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(71) Applicant (for all designated States except US): **SURFACE SPECIALTIES, S.A.** [BE/BE]; Allée de la Recherche, 60, B-1070 Brussels (BE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **CHEW, Kong, Chin** [MY/MY]; Surface Soecialties Malaysia SDN.BHD. (337603-V), PT 12701, Tuanku Jaafar Industrial Park, 71450 Seremban, Negeri Sembilan (MY).

(74) Agent: **DESTRYKER, Elise**; UCB, S.A., Allée de la Recherche, 60, B-1070 Brussels (BE).

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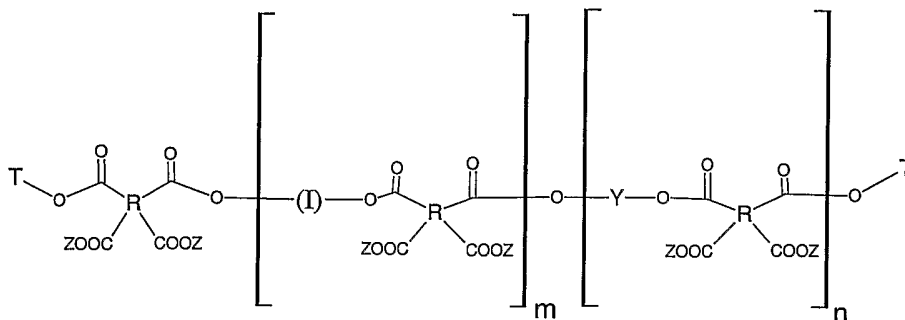
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(54) Title: ALKALI-DEVELOPABLE RADIATION CURABLE COMPOSITION

(θ)



(57) Abstract: The invention provides a radiation curable polymer described as dianhydride- polyol extended epoxy acrylate bearing carboxylic groups, as represented by Formula (θ) below; which is useful in alkali-developable photosensitive formulations for the fabrication of printed circuit boards or flat panel displays.

Alkali-developable radiation curable composition

Field of invention

This invention relates to radiation curable composition which can be used
5 as alkali-developable photosensitive or photoimageable materials for the
fabrication of articles such as printed circuit boards and liquid crystal displays. The
radiation curable compositions used as alkali-developable photosensitive materials
are removable by aqueous alkaline solution when they are not cured by radiation.
The alkali-developable photosensitive materials can be utilized as photoimageable
10 etching resist or plating resist inks in formation of circuit pattern, as
photoimageable solder mask to protect circuit pattern on printed circuit board, or
as photoresist ink in preparation of color filters for liquid crystal display.

Typically printed circuit boards are fabricated by applying a radiation curable
coating to the copper surface of the board. A negative film of the desired circuit
15 image is then applied to the curable coating and the film is exposed to a UV light
source. After the coating is cured the printed circuit board is washed in an
aqueous alkaline solution to remove the coating areas that were not exposed to
the UV light source. The board is then etched to remove the uncoated copper
regions. Other imaging techniques may be used. In addition to this use for
20 forming printed circuit boards, these techniques can be used to form other
surfaces such as printing plate surfaces. In this field radiation curable
compositions are often termed photo-resist compositions.

Background to the invention

25 US Patent 5002977 teaches the synthesis of a radiation curable polymer
made from the reaction of an acrylic binder based on methyl methacrylate, and
methacrylic acid further reacted with a cycloaliphatic unsaturated epoxy, 3,4-
epoxycyclohexyl methyl (meth)acrylate. The use of this polymer in liquid
photoimageable solder mask gives coatings that are excellent in tack-free property
30 before cure, and high photosensitivity. However, a main disadvantage with this
material is the excessive brittleness.

US Patent 4943516 teaches the synthesis of a radiation curable polymer
made from the reaction of an epoxy resin such as epoxy cresol novolak with

(meth)acrylic acid. This material is then further reacted with a cyclic anhydride such as 1,2,3,6-tetrahydrophthalic anhydride to provide acid functionality to the epoxy (meth)acrylate. The use of this polymer in liquid photoimageable composition gives coatings that are good in hardness but are tacky before curing. This results
5 in the coating sticking to the phototool, which is undesirable.

US Patent 5858618 also teaches a technique similar to US4943516. The difference is that instead of reacting the epoxy novolak with (meth)acrylic acid, it is reacted with a (meth)acrylated half-ester, which is a product of a cyclic anhydride with a hydroxy-group containing (meth)acrylate. This material is also known to
10 have similar performance as the product of US4943516.

WO 9800759 attempts to address the issue of the brittleness of the material taught in US5002977 by blending it with the novolak-based material taught in US4943516. However, the resulting material is still quite brittle.

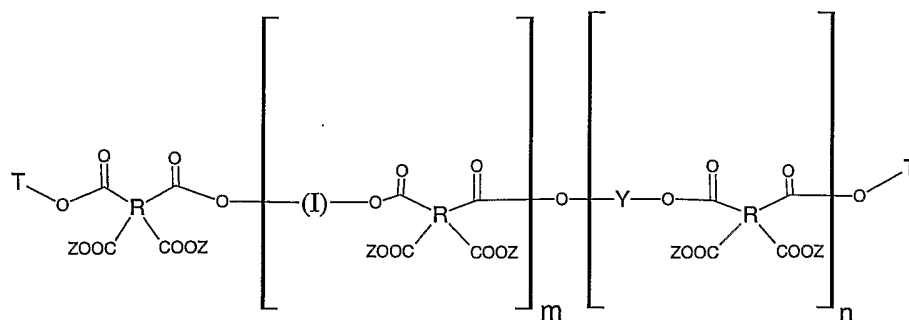
JP2000143579 attempts to solve the problem of brittleness by using as
15 additive a material prepared from a dianhydride reacted with 2 equivalents of a (meth)acrylate and subsequently with 2 equivalents of an unsaturated epoxy. However, although this may reduce the problem of brittleness, the tackiness of the formulation becomes an issue.

JP 2000297137 and JP 07092674 teach a photoimageable composition based on
20 the product of an epoxy acrylate with a dianhydride. However, the process based on this composition can take a long time to completion if the epoxy acrylate is used in only slight equivalent excess to the dianhydride, in order to synthesize a high molecular weight copolymer. The present invention aims to find an improved process and an improved radiation curable polymer that overcomes these
25 problems.

There is a need for novel radiation curable unsaturated compounds having free carboxyl groups which impart high flexibility and impact resistance. It was found that the present invention has found utility in alkali-developable photosensitive formulations for circuit formation as etching or plating resists, for
30 protection of circuit board as solder mask and for formation of color filters in liquid crystal display.

