction. The carboxyl-containing polyol may be any carboxylic acid containing 2 or more hydroxyl moieties. Suitably, there are from 2 to 5 hydroxyl groups. Preferably, the compound is either a carboxylic acid diol or triol.

Advantageously, therefore, the carboxylic acid polyol has the formula shown in Formula 2 as follows:



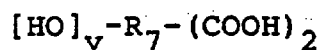
Formula 2

wherein x is an integer from 2 to 5 and R_6 is a branched, cyclic or linear, saturated or unsaturated, aliphatic or an aromatic hydrocarbon moiety having from 2 to 29 carbon atoms. Where x represents 3 or more, R_5 in Formula 1 may be linked to a further (meth)acrylated isocyanate group or further such groups to give tri or higher poly(meth)-acrylates. Preferably, R_6 has from 2 to 24 carbon atoms while x is 2 or 3. Most preferably, x is 2 and R_6 is a branched or linear, saturated or unsaturated aliphatic or an aromatic hydrocarbon structure with from 2 to 20 carbon atoms. A preferred embodiment uses an α,α -dimethylol alkanoic acid as the carboxylated diol, most preferably having an alkyl group having from 1 to 8 carbon atoms. Preferred diol carboxylic acids are selected from: α,α -dimethylolacetic acid; α,α -dimethylolpropionic acid, α,α -dimethylolbutyric acid, α,α -diethylolacetic acid; α,α -diethylolpropionic acid; α,α -dipropylolpropionic acid, α,α -dipropylolbutyric acid, and 2,3-dihydroxypropanoic acid.

Optionally, a polyol may also be included in the reaction mixture. This will increase the molecular weight of the product. The presence of the polyol results in materials as depicted under Formula 1 wherein $k = 1$.

One embodiment of the instant invention may preferably be taken advantage of when a higher concentration of hydroxyl groups is provided (such as by the

addition of a polyol or by the use of a carboxylic acid as shown in Formula 2 where x is 3, 4, or 5). In this embodiment, a hydroxy dicarboxylic acid is added to the reaction mixture. Formula 3 below shows a formula for
 5 some suitable hydroxyl carboxylic acids:



Formula 3

where y represents an integer from 1 to 5 (preferably from 1 to 3) and R_7 is a linear, cyclic, or branched,
 10 saturated, or unsaturated aliphatic or an aromatic hydrocarbon moiety having from 1 to 28 carbon atoms, preferably having from 1 to 18 and most preferably from 1 to 12 carbon atoms. If y is from 2 to 5, R_7 preferably ranges from 2 to 18 carbon atoms. Preferably, these diacids
 15 should be used when the hydroxyl concentration of the total reaction mixture is at least about 0.3 milliequivalents of OH per gram of the combined amount of the reactants (the diisocyanate, the carboxylic acid polyol, the hydroxyl alkyl(meth)acrylate, the hydroxydicarboxylic
 20 acid and the polyol if present). These diacids may suitably be used in an amount of from 0.3 to 0.7 milliequivalents of acid per gram of the combined amount of the reactants. Suitable hydroxy dicarboxylic acids may be selected from the group consisting of: malic acid,
 25 tartaric acid, dihydroxy tartaric acid, hydroxy adipic acid, dihydroxy adipic acid, and trihydroxy adipic acid.

These dicarboxylic acids may be used to provide thermally curable pendant or terminal end-groups. Advantageously, these ends also provide reactive sites for future reaction with other materials. Melamine and epoxy
5 for example are two compounds or moieties that may be reacted with the terminal carboxyl groups. By such reactions the characteristics of the material may be further modified or enhanced. The specific characteristics or qualities desired will depend on the intended use
10 of the material.

To prepare the instant carboxylated urethane di (and/or) tri(meth)acrylate coating composition, the reaction is advantageously carried out in a dry solvent solution which itself is non-reactive to the isocyanate.
15 Suitable examples of such solvents are esters, for example, ethyl acetate and propyleneglycol monomethyl ether acetate; ketones, for example, methyl ethyl ketone, methyl isobutyl ketone, and N-methylpyrrolidone; aromatic hydrocarbons, for example, toluene and xylene; and mixtures of the
20 above.

The reaction preparing the instant coating composition is advantageously conducted with the solids content of the solution in the range of from 20 to 100%, preferably in the range of from 35 to 95% and, most preferably,
25 from 65 to 85% by weight. The reaction temperature is generally from 50 to 95°C., and preferably from 65 to 85°C. Preferably, homopolymerization is inhibited by

the addition of a free radical polymerization inhibitor such, for example, as hydroquinone, m-dinitrobenzene or phenothiazine. Most preferably, these are used in an amount of from about 0.005% to about 1% by weight based
5 on the weight of the solids.

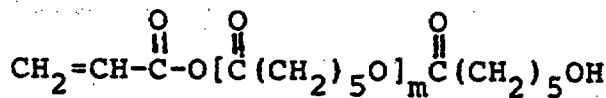
It is also preferred to use a condensation catalyst such as a tin or amine catalyst. Such catalysts may be selected from di-butyl tin dilaurate, dimethyl tin dineodecanoate, dibutyltin bisoctylthioglycolate, tri-
10 ethylamine, and triethylenediamine. For best results, the reaction is carried out under a dry air blanket.

The diisocyanate may be a hydrocarbon that is branched, linear, or cyclic, saturated or unsaturated aliphatic or aromatic. Advantageously, it has from 4 to
15 20 carbon atoms, preferably, it has from 6 to 18 carbon atoms. Diisocyanates may be selected from xylylene diisocyanate; 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane; 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate; 2,4-tolylenediisocyanate; 2,6-tolylenediisocyanate;
20 cyanate; 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate; methylene-bis(4-cyclohexalisocyanate); hexamethylenediisocyanate; meta-tetramethylxylenediisocyanate; para-tetramethylxylenediisocyanate; methylene-bis-phenyldiisocyanate;
25 1,5-naphthylene diisocyanate; metaphenylene diisocyanate and mixtures of the above. The most preferred diisocyanates are: 2,6-tolylene diisocyanate; 2,4-tolylene

diisocyanate; 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane; 2,2,4-trimethylhexamethylene diisocyanate, and 2,4,4-trimethylhexamethylene diisocyanate.

5 When a polyol is included, the molecular weight, cure speed, and crosslinking density will be increased. The polyol may have from 2 - 28 carbon atoms. The hydrocarbon portion may be cyclic, branched or linear, saturated or unsaturated aliphatic or aromatic, and have
10 from 2 - 5 hydroxyl moieties. Preferably, the polyol is a diol or triol having from 2 to 16 carbon atoms. Preferred diols may be selected from: ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, octanediol, neopentyl glycol, 2-methylpropane-1,3-diol,
15 cyclohexanedimethanol, and diethylene glycol. Other preferred polyols include glycerol, trimethylolpropane, and hexanetriol.

 The hydroxyaliphatic (meth)acrylate may have an aliphatic group with from 2 to 28 carbon atoms. The
20 aliphatic moiety may be linear, cyclic, or branched, saturated or unsaturated, but is advantageously an alkyl group. Preferably, the alkyl group of the hydroxy alkyl (meth)acrylate has from 2 to 12 carbon atoms. Some preferred hydroxyalkyl (meth)acrylate can be selected
25 from: hydroxyethyl(meth)acrylate, hydroxy propyl (meth)acrylate, hydroxy butyl (meth)acrylate. Also preferred are having the general formula:



where m is one or two.

When the coating composition of the invention is prepared, the concentrations of the reactants should advantageously be such that the total concentration of the hydroxyl groups is at least approximately equal to the amount of diisocyanate present. Broadly, this means that the total concentration of the polyol, the diol of the dialkylol carboxylic acid, and the hydroxyalkyl (meth)-
 10 acrylate is sufficient to bring the ratio of hydroxyl to diisocyanate advantageously to at least about 0.95:1, and, preferably, to at least 1:1. Most preferably, the hydroxyl moiety is present in excess. Preferably, the hydroxyl should be present relative to the diisocyanate in the molar range
 15 of from 1.05:1 to .95:1, most preferably, it is in the range of from 1.02:1 to 1:1.

The carboxylic acid polyol is an important ingredient of the instant coating composition, and is preferably present in an amount sufficient to allow the uncured
 20 copolymer to be soluble or swellable in aqueous alkali solutions.

We have found that enhanced polar solubility results when, according to the invention, the carboxylic acid polyol is used in the reaction mixture in an amount
 25 greater than 0.8 acid milliequivalents per gram of the total amount of the reactants (meq/g of TR).

A preferred range of acid meq/g of TR is from 0.8 to 1.6 acid meq/g of TR. If a highly viscous product, extremely suitable for combination with other materials, is desired it is most preferred that the reaction mixture contains a proportion of at least 1 acid meq/g of TR; a most preferred range is from 1 to 1.6 acid meq/g of TR. The use of the diacid of Formula 3 may also be used to add to the amount of acid milliequivalents.

Another advantage provided by the carboxylation of the urethane di and tri(meth)acrylates is that the UV sensitive compound may be combined with hydrophilic resins. Furthermore, by varying the concentration of the carboxylation in the urethane di and tri(meth)acrylates, the hydrophilic nature of this UV sensitive compound may, to an extent, be controlled. This allows the hydrophilic character to be set for a specific resin. Thus, when one desires to use a more hydrophobic or less hydrophilic resin, a low concentration of carboxylation can be used in the urethane di and tri(meth)acrylate, to increase compatibility with the selected resin. Conversely, if one desired to use a hydrophilic resin, the carboxyl concentration would be increased so that the resin and the

urethane di and tri(meth) acrylate could be mixed in larger concentrations. Advantageously the carboxylic acid polyol is used in the reaction mixture in concentrations having the carboxylated polyol in an amount of from 5 to 45% by weight of the total amount of reactants (by weight of TR), preferably, from 5 to 25% by weight of TR, most preferably, from 12 to 25% by weight of TR.