Summary of the invention

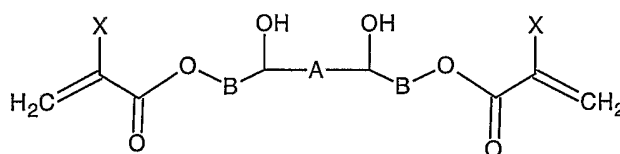
The invention provides a radiation curable polymer. This polymer is generally described as dianhydride-polyol extended epoxy acrylate bearing carboxylic groups, as represented by Formula (θ) below;

Formula (θ)

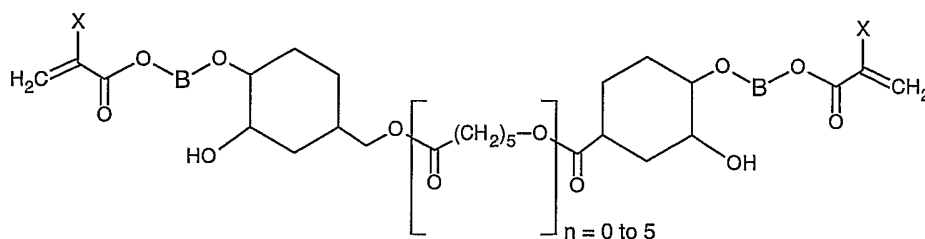
wherein;

the radiation curable polymer is derived by reacting Compound (I), Compound (II), and Compound (III), optionally further reacting with Compound (IV) and Compound (V);

- 10 wherein (I) is derived from compound (I-a) and/or Compound (I-b) which is reacted with Compound (II) through the hydroxyl groups of Compound (I-a) and/or (I-b);

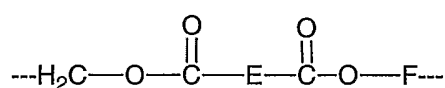


Compound (I-a)



Compound (I-b)

B designates $-\text{CH}_2-$ or

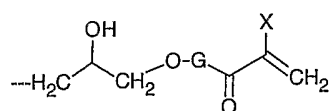


X designates H or $-\text{CH}_3$;

Y designates a compound derived from polyols of Compound (III);

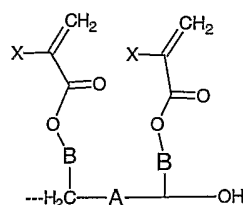
- 5 R represents an optionally substituted organo moiety which links the two anhydride groups on Compound (II), such that each anhydride group forms a five-membered cyclic structure with two atoms on R,

Z designates $-\text{H}$ or



in which the latter is derived from unsaturated epoxy compound (V);

- 10 and T designates $-\text{Q}$, $-\text{Y}-\text{OH}$, or



in which Q is derived from mono-alcohol compound (IV).

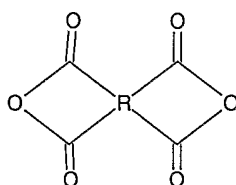
- 15 The radiation curable polymer according to the invention permits to solve the above-mentioned problems, including brittleness.

The invention provides a process for producing a radiation-curable polymer comprising :

(i) reacting together compounds (I), (II) and (III) optionally in the presence of solvent or multifunctional (meth)acrylate diluting monomer or mixture of both, polymerization catalyst and inhibitors, generally at 95 to 100°C between 5-20 hours wherein:

- compound (I) has at least 2 secondary hydroxyl groups and at least 2 (meth)acrylate groups and is of formula (I-a) and/or (I-b):

- compound (II) is a dianhydride compound of formula:



II

R represents an optionally substituted organo moiety which links the two anhydride groups, such that each anhydride group forms a five-membered cyclic structure with two atoms on R,

- compound (III) is a polyol with at least 2 primary hydroxyl groups,

(ii) optionally reacting any excess of anhydride groups from (i) with a mono alcohol compound (IV).

and (iii) optionally reacting the reaction products from (i) or (ii) with an epoxy-containing unsaturated compound (V).

This process can be faster and more complete than known prior art processes. Reactivity of a reaction mixture containing together a dianhydride compound, a polyol compound with at least 2 primary hydroxyl groups, and a compound containing at least two secondary hydroxyl groups is greater than the reactivity of a mixture of epoxyacrylate with dianhydride as described in JP

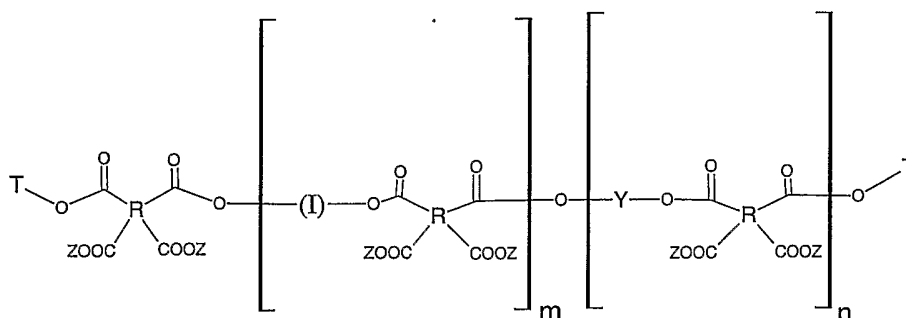
2000297137 and JP 07092674 for the synthesis of high molecular weight polymers.

The radiation curable polymer according to this invention is useful in alkali-developable photosensitive formulation for the fabrication of printed circuit boards or flat panel displays.

The invention provides a radiation curable and/or alkali developable photosensitive and/or thermosetting formulation comprising; 50 to 100 parts by weight of radiation curable polymer of Formula (θ), 0 to 100 parts of COOH-functional-acrylic polymer, 0 to 100 parts of COOH-functional acrylated acrylic polymers, 0 to 50 parts of multifunctional monomers, 1-20 parts of photopolymerization initiators, 1-20 parts of pigments or dyes, and 0-50 parts of epoxy-group containing resin.

Detailed description of the invention

The alkali-developable radiation curable polymer of Formula (θ) is further described as having structural unit (m) and (n) at a ratio of (m/n) between 1/99 to 90/10, described as the following



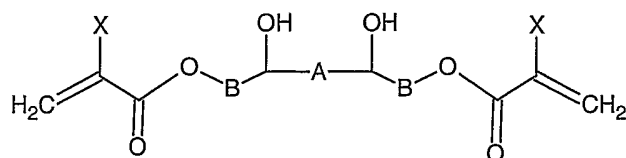
Formula (θ)

wherein;

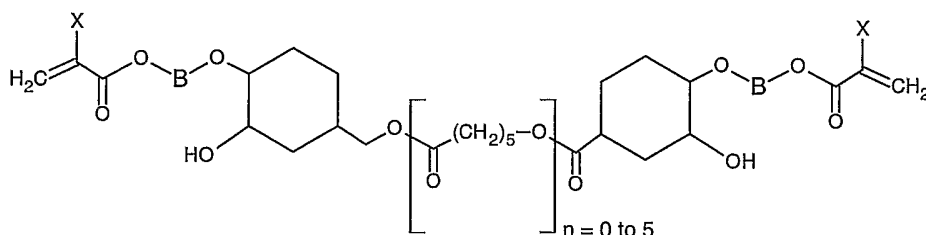
the radiation curable polymer is derived by reacting Compound (I), Compound (II), and Compound (III), optionally further reacting with Compound (IV) and Compound (V);

wherein (I) is derived from compound (I-a) and/or Compound (I-b) which is

reacted with Compound (II) through the hydroxyl groups of Compound (I-a) and/or (I-b);

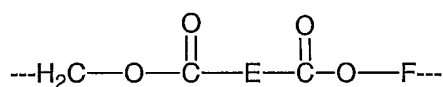


Compound (I-a)



Compound (I-b)

5 B designates -CH₂-- or



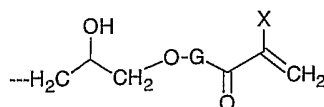
X designates H or -CH₃;

Y designates a compound derived from diols of Compound (III);

R represents an optionally substituted organo moiety which links the two anhydride groups of Compound (II), such that each anhydride group forms a five-membered cyclic structure with two atoms on R,

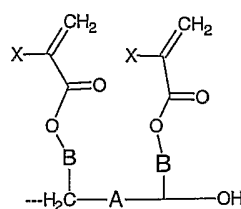
10

Z designates -H or



in which the latter is derived from unsaturated epoxy compound (V);

and T designates -Q, --Y--OH, or



in which Q is derived from mono-alcohol compound (IV).

Further embodiments of the invention will be described in detail below.

The structure as described in Formula (θ) can be synthesized through
 5 various ratios of compound (I), compound (II), compound (III), compound (V), and compound (IV).

The reaction can be conducted as follows: first reacting compound (I), compound (II) and compound (III), along with solvent, polymerization catalyst, and inhibitors in a reaction flask at 95-100 degree Celsius between 5 to 20 hours. The
 10 mixture is continuously stirred while maintaining temperature between 95 to 100 degrees Celsius, until more than 95% of all the anhydride groups are reacted to the hydroxyl groups. Then the final mixture is post-stabilized with hydroquinone or its derivatives to improve shelf stability of the final products.

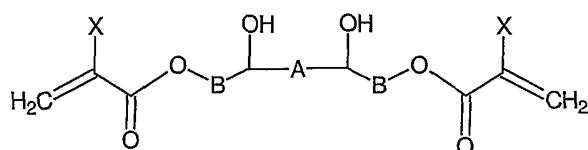
The preferred ratio of compound (I), Compound (II), and compound (III) are
 15 defined below such that based on number of carboxylic acid equivalents of the anhydride of compound (II) and hydroxyl equivalents of compounds (I) and (III);

- (i) $6 \leq (x + y + z) \leq 400$,
- (ii) $y \geq 3$,
- (iii) $x + z \geq y$,
- 20 (iv) x/y is between 0.2 and 0.9, and
- (v) z/y is between 0.1 and 0.8,

where x, y and z are the number of equivalents of compounds (I), (II), and (III), respectively.

The radiation curable polymer of Formula (θ) generally has theoretical molecular weight ranging from 1000 to 150,000 based on weight-average molecular weight as measured by Gel Permeation Chromatography. The range of final acid number is preferably between 50 and 200 mg KOH/gm.

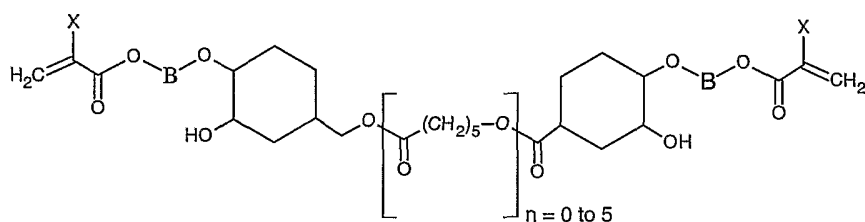
- 5 Compound (I) is preferably selected from di(meth)acrylate compounds having at least 2 secondary hydroxyl groups which are described below by



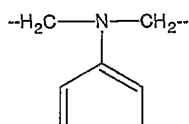
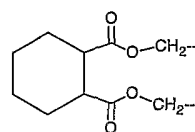
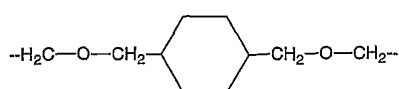
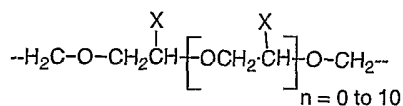
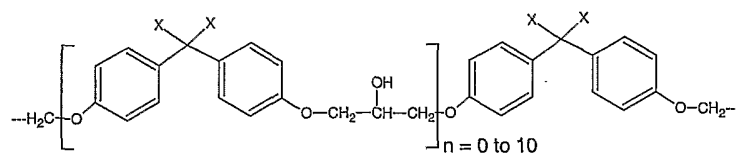
compound (I-a),

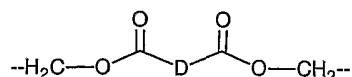
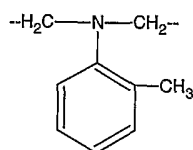
or, by compound (I-b),

10



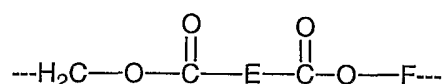
wherein A is selected from one of the following:





where D is derived from C8-C20 fatty acids, poly(butadiene), poly(butadiene-acrylonitrile).

5 and, B is $\text{--CH}_2\text{--}$ or:



such that E is a structure preferably derived from acid anhydrides based on maleic, succinic, glutaric, phthalic, tetrahydrophthalic, alkyl substituted tetrahydrophthalic, endomethylene tetrahydrophthalic, hexahydrophthalic, methyl-hexahydrophthalic anhydrides, but not limited to these;

10 and F is a structure derived from hydroxyl-functional (meth)acrylates preferably based on alkyl, alkyl ether, alkyl ester, alkyl ester ether, and cycloalkyl, wherein the alkyl is C2-C20;

and, X is H or --CH_3 .

Compound (I) is preferably a bisphenol-A epoxy acrylate.

15 Compound (II) is preferably selected from dianhydrides based on pyromellitic dianhydride, benzophenonetetracarboxylic acid dianhydride, 4,4'-bisphenol-A dianhydride, biphenyltetracarboxylic acid dianhydride, biphenylether tetracarboxylic acid dianhydride, 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexane-1,2-dicarboxylic acid dianhydride, 1,4,5,8-naphthalene tetracarboxylic
20 dianhydride, and 3,4,9,10-perylene tetracarboxylic dianhydride.

Preferred compound (II) is pyromellitic dianhydride.