When a polyol is also included, it is advantageously used in the reaction mixture in an amount of from 2 to 18% by weight of TR; and preferably, from 2 to 15% by weight of TR.

For the diisocyanate, an advantageous concentration range is from 30 to 80% by weight of the TR. Preferably, it is in the range of from 50 to 75% by weight of TR.

The hydroxyalkyl (meth)acrylate should be present in the reaction mixture in a proportion of at least 0.50 meq of acrylate/g of TR to assure suitable UV sensitivity if the composition contains no other photosensitive component. A suitable range is from 0.5 to 1.6 meq of acrylate/g of TR. An advantageous weight percent range is in an amount of from 5 to 50% by weight of TR and, preferably, it is used in an amount of from 10 to 30% by weight of TR.

The instant carboxylated urethane di (and/or) tri(meth)acrylate copolymer coating composition advantageously has a weight average molecular weight of from 500 to 6,500, preferably, from 800 to 3,000, and, most

preferably, from 1,000 to 2,500 (determined by Gel Permeation Chromatography and based on a standard polystyrene calibration curve).

As indicated above, the coating composition of the invention comprises a binder. The resin which is used for this preferably should have a glass transition temperature (T_g) of about 155°C. or greater, and most preferably is hydrophilic. The high T_g will improve temperature resistance. Several commercially available
 10 resins are available for this purpose. Compatible mixtures can be achieved with the instant carboxylated urethane di (and/or) tri(meth)acrylates especially by appropriately varying the carboxyl concentration. Resins that may be used for this purpose are styrene/maleic
 15 anhydride copolymers, particularly those which have been partially esterified with low molecular weight alcohols. Copolymers of styrene/maleic anhydride are commercially available which have been esterified with mixtures of alcohols from methyl to butyl. Such copolymers are
 20 commercially available in a wide range of molecular weights. The molecular weight of this resin binder should preferably be in the range of from 25,000 to 300,000; and most preferably from 60,000 to 250,000. Preferably, the copolymer used has a ratio of styrene to maleic anhydride in the
 25 range of from 1:1 to 2:1. A preferred T_g range for the binder is from 155°C. to 200°C.

The binder may be used in an amount of from 85 to

25% by weight of the total composition, and, preferably, from 17 to 60% by weight of the total composition.

Preferably, the carboxylated urethane di (and/or) tri(meth)acrylate coating composition is mixed with the binder so that the Tg of the end product is from 70 to 190°C. Preferably, the binder acid number is from 120 to 280 mg of KOH/g. Other polymers having the above described molecular weight, Tg and acid number may also be used as a binder with the carboxylated urethane di (and/or) tri(meth)acrylate coating composition. Suitable polymers for use as binders include: methyl methacrylate-methacrylic acid and methyl methacrylate-methyl acrylate-methacrylic acid.

When the instant carboxylated urethane di (and/or) tri(meth)acrylate composition is used with other additives such, for example, as crosslinkers, dyes, solvents, pigments, photoinitiators and thermal inhibitors, the concentration of the UV sensitive carboxylated coating ingredient advantageously is in the range of from 10 to 85% by weight of the total composition. Preferably, it is in the range of from 15 to 75% and, most preferably, it is in the range of from 17 to 60% by weight of the total combined composition.

Preferred crosslinkers are the (meth)acrylate monomers. Crosslinkers are used when it is desirable to obtain a composition having a greater crosslinking density,

which in turn improves resistance to solvents such as methylene chloride. More preferred are polyfunctional (meth)acrylate monomers. Such polyfunctional monomers can be selected from trimethylolpropane tri(meth)acrylate, 5 trimethylpropane ethoxylated tri(meth)acrylate, dipentaerythritol hydroxypentaacrylate, and ditrimethylolpropane tetraacrylate.

Other crosslinkers which may be used include divinyl ethers, acrylated epoxies, epoxy resins, and 10 aminoplast resins. The acrylated epoxies are preferred since they improve overall heat resistance, solvent resistance, and overall adhesion.

When the instant carboxylated coating composition is used as a solder mask, the composition is advantageous- 15 ly coated on an appropriate substrate and dried to a tack-free condition. The coated substrate is then advantageously photoimaged with from 75 to 105 mJ/sq. cm. of UV radiation, and may then be developed with an aqueous alkali solution. Preferably, the aqueous alkali solution 20 is potassium or sodium carbonate.