Compound (III) is selected from polyol with at least two primary hydroxyl groups such as, for example, polyester polyol, polyether polyol, polycaprolactone polyol, and polycarbonate polyol, poly(tetrahydrofuran) diol, poly(tetramethylene glycol) diol, 1,4-cyclohexanedimethanol, diol of poly(1,4-cyclohexanedimethanol) and diol of poly(alkylene carbonate), tricyclodecane dimethanol, diol of poly(tricyclodecane dimethanol) and diol of poly(alkylene carbonate), diol of poly(alkylene glycol) and diol of poly(isophthalic acid), bisphenol-A, hydrogenated bisphenol-A, and alkoxyated bisphenol-A, poly(urethane) diol derived from di-carbonate and primary or secondary amines, trimethylolpropane and its alkoxyated and/or lactone modified polyol, glycerol and its alkoxyated derivatives, pentaerythritol and its alkoxyated derivatives, dipentaerythritol and its alkoxyated derivatives, but not limited to these.

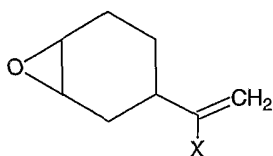
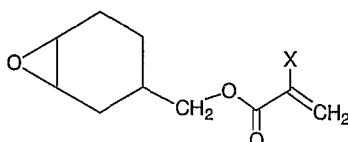
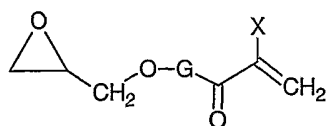
In order to obtain complete reaction of the dianhydrides, very small amount of mono alcohol, compound (IV), can be added to the reaction product of (I), (II), and (III). The range of compound (IV) added to the mixture is generally between 0 and 10 % by weight of the final product.

Compound (IV) can be selected from mono-functional alcohol such as alkyl alcohols of C2-C20 and methoxy alkyl alcohols of C2-C20. Preferably compound (IV) is methoxy propanol. Compound (IV) also can be selected from any (meth)acrylate compound containing a primary or secondary hydroxyl group. Such compound can be any hydroxyl alkyl (meth)acrylates with alkyl group of C2-C20. Example of hydroxyl alkyl (meth)acrylates are hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate.

Optionally, the reaction product of compound (I), (II), and (III), and optionally with (IV), can be further reacted with epoxy-containing unsaturated compound (V) to adjust the acid number.

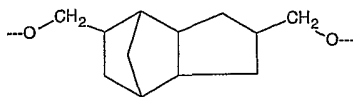
The range of compound (V) to be added is preferably from 0.1 to 0.8 epoxy equivalent to each equivalent of carboxylic acid. Preferred amount of compound (V) is not more than 0.50 epoxy equivalent to each equivalent of carboxylic acid.

Compound (V) is preferably selected from the followings;

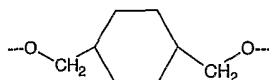


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wherein G can be absent, or --(C2-C10 alkyl)-O--, or



or



10 Among the above-mentioned compounds (V), the preferred ones are glycidyl methacrylate (G is absent, X=CH₃) and 4-hydroxybutyl acrylate glycidyl ether (G = -(C₄alkyl)-O-, X=H).

When Compound (V) is further reacted with reaction product of compounds (I), (II), and (III), this is preferably done by heating the mixture at 95 to 100 Celsius,
15 until the final epoxy content is less than 0.4% in the final product.

A radiation curable polymer according to the invention can be prepared in solvents or in multifunctional (meth)acrylate diluting monomers, or in a mixture of

both. Type of solvents recommended to use must not contain any hydroxyl group which can react with the dianhydride compounds. Organic solvents that could be used effectively includes ketones such as methyl ethyl ketone, methyl iso-butyl ketone or cyclohexanone; aromatic hydrocarbons such as toluene, xylene; esters
5 such as ethyl acetate and butyl acetate; and esters of glycol ethers such as cellosolve acetate, butyl cellosolve acetate, carbitol acetate, butyl carbitol acetate, and propylene glycol methyl ether acetate. The organic solvent is preferred to be highly compatible with the extended epoxy acrylate of Formula (θ). Multifunctional (meth)acrylate diluting monomers can be selected from any (meth)acrylate
10 containing monomers containing from 1 to 10 (meth)acrylate groups derived from any alcohols or polyols of C2-C50.

The reaction between anhydride and hydroxyl group can be catalyzed by inorganic alkaline salts such as sodium carbonate, lithium carbonate, sodium hydroxide; organometallic salts such as lithium octanoate, dibutyltin oxide, and
15 dibutyltin dilaurate, or basic organic compounds such as tertiary amines like ethylmorpholine, triethylamine, and phosphines like tri-phenyl phosphine.

Thermal polymerization of the (meth)acrylate unsaturation can be suppressed by adding thermal polymerization inhibitors based on quinones such as hydroquinones, methyl ether of hydroquinone, and ditertibutyl hydroquinone;
20 organometallic stabilizers based on phosphorus such as triphenyl phosphite, tris(nonylphenyl) phosphine; organo-antimony such as triphenyl antimony; and phenothiazine. These inhibitors are used for retarding thermal polymerization of the (meth)acrylate unsaturation in presence of oxygen. These stabilizers can be added to the extended epoxy acrylate during the preparation step, or after the
25 completion of the preparation to improve the shelf-life of the final product.

Carboxylic functional acrylic polymers suitable for the alkali-developable photosensitive formulation can be selected from any acrylic copolymer prepared from carboxylic group bearing (meth)acrylate such as (meth)acrylic acid, dimer of (meth)acrylic acid, with any of these alkyl (meth)acrylate, styrene and its
30 derivatives, hydroxyl-containing (meth)acrylates, vinyl ether, butadiene, vinyl

acetate. Such carboxyl functional polymers can also be obtained from the partial esterification of maleic anhydride copolymers selected from styrene-maleic anhydride copolymers, alkylene-maleic anhydride copolymer, and poly(butadiene)-maleic anhydride copolymer with mono-alcohols. Opening of the anhydride groups
5 by the monoalcohols formed pendant carboxylic groups on these copolymers. These carboxyl-functional acrylic polymers preferably have weighted average molecular weight between 5000 and 200,000; acid number between 50 and 250 mg KOH/gm; and glass transition temperature higher than 60 degree Celsius.

Carboxyl-functional acrylated acrylic polymers can be prepared via solution
10 polymerization of (meth)acrylate monomers selected from any of these (meth)acrylic acid, alkyl (meth)acrylate, styrene and its derivatives, hydroxyl-containing (meth)acrylates, vinyl ether, butadiene, and vinyl acetate. This resulted in carboxylic functional acrylic copolymer which is then further reacted to epoxy-containing unsaturated (meth)acrylate such as glycidyl methacrylate or 3,4-
15 epoxycyclohexyl methyl acrylate. Particular example is unsaturated acrylic polymer as described in US Patent 5,002,977. Furthermore, polymers prepared by partial esterification of styrene-maleic anhydride and hydroxyl (meth)acrylates could be used in the alkali-developable photosensitive formulation.

Multifunctional (meth)acrylate monomers or (meth)acrylate diluents are
20 useful for adjusting the ink viscosity and increasing the photo-resist compositions. Typical multifunctional (meth)acrylates or (meth)acrylate diluents are hydroxyethyl (meth)acrylate, hydroxypropyl acrylate and methacrylate, trimethylolpropane triacrylate and trimethacrylate, pentaerythritol triacrylate and tetraacrylate, dipentaerythritol hexaacrylate, and any mixtures of these.

Suitable photo-initiators for photo-resist application include 2-benzyl-2-N,N-
25 dimethylamino-1-(4-morpholinophenyl)-1-butanone commercially available as Irgacure 369 and 2-methyl-1-(4-methylthiophenyl)-2-morpholino propan-1-one commercially available as Irgacure 907. These photo-initiators are typically used in combination with thioxanthone sensitizers such as 2,4-diethylthioxanthone, 2-
30 and 4-isopropylthioxanthone, and 2- and 4-chlorothioxanthone.

Typical pigments used in the formulation are organic pigments such as phthalocyanines, quinacridones, dioxazines, isoindolinones, perinones, anthraquinones, and their mixtures. Inorganic pigments such as iron oxide, cobalt-based pigments, manganese-based pigments, ultramarine, Prussian blue, cobalt
5 blue, cerulean blue, viridian, emerald green, cobalt green and their mixtures are also used in the formulation.

Epoxy-group containing resins are necessary in formulation for solder mask or color filter resist. Suitable epoxy-containing resins are bisphenol-A epoxy and its polymer with bisphenol-A, cycloaliphatic epoxy, epoxy phenol novolak, epoxy
10 cresol novolak, triglycidyl of isocyanurate, triglycidyl ether of trimethylolpropane, bisphenol-A novolak, and epoxy containing (meth)acrylate.

Additionally organic solvents can be required to adjust the viscosity of the photo-resist ink for different applications. These solvents can be used alone or in any combination. Suitable organic solvents include butyl cellosolve, butyl
15 cellosolve acetate, propylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol and diethyl ether.

In the present invention the following general definitions are used : A monomer is a polymerisable compound with a low molecular weight (e.g. <1000 g/mol). An oligomer is a polymerizable compound of intermediate molecular weight, higher
20 than a monomer. Preferably, the molecular weight of an oligomer is comprised between about 250 and about 4,000 daltons. A monomer is generally a substantially monodisperse compound whereas an oligomer or a polymer is a polydisperse mixture of compounds. A polydisperse mixture of compounds prepared by a polymerisation method is a polymer. A polymer precursor is an
25 oligomer or a polymer which can be (further) polymerized. Curable resin as well as curable polymer refer to polymer or polymer precursor having at least ethylenically unsaturated group that can be polymerized i.e. cured. A composition is a mixture of compounds. A formulation is a mixture of compounds containing ingredients able to react together upon exposure to radiation.

The polymerisation of polymerisable compounds may be achieved by thermal curing or irradiation, irradiation curing being often called radiation curing. An irradiation curing can be done for example by using ultraviolet radiation and/or ionising radiation, such as gamma rays, X-rays or an electron beam. Radiation curing can be a free radical polymerization initiated by any free radical initiator, preferably a photochemical initiator. Radiation-curable polymer precursors can be acrylated oligomers or monomers i.e. compound containing radiation-curable acrylate functionalities.

Certain moieties, species, groups, repeat units, compounds, oligomers, polymers, materials, mixtures, compositions and/or formulations which comprise some or all of the invention as described herein may exist as one or more stereoisomers (such as enantiomers, diastereoisomers, geometric isomers, tautomers and/or conformers), salts, zwitterions, complexes (such as chelates, clathrates, crown compounds, cyptands / cryptades, inclusion compounds, intercalation compounds, interstitial compounds, ligand complexes, non-stoichiometric complexes, organometallic complexes, π -adducts, solvates and/or hydrates); isotopically substituted forms, polymeric configurations [such as homo or copolymers, random, graft or block polymers, linear or branched polymers (e.g. star and/or side branched polymers), hyperbranched polymers and/or dendritic macromolecules (such as those of the type described in WO 93/17060), cross-linked and/or networked polymers, polymers obtainable from di and/or tri-valent repeat units, dendrimers, polymers of different tacticity (e.g. isotactic, syndiotactic or atactic polymers)]; polymorphs [such as interstitial forms, crystalline forms, amorphous forms, phases and/or solid solutions] combinations thereof where possible and/or mixtures thereof. The present invention comprises all such forms which are effective.

It is appreciated that certain features of the invention, which are for clarity described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely various features of the invention, which are for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

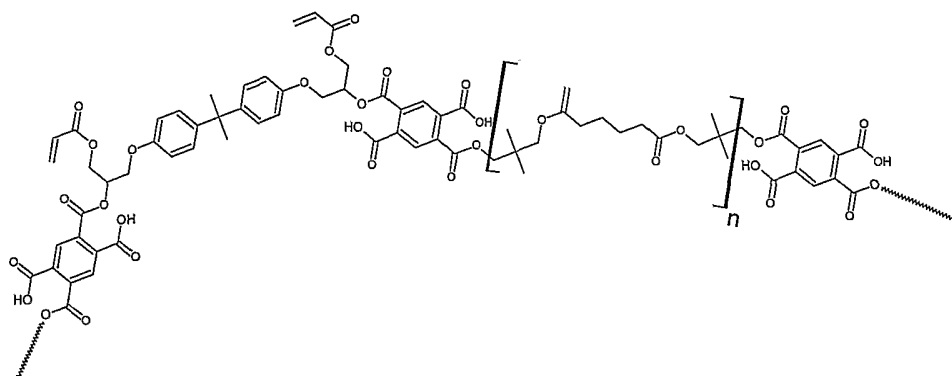
The term "comprising" as used herein will be understood to mean that the list following is non-exhaustive and may or may not include any other additional suitable items, for example one or more further feature(s), component(s), ingredient(s) and/or substituent(s) as appropriate. The formula of a compound X is
5 mentioned as (X).

The invention will be described by reference to the following examples, which are non-limiting.