Generally, the photoimaged coated substrate is inspected at this point. The instant coating composition has the advantage in that, if desired, a coating can be easily stripped with an aqueous alkaline stripper, and 25 redone. The amount of alkali needed in the stripping or developing solution is very low. A solution which comprises 1% by weight of base may be used.

When the desired quality of image is obtained, the coating may be given a post UV cure of 3 - 5 J/sq. cm. This is followed by a heat cure, preferably at 150°C. for a sufficient curing time. The instant compositions have
5 excellent resolution, flexibility, and adherence to metals.

The following examples illustrate the invention. All parts and percentages are by weight unless otherwise indicated.

10

Example 1

This example illustrates the preparation of the photoimagable coating composition.

The following ingredients were added to a 5 liter round-bottomed flask, fitted with a mechanical stirrer,
15 a thermometer, a condenser, a gas inlet, and a heating mantle: 236.0 grams (g) (about 4 equivalents) of 1,6-hexanediol; 268.0 g. (about 4 equivalents) of dimethylolpropionic acid; 951.2 g. (about 8.2 equivalents) of 2-hydroxyethyl acrylate; 0.23514 g. of phenothiazine
20 as a free radical inhibitor; 783.8 g. of N-methyl-2-pyrrolidone as a solvent; and 31.35 g. of dibutyltin dilaurate (T-12) as a catalyst. Under a dry-air blanket with agitation, 1,680.0 g. (about 16 equivalents) of trimethylhexamethylene diisocyanate were charged into the
25 mixture in two equal portions 30 minutes apart. An exotherm took place for each addition. The reaction temperature was kept under 85°C. by cooling with

an ice-water bath, and after the second addition of trimethylhexamethylene diisocyanate the reaction temperature was maintained at a constant 85°C. for 10-12 hours until the isocyanate infra-red absorption peak had
5 disappeared, which indicated that the reaction had gone to completion.

Example 2

The photosensitive coating composition which was prepared in Example 1 was used to prepare a photoimagable
10 solder mask. The solder mask was prepared by charging the following ingredients to a 500 ml. roundbottom flask, equipped with a stirrer, a gas inlet, a thermometer, and a condenser: 6.5 g. of a low molecular weight copolymeric defoaming agent; 91.25 g. of N-methyl-2-pyrrolidone as a
15 solvent; 82.0 g. of an esterified styrene/maleic anhydride copolymer as binder. (The resin used here was Scripset 550 by Monsanto). The mixture was agitated and heated to 95°C. for 30 minutes to obtain a hazy solution. After this, the temperature was lowered to 70°C., and then the
20 following ingredients were added to the mixture: 0.004 g. of the free radical polymerization inhibitor phenothiazine; 77.5 g. of the UV sensitive coating composition prepared in Example 1, and 9.0 g. of a green pigment. While the mixture was blanketed with a flow of dry air, a premixed
25 solution containing the following was added: 47.8 g of trimethylolpropane triacrylate (SR351) as a crosslinker, 6.5 g. of isopropylthioxanthone (ITX) as a photoinitiator

and 8.4 g. of ethyl p-dimethylaminobenzoate (EPD) as a sensitizer.

The above ingredients were allowed to mix under a dry air blanket for 30 minutes at 70°C., after which time they were discharged into an amber jar. The solder masking this composition prepared was used as described in Example 3.

Example 3

The composition prepared in Example 2 was applied as a coating to two 6" x 8" (153 x 203 mm) bare copper clad epoxy boards at a wet thickness of about two mils (0.05 mm), using a 75 mesh monofilament polyester screen, and a rubber squeegee having 70 durometer hardness. This wet coating was dried to a 1.4 mil (0.035 mm) tack-free film in a forced-air oven at 100°C. in a period of 12 minutes.

After these dried films were cooled to room temperature, they were exposed at 75 mJ/sq. cm. through an IPC (Institute for Interconnecting Packaging electronic circuits) No. B-25 negative artwork with a 400 watt mercury vapor lamp. The exposed films were then developed manually in a 1% solution of K_2CO_3 for 45 seconds, and then rinsed with fresh water.

An excellent resolution of the IPC B-25 was produced.

After this development, the boards were cured at 3 J/sq. cm., and thermally baked at 150°C. for one hour as a post-cure process.

One of the boards was then soaked in methylene chloride (MeCl_2) for 15 minutes, and no degradation was found on the mask (solvent resistance test).

The other board was given a cross-hatch adhesion test according to ASTM D3359-78 method B, and was found to have no adhesion loss. The board was then painted with a resin flux, and floated with the face having the solder mask down on a molten solder pot at 260-275°C. for 10 seconds. After the solder pot test, the board was immediately rinsed with 1,1,1-trichloroethane while the board was still warm. One hour later, the board was given the same cross-hatch adhesion test and found to have no adhesion loss.