Example 1 (resin A)

262g Fomrez 55-112 (neopentyl glycol-adipic acid polyester diol, hydroxyl
10 number 112 mgKOH/g, commercially available from Crompton Chemicals) and 206g of Ebecryl (Trade Mark) 3700 (bisphenol A diglycidyl ether diacrylate commercially available from UCB Surface Specialties) were charged into a reaction vessel. 400g methoxy propyl acetate, 0.7g hydroquinone and 0.7g methyl ether hydroquinone were subsequently added. The mixture was heated to 96°C
15 and 1g 4-ethylmorpholine was added. Lastly, 130g pyromellitic dianhydride was charged. The mixture was stirred and maintained at this temperature for 11h, after which 0.1g hydroquinone and 0.1g methyl ether hydroquinone were added. Final acid value of the mixture was 124 mgKOH/g. This material is designated as Resin A. Mole equivalent ratio of Compound (I): Compound (II): Compound (III) for Resin
20 A is 0.67:1.00:0.44.

Resin A can be schematically described as in Formula (2) based on reaction scheme of pyromellitic dianhydride, bisphenol-A epoxy acrylate and polyester diol (based on neopentyl glycol and adipic acid)



Formula (2)

Example 2 (resin B)

335.8g of Resin A, 13.4g of 4-hydroxybutyl acrylate glycidyl ether, 0.35g AMC-2,
 5 0.25g hydroquinone and 0.25g methylether hydroquinone were charged into a flask and heated to 96°C. The mixture was stirred at this temperature for 6h. The final acid value of this material is 90 mgKOH/g. This material is designated as Resin B. Mole equivalent of Compound (V) to COOH-group of Resin A: Resin B is 0.15: 1.00.

10 Example 3 (resin C)

330.49g of Resin A, 0.35g AMC-2, 0.25g hydroquinone and 0.25g methyl ether hydroquinone were charged into a reaction vessel and the mixture was heated to 96°C. 18.67g glycidyl methacrylate was then added and the resulting mixture was then added and the resulting mixture was stirred and heated for 6h. The final acid
 15 value was 78mgKOH/g. Mole equivalent of Compound (V) to COOH-group of Resin A: Resin C is 0.30:1.00.

Comparative example 1

As a comparison, in a separate synthesis, 211.4 g Eb3700 was charged
 20 into a reaction vessel (no diol added). 200g methoxy propyl acetate, 0.25g triphenyl antimony and 0.25g hydroquinone were subsequently added. The mixture was heated to 96°C and 0.5g 4-ethylmorpholine was added. Lastly, 87.6g

pyromellitic dianhydride was charged. The mixture was stirred and maintained at this temperature. After 7h, the partial acid value was 151mgKOH/g while the total acid value was 170mgKOH/g. One hour later, the total acid value has only decreased to 168mgKOH/g, indicative of a very slow reaction. After 10 hours of heating, gelling of the mixture occurred.

Examples 4 and 5

Furthermore Resin A and Resin B, are evaluated in formulation containing Cyclomer-P ACA250.

Coatings manufacture

Photoinitiator, Irgacure 907 commercially available from CIBA), based on 2-methyl-1-(4-methylthiophenyl)-2-morpholino propan-1-one is added to these resins to make it easily curable by UV source.

The formulations comprising a photoinitiator are applied onto a steel panel using bar coater, and dried in the oven at 80 degrees Celsius to evaporate the solvent. The final coating thickness after drying is between 10-15 microns.

The coated steel is exposed to UV source of Fe-doped metal halide for 60 seconds, through a glass in a vacuum condition. Intensity of the UV source at the coating surface is approximately 10 mW/cm².

Evaluation tests

Time to tack-free is measured by first placing the coated steel panel in the oven at 80 degrees Celsius, and taken out at 5 minutes increment. Tackiness of coating is measured by pressing a finger onto the coating. The coating is considered tack-free when there is no finger mark is left on the coating after pressing the finger onto the coating. Coating with shorter time to tack-free has the better tack-free property.

Hardness test is conducted by scratching the coating using pencils ranging from HB to 9H:

9H, 8H,..., 2H, 1H, F, HB

where 9H is the hardest, HB the softest. The hardest is the best.

Deformation resistance is measured on an Erichsen deformation tester and failure is measured based on cracks first appearing on the coating at a particular penetration depth in millimetre. A high penetration depth indicates a high deformation resistance.

- 5 Reverse impact resistance is measured by dropping a 1.7kg steel ball, raised at different height, onto the back of the coated steel. This is done at increment of 20 kg.cm of impact load. Failure is measured based on cracks first appearing on the coating. Coating which cracks at higher impact load has the higher reverse impact resistance, which is preferred. Coatings made from Resin A and Resin B are evaluated for time to tack-free, pencil hardness, deformation resistance, and reverse impact resistance.

A high resistance to cracks in reverse impact resistance test and/or in deformation resistance test indicates a low brittleness of the coating.

A comparison is made with coatings resulting from:

- 15 ▪ a resin made from epoxy acrylate and pyromellitic dianhydride (Comparative 1)
- an unsaturated acrylic binder, commercially available as Cyclomer-P ACA250 from Daicel Chemical (Comparative 2)
- 20 ▪ an epoxy novolak (meth)acrylate (prepared by reaction of epoxy cresol novolak, carboxyl-functional acrylonitrile butadiene and methacrylic acid; then further reacted to tetrahydrophthalic anhydride) as Comparative 3.
- a mixture of the above-mentioned binders in equal proportions (Comparative 4).

The comparison is shown in Table 1.

- 25 Improvement in deformation resistance and reverse impact resistance are achieved through the Resin A and Resin B.

Improvement in coating hardness was observed in formulation containing Resin A and Resin B compared to "ACA250" formulation.

- 30 Improvement in Erichsen penetration depth was achieved for ACA250-based formulation without significant reduction in tack-free. This indicates that the flexibility of the ACA250-based formulation has been significantly improved by the incorporation of Resin A and Resin B.

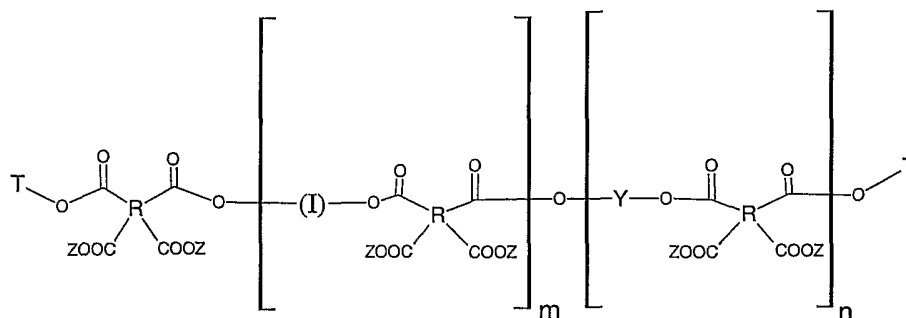
Table 1

	C1	C2	C3	C4	1	2	4	5
ACA250 (parts by weight)		10	-	5	-	-	8	8
Epoxy novolak (meth)acrylate (parts by weight)		-	10	5	-	-	-	-
Resin A (parts by weight)		-	-	-	10	-	2	-
Resin B (parts by weight)		-	-	-	-	10	-	2
Epoxy acrylate+pyromellitic dianhydride (parts by weight)	10	-	-	-	-	-	-	-
Irgacure 907 (parts by weight)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Time to Tack-free	X	5 minutes	20 minutes	10 minutes	30 minutes	30 minutes	5 minutes	5 minutes
Pencil Hardness	X	<1H	3H	<1H	~1H	~1H	1H	1H
Deformation Resistance	X	Failed at 1.0mm	Passed at 7.5mm	Failed at 1.5mm	Passed at 8.0mm	Passed at 8.0mm	Passed at 7.5mm	Passed at 7.5mm
Reverse Impact Resistance	X	Failed at 20kgcm	Failed at 20kgcm	Failed at 20kgcm	Passed at 40kgcm	Passed at 160kgcm	Failed at 20kgcm	Failed at 20kgcm

X: gelling of the reaction mixture impedes evaluation

Claims

1. A radiation curable polymer represented by Formula (θ) :



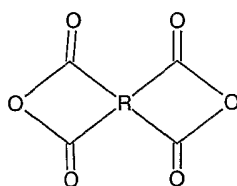
Formula (θ)

5 wherein;

the radiation curable polymer is derived by reacting Compound (I), Compound (II), and Compound (III), optionally further reacting with Compound (IV) and Compound (V);

10 wherein the compound (I) has at least 2 secondary hydroxyl groups and at least two (meth)acrylate groups;

wherein the Compound (II) is a dianhydride compound of formula:



wherein the Compound (III) is selected from polyols with at least 2 primary hydroxyl groups;

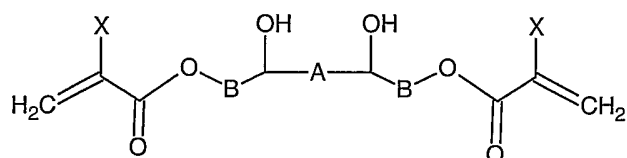
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wherein the Compound (IV) is a mono-functional alcohol selected from alkyl alcohols of C2-C20, methoxy alkyl alcohols of C2-C20 or any (meth)acrylate compound containing a primary or secondary hydroxyl group;

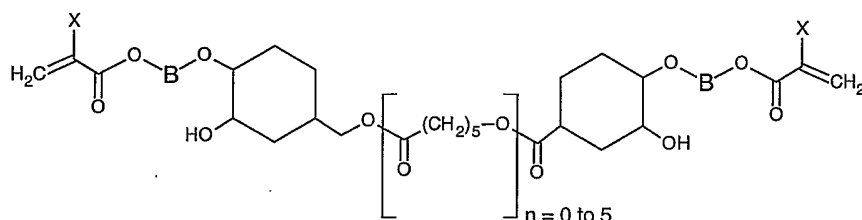
wherein the Compound (V) is a epoxy containing unsaturated compound;

wherein (I) is derived from compound (I-a) and/or Compound (I-b) which is reacted with Compound (II) through the hydroxyl groups of Compound (I-a) and/or (I-b);

5



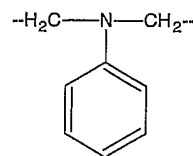
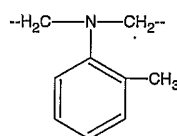
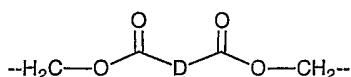
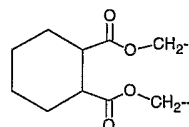
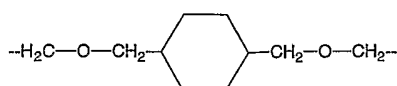
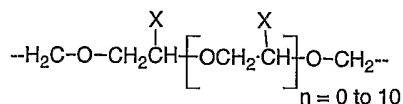
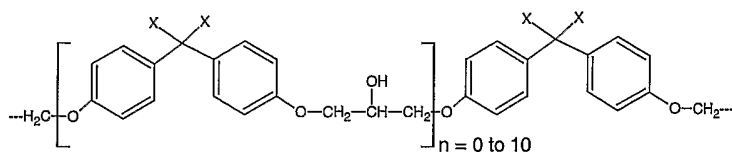
Compound (I-a)



Compound (I-b)

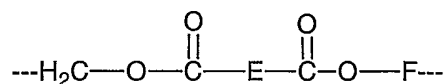
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wherein A is selected from one of the following:



wherein D is derived from C8-C20 fatty acids, poly(butadiene), poly(butadiene-acrylonitrile)

wherein B is—CH₂— or:



- 5 wherein E is a structure preferably derived from acid anhydrides based on maleic, succinic, glutaric, phthalic, tetrahydrophthalic, alkyl substituted tetrahydrophthalic, endomethylene tetrahydrophthalic, hexahydrophthalic, methyl-hexahydrophthalic anhydrides;

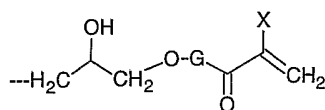
- 10 wherein F is a structure derived from hydroxyl-functional (meth)acrylates preferably based on alkyl, alkyl ether, alkyl ester, alkyl ester ether, and cycloalkyl, wherein the alkyl is C2-C20;

X is H or —CH₃,

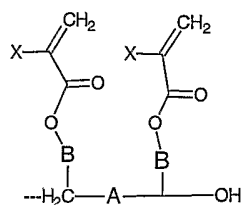
Y designates a compound derived from polyols of Compound (III),

- 15 R represents an optionally substituted organo moiety which links the two anhydride groups of Compound (II), such that each anhydride group forms a five-membered cyclic structure with two atoms on R,

Z is : —H or



T is: —Q, —Y—OH, or:



in which Q is derived from mono-alcohol compound (IV),

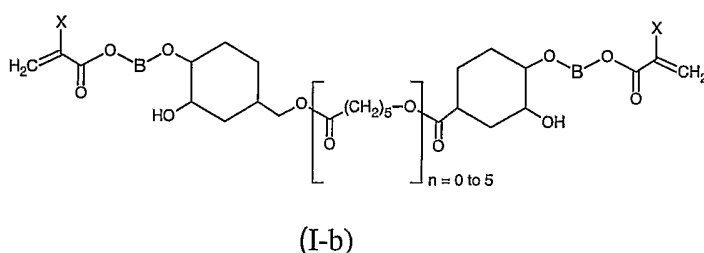
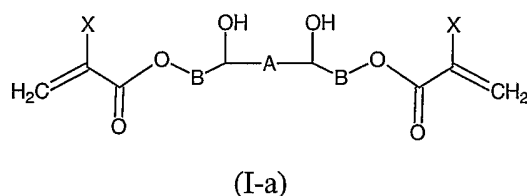
and where Y, A, B and X are as described above.

wherein structural units (m) and (n) are in a ratio of (m/n) between 1/99 to 90/10, with m between 1 and 100 and n between 1 and 100.