Example 4

Using the apparatus and general procedure as described in Example 1, urethane diacrylate oligomers were prepared which varied in the amount of carboxylation. Sample 4 contained no carboxylation and Sample 9 contained the highest amount of carboxylation. All of the samples were prepared at 80% solids. The formulation used for each individual sample is shown in Table 1 below; the weights are given in grams.

Table 1

The following abbreviations have been employed.

DMPA = dimethylolpropionic acid
2HEA = 2-hydroxyethyl acrylate
TMDI = trimethylhexamethylene diisocyanate

DTN = dimethyl tin dineodecanoate

M-Pyrol = N-methylpyrrolidone

eq. = equivalent

		<u>Sample 4</u>		<u>Sample 5</u>	
		<u>eq.</u>	<u>Weight</u>	<u>eq.</u>	<u>Weight</u>
5	1,6 Hexanediol	8	472	7.0	413.0
	DMPA	-	-	1.0	67.0
	2HEA	8.1	939.6	8.2	951.2
	TMDI	16	1680.0	16.0	1680.0
10	DTN	-	15.46	-	15.56
	M-Pyrol	-	772.9	-	777.8
	Phenothiazine	-	0.309	-	0.311

		<u>Sample 6</u>		<u>Sample 7</u>	
		<u>eq.</u>	<u>Weight</u>	<u>eq.</u>	<u>Weight</u>
15	1,6-Hexanediol	3.0	177.0	2.0	118.0
	DMPA	5.0	335.0	6.0	402.0
	2HEA	8.2	951.2	8.2	951.2
	TMDI	16.0	1680.0	16.0	1680.0
	DTN	-	15.72	-	15.76
20	M-Pyrol	-	785.8	-	762.8
	Phenothiazine	-	0.314	-	0.315

		<u>Sample 8</u>		<u>Sample 9</u>	
		<u>eq.</u>	<u>Weight</u>	<u>eq.</u>	<u>Weight</u>
	1,6-Hexanediol	1.0	59.0	0	0
	DMPA	7.0	469.0	8.0	536.0
5	2HEA	8.2	951.2	8.2	951.8
	TMDI	16.0	1680.0	16.0	1680.0
	DTN	-	15.8	-	31.67
	M-Pyrol	-	789.8	-	791.8
	Phenothiazine	-	0.316	-	0.317

10 The viscosities of Samples 4 - 9 were measured (in cP) at 75°F. (24°C.) using a Brookfield RVT Viscometer, # 6 spindle at 10 RPM.

Sample	4	5	6	7	8	9
Viscosity	20400	22400	41600	44800	68800	86400

15 Example 5

 Samples 5-9 of the carboxylated urethane acrylates were used to prepare solder masks, and the properties of the solder masks were compared. This example, along with examples 6 and 7 which follow, may be used to
20 compare the properties of the carboxylated urethane acrylates with those of masks containing noncarboxylated urethane acrylates.

 The solder masks designated herein as Samples D - H were prepared using the apparatus and by the
25 general procedure described in Example 2, Sample D employs

the acrylate of Sample 5, Sample E that of Sample 6, etc.

The proportion of each ingredient is given in the following table:

Table 2

5	<u>Common Solder Mask Formulation for Samples D-H</u>	
	Modaflow*(a low molecular weight copolymer)	6.5
	N-methyl pyrrolidone	91.25
	Styrene/maleic anhydride (Scripset *550)	82.0
	Phenothiazine	0.004
10	Carboxylated Urethane Acrylate	77.5
	Green Pigment (9G5)	9.0
	Isopropyl Thioxanthone	6.5
	Ethyl p-dimethylamino benzoate	8.4
	Trimethylolpropzyl triacrylate (SR351)	47.8

15 Summary of Properties of Solder Masks
 Containing Carboxylation

 Using the solder masks of Samples D-H, bare, copper clad epoxy boards were coated using the general method as described in Example 3. The boards were then
 20 tested and evaluated.

Photospeed - was excellent at 75 mJ/cm^2 for all Samples D-H.

Development: For Samples D-H in a 1% aqueous K_2CO_3 solution development was excellent.

In 1,1,1-trichloroethane development for Samples D-H was
 25 poor.

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Adhesion Test Method: ASTM-D3359-78 Method B.

(Scale 5 = No adhesion loss)

(Scale 0 = Complete adhesion loss)

Sample Number	D	E	F	G	H
5 Adhesion before molten solder	5	4-5	4-5	5	4-5
Adhesion after molten solder was applied	5	5	5	5	5

Example 6

Samples of a solder mask composition, using the 10 Sample 4 noncarboxylated material, were prepared as follows and as described in Example 2.

The ingredients and amounts of the ingredients are given in the following table:

Table 3

15	Solder Mask	Solder Mask
<u>Formulation</u>	<u>Sample A</u>	<u>Sample B</u>
Defoamer	1.10	1.30
N-methylpyrrolidone	41.8	50.35
Scripset	30.68	36.50
20 Phenothiazine	0.0024	0.003
Green Pigment (9G5)	3.1	3.1
Sample 4 acrylate	29.0	75.0
SR351	16.2	---
ITX	2.25	3.0
25 EPD	3.1	4.0

To provide a comparison using the procedures as described in Example 3 each of these formulations (A&B) were tested and used to coat a bare copper clad epoxy board. The results are given below:

5	Solder Mask		Solder Mask
	<u>Sample A</u>		<u>Sample B</u>
	Stability at 24°C: Limited Compatibility	(1 month)	Total Phase Separation
	<u>Development</u>		
10	1 % aq. K_2CO_3	excellent	---
	1,1,1-trichloroethane	poor	---
	<u>Property</u>		
	Methylene Chloride Resistance was poor showing the solvent's effect after only a 2 min. exposure.		
15	Adhesion before molten solder*	5	
	after molten solder*	5	

SR351 = Trimethylolpropane triacrylate

* crosshatch adhesion - ASTM-D3359-78 Method B

Scale 5 = no adhesion loss

20 Scale 0 = complete adhesion loss

Example 7

Also for the purpose of comparison, Sample 4 material was used to prepare a photosensitive element which was then evaluated for development in different types of solvents. The photosensitive element (Sample C)

was prepared by mixing the ingredients in Table 3, at 50°C., in a 500-ml round-bottom flask equipped with a stirrer, a gas inlet, a thermometer, and a condenser.

The table below indicates the amount of each
5 ingredient.

Table 3

A Solder Mask Composition (Sample C) Containing
Non-Carboxylated Urethane Diacrylate (Sample 4)

<u>Formulation</u>	<u>(g)</u>
10 Sample 4 acrylate	122.5
Elvacite*2008	94.0
PMA	131.0
Phenothiazine	0.0044
Irgacure*651	6.2
15 Leuco Crystal Violet (dye)	0.2

Development

in 1,1,1 trichloroethane	excellent
in 1% aqueous K ₂ CO ₃	no development

Materials and Abbreviations Used Above:

- 20 Elvacite 2008 = polymethyl methacrylate (M.W. = 79,000)
PMA = propylene glycol monomethyl ether acetate
Irgacure 651 = 2,2-dimethoxy-2-phenylacetophenone

The noncarboxylated urethane diacrylate (Sample 4) had a very limited compatibility with the styrene/
25 maleic anhydride resin (Scripset 550). Homogeneous mixtures of the noncarboxylated urethane diacrylate and

* Trade Marks

the styrene/maleic anhydride resin could be obtained only for a relatively short period of time (less than one month) but only when the ratio of the urethane diacrylate to the resin was less than one. When the ratio is
5 increased, phase separation occurred (Sample B).

The carboxylated urethane di or tri (meth)acrylate, however, can have varying concentrations of carboxylation, allowing them to be miscible and compatible in all proportions with the styrene/maleic anhydride resin and
10 other binder resins. The results are excellent shelf life, uniformity, and high performance properties of the products.

Example 8

Carboxylated urethane triacrylate samples were prepared using the apparatus and general procedure
15 as described in Example 1. The specific ingredients for each triacrylate sample is given in the table below:

Table 5

		Sample 10		Sample 11	
		(eq.)	(wt. in g)	(eq.)	(wt. in g)
	1,6-Hexanediol	2.0	118.0	---	---
5	Tone *0301	---	---	4.0	400.0
	Glycerol DMPA	2.0	61.4	---	---
	DMPA	4.0	268.0	4.0	268.0
	2HEA	8.1	939.6	---	---
	Tone M-100	---	---	8.2	2820.8
10	TMDI	16.0	1680.0	---	---
	IPDI	---	---	16.0	1777.6
	DTN	---	---	---	52.66
	T-12	---	30.67	---	---
	M-Pyrol	---	766.8	---	1316.6
15	Phenothiazine	---	0.23	---	0.395

Materials and Abbreviations Used Above:

Tone 0301 = polycaprolactone triol with molecular weight
of 300

Tone M-100 = a reactive caprolactone acrylate

20 IPDI = isophorone diisocyanate

= 1-Isocyanate-3-isocyanato-methyl-3,5,5-trimethyl-
cyclohexane

The solder mask compositions were prepared using
the apparatus and general procedure described in Example 2,
the products of Samples 10 and 11 being used to prepare the
solder masks of Samples I and J respectively.

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Table 6

Solder Mask Composition Based On

Carboxylated Urethane Triacrylates

	<u>Formulation</u>	<u>Sample I</u>	<u>Sample J</u>
5	Modaflow	1.10	1.10
	N-methyl pyrrolidone	41.8	41.8
	Scripset 550	30.68	30.68
	Phenothiazine	0.0024	0.0024
	(Sample 10)	29.0	---
10	(Sample 11)	---	29.0
	Green Pigment 9G5	3.1	3.1
	ITX	2.25	2.25
	EPD	3.10	3.10
	SR351	16.2	16.2
15	The compositions of Sample I and J were then used to make boards by the procedure described in Example 3, and tested.		
	<u>Development properties:</u>		
	in 1% by weight aqueous K_2CO_3	Excellent	Excellent
20	$MeCl_2$ resistance	6 min. (good)	8 min. (good)
	(Tested by immersing in the solvent for stated period of time and evaluating the results as good if no effect is seen, poor if a solvent effect is seen.)		
	Crosshatch adhesion - ASTM-D3359-78 Method B		
25	Scale 5 = no adhesion loss		
	Scale 0 = complete adhesion loss		
	Adhesion before molten solder	5	4
	after molten solder	5	3



CLAIMS

1. A photoimable coating composition comprising: a polymer selected from carboxylated urethane polymethacrylates and carboxylated urethane polyacrylates; said polymer being made by condensing a reaction mixture comprising component (a) a diisocyanate having from 6 to 18 carbon atoms, component (b) a carboxylic acid polyol having the formula $[HO]_x-R_6-COOH$; wherein x represents an integer from 2 to 5, and wherein R_6 is a cyclic, linear or branched, saturated or unsaturated aliphatic, or aromatic, hydrocarbon moiety having from 2 to 29 carbon atoms, and component (c) selected from hydroxyalkyl acrylates and hydroxyalkyl methacrylates, wherein each alkyl has from 2 to 28 carbon atoms; provided that component (a) is present in an amount of from 30 to 80% by weight of the total amount of the reaction mixture; component (b) is present in an amount of from 5 to 45% by weight of the total amount of the reaction mixture, there being at least 0.8 milliequivalents of acid per gram of the total amount of the reaction mixture, and component (c) is present in an amount of from 5 to 50% by weight of the total amount of the reaction mixture, there being at least 0.5 milliequivalents of (meth)acrylate per gram of the total amount of the reaction mixture, the composition also comprising a binder.

2. A composition as claimed in claim 1, wherein



the diisocyanate is selected from 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane; xylene diisocyanate; 3,3'-dimethyl diphenylmethane-4,4'-diisocyanate; 2,4-tolylenediisocyanate; 2,6-tolylenediisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; methylenebis(4-cyclohexyldiisocyanate); hexamethylene diisocyanate; 1,5-naphthylene diisocyanate; meta-phenylenediisocyanate; meta-tetramethylxylene diisocyanate; para-tetramethylxylene diisocyanate; and methylenebisphenyl diisocyanate.

3. A composition as claimed in claim 1 or claim 2, wherein component (b) is selected from alpha-alpha-dimethylol acetic acid, alpha-alpha-dimethylol propionic acid, alpha-alpha-dimethylol butyric acid, alpha-alpha-diethylol acetic acid, alpha-alpha-diethylol propionic acid and alpha-alpha-diethylol butyric acid.

4. A composition as claimed in any one of claims 1 to 3, wherein the binder is a styrene/maleic anhydride copolymer having a glass transition temperature of at least 155°C.

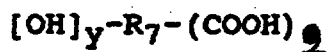
5. A composition as claimed in any one of claims 1 to 4, wherein the reaction mixture also includes a polyol having from 2 to 28 carbon atoms, and from 2 to 5 hydroxyl moieties.

6. A composition as claimed in any one of claims 1 to 6, wherein the reaction mixture also includes



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a dicarboxylic acid having the formula:



wherein y is an integer from 1 to 5 and wherein R₇ is a hydrocarbon moiety having from 1 to 28 carbon atoms.

7. A composition as claimed in any one of claims 1 to 6, wherein the poly(meth)acrylate is selected from di(meth)acrylates and tri(meth)acrylates.

8. A composition as claimed in any one of claims 1 to 7, wherein the reaction mixture has from 0.8 to 1.6 milliequivalents of acid per gram of the total amount of the reaction mixture.

9. A composition as claimed in any one of claims 1 to 8, which also contains a crosslinker.

10. A method for the preparation of a UV sensitive polymeric composition comprising conducting a condensation reaction with a reaction mixture comprising: component (a) a diisocyanate having from 6 to 18 carbon atoms, component (b) a carboxylic acid polyol having the formula $[\text{OH}]_x\text{-R}_6\text{-COOH}$; wherein x represents an integer from 2 to 5, and wherein R₆ is a cyclic, linear or branched, saturated or unsaturated aliphatic, or aromatic, hydrocarbon moiety having from 2 to 29 carbon atoms, and component (c)^{is} a hydroxyalkyl acrylate or a hydroxyalkyl methacrylate wherein each alkyl has from 2 to 28 carbon atoms; provided that component (a) is present in an amount of from 30 to 80% by weight of the total amount of the reaction mixture; component (b) is



present in an amount of from 5 to 45% by weight of the total amount of the reaction mixture, there being at least 0.8 milliequivalents of acid per gram of the total amount of the reaction mixture, and component (c) is present in an amount of from 5 to 50% by weight of the total amount of the reaction mixture, there being at least 0.5 milliequivalents of (meth)acrylate per gram of the total amount of the reaction mixture, and mixing the condensation product with a binder.

11. A method as claimed in claim 10, wherein the diisocyanate is as defined in claim 2.

12. A method as claimed in claim 10 or claim 11, wherein component (b) is as defined in claim 3.

13. A method as claimed in any one of claims 10 to claim 12, wherein the reaction mixture also contains a polyol having from 2 to 5 hydroxyl groups and from 2 to 28 carbon atoms.

14. A method as claimed in any one of claims 10 to 13, wherein the reaction mixture also includes a dicarboxylic acid as specified in claim 6.

15. A method as claimed in any one of claims 10 to 14, wherein the reaction mixture contains from 0.8 to 1.6 milliequivalents of acid per gram of the total reaction mixture.

16. A method as claimed in any one of claims 10 to 15, carried out at a temperature in the range of from 50 to 95°C.



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17. A method as claimed in any one of claims 10 to 16, wherein the reaction mixture also contains a free radical polymerization inhibitor and a condensation catalyst.

18. A method as claimed in any one of claims 10 to 17, carried out under dry air.

19. A photosensitive coating composition comprising a binder and a carboxylated urethane poly-(meth)acrylate, said poly(meth)acrylate being obtainable by reaction of

- (a) a diisocyanate
- (b) a carboxylic acid polyol, and
- (c) a hydroxyaliphatic (meth)acrylate

the proportion of acid groups being at least 0.8, and the proportion of (meth)acrylate groups optionally being at least 0.5, milliequivalents per gram of carboxylated urethane poly(meth)acrylate.

20. A photosensitive coating composition comprising the reaction product of

- (a) a diisocyanate,
- (b) a carboxylic acid polyol, and
- (c) a hydroxyaliphatic (meth)acrylate,

the proportion of acid groups being at least 0.8 milliequivalents, and the proportion of (meth)acrylate groups optionally being at least 0.5 milliequivalents, per gram of reaction product, in admixture with a binder.

21. A composition as claimed in claim 19 or



claim 20, wherein the diisocyanate contains from 4 to 20 carbon atoms.

22. A composition as claimed in claim 21, wherein the diisocyanate contains from 6 to 18 carbon atoms, excluding the carbon atoms of the isocyanate groups.

23. A composition as claimed in any one of claims 19 to 22, wherein the carboxylic acid polyol is of the formula



wherein x represents an integer from 2 to 5, and R₆ is a straight, branched, or cyclic, saturated or unsaturated aliphatic or aromatic moiety having from 2 to 29 carbon atoms.

24. A composition as claimed in claim 23, wherein x represents 2 or 3.

25. A composition as claimed in any one of claims 19 to 24, wherein the aliphatic moiety of component (c) is a cyclic, linear, or branched, saturated or unsaturated aliphatic group, which may contain one or more oxygen atoms in its chain.

26. A composition as claimed in any one of claims 19 to 24 wherein the aliphatic moiety of component (c) is an alkyl group.

27. A composition as claimed in any one of claims 19 to 26, which is the reaction product of, or is



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derivable from, a reaction mixture also comprising a hydrocarbon polyol.

28. A composition as claimed in any one of claims 19 to 27, which is the reaction product of, or is derivable from, a reaction mixture also comprising a hydroxydicarboxylic acid.

29. A composition as claimed in any one of claims 19 to 28, which also comprises a crosslinking agent.

30. A composition as claimed in any one of claims 19 to 29, which also comprises a photoinitiator.

31. A composition as claimed in any one of claims 19 to 30, which comprises a carboxylated urethane di(meth)acrylate.

32. A composition as claimed in any one of claims 19 to 31, which comprises a carboxylated urethane tri(meth)acrylate.

33. A photosensitive composition substantially as described in any one of Example 2, Example 5, and Samples I and J of Example 8 herein.

34. A composition as claimed in any one of claims 1 to 9 or 19 to 33, that has been exposed to actinic radiation.

35. A composition as claimed in any one of claims 1 to 9 or 19 to 33, in the form of a solder masking composition.

36. A composition as claimed in any one of



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claims 1 to 9 or 19 to 33, that has been imagewise exposed to actinic radiation, developed, and optionally fixed by post-development exposure.

37. A composition as claimed in any one of claims 1 to 9 or 19 to 33, in the form of a dry coating on a substrate.

38. A photoresist comprising a composition as claimed in any one of claims 1 to 9 or 19 to 33.

39. A paint or ink comprising a composition as claimed in any one of claims 1 to 9 or 19 to 33.