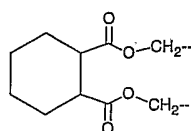
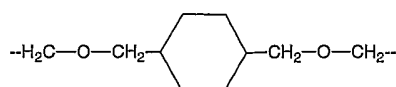
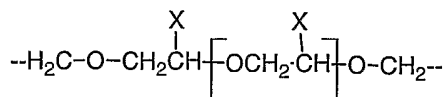
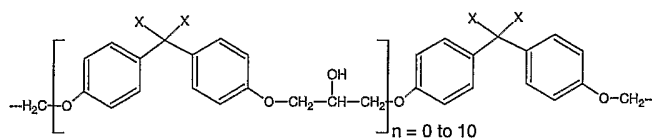
2. Process for producing a compound of Formula (θ) as claimed in Claim 1 comprising :

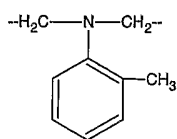
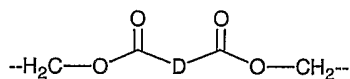
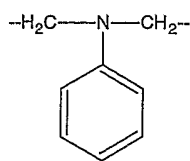
(i) reacting together Compounds (I), (II) and (III) optionally in the presence of solvent or multifunctional (meth) acrylate diluting monomers or mixture of both, polymerization catalyst and inhibitors,

wherein compound (I) has at least 2 secondary hydroxyl groups and at least 2 (meth)acrylate groups and is of formula (I-a) and/or (I-b):



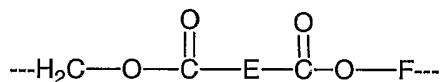
wherein A is selected from one of the following:





5 wherein D is derived from C8-C20 fatty acids, poly(butadiene), poly(butadiene-acrylonitrile).

wherein B is $\text{--CH}_2\text{--}$ or:

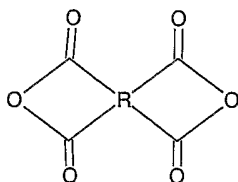


wherein E is derived from acid anhydride,

10 wherein F is a structure derived from hydroxyl-functional (meth)acrylates based on alkyl, alkyl ether, alkyl ester, alkyl ester ether, and cycloalkyl, wherein the alkyl is C2-C20;

and X is H or --CH_3 .

wherein Compound (II) is a dianhydride compound of formula:

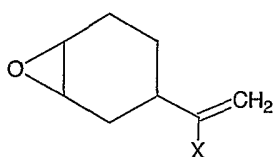
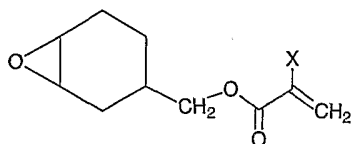
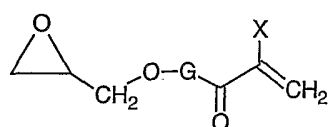


(II)

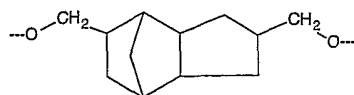
wherein R represents an optionally substituted organo moiety which links the two anhydride groups, such that each anhydride group forms a five-membered cyclic structure with two atoms on R, and

wherein Compound (III) is a polyol with at least 2 primary hydroxyl groups,

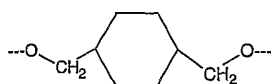
- 5 (ii) optionally Compound (IV) which is a mono-functional alcohol selected from alkyl alcohols of C2-C20, methoxy alkyl alcohols of C2-C20 or any (meth)acrylate compound containing a primary or secondary hydroxyl group, is added to the product of reaction (i), and
- (iii) optionally the product of reaction (i) or (ii) is reacted with Compound (V)
- 10 selected from one of the following:



wherein G can be absent, or --(C2-C10 alkyl)-O--, or



15 or



3. Process according to claim 2 wherein solvent is selected from ketones, aromatic hydrocarbons, esters or acetic esters of glycol ethers or a combination thereof and; wherein the ketones is selected from one or more from the groups consisting of methyl ethyl ketone, methyl iso-butyl ketone and cyclohexane;
5 wherein the aromatic hydrocarbon is either toluene or xylene or a mixture thereof; wherein the esters is either ethyl acetate or butyl acetate or a mixture thereof; wherein the esters of glycol ethers is selected from the group consisting of cellulose acetate, butyl cellulose acetate, carbitol acetate, butyl carbitol acetate or propylene glycol methyl ether acetate or a mixture thereof.
- 10 4. Process according to claim 2 wherein the reaction is conducted at 95 to 100°C between 5-20 hours.
- 15 5. Process according to claim 2 wherein the multifunctional (meth)acrylate diluting monomers is selected from (meth)acrylate containing monomers containing from 1 to 10 (meth)acrylate groups derived from any alcohols or polyols of C2-C50.
- 20 6. Process according to claim 2 wherein the catalyst is selected from inorganic alkaline salts, organometallic, tertiary amines or phosphines and; wherein the inorganic alkaline salt is selected from one or more from a group consisting of sodium carbonate, lithium carbonate and sodium hydroxide; wherein the organometallic salt is selected from a group consisting of lithium octanoate, dibutyltin oxide, and dibutyltin dilaurate; wherein the tertiary amines is either
25 ethylmorphine or triethylamine; the phosphines is tri-phenyl phosphine.
- 30 7. Process according to claim 2 wherein the polymerization inhibitor is selected from quinones, organometallic stabilizers based on phosphorus or organo-antimony and; wherein the quinones is selected from a group consisting of hydroquinones, methyl ether of hydroquinone and ditertibutyl hydroquinone; wherein the organometallic stabilizers is either triphenyl phosphite,

tris(nonylphenyl) phosphite; wherein the organo-antimony is either triphenyl antimony or phenothiazine.

5 8. Process according to claim 2, wherein compound (I) is a bisphenol-A epoxy acrylate compound.

9. Process according to claim 2 wherein compound (II) is selected from pyromellitic dianhydride, benzophenonetetracarboxylic acid dianhydride, 4,4'-bisphenol-A dianhydride, biphenyltetracarboxylic acid dianhydride, biphenylether
10 tetracarboxylic acid dianhydride, 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexane-1,2-dicarboxylic acid dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, and 3,4,9,10-perylene tetracarboxylic dianhydride.

10. Process according to claim 2, wherein compound (III) is selected from the
15 following: polyester polyol, polyether polyol, polycaprolactone polyol, and polycarbonate polyol, poly(tetrahydrofuran) diol, poly(tetramethylene glycol) diol, 1,4-cyclohexanedimethanol, diol of poly(1,4-cyclohexanedimethanol and alkylene carbonate), tricyclodecane dimethanol, diol of poly(tricyclodecane
20 dimethanol and alkylene carbonate), diol of poly(alkylene glycol and isophthalic acid), bisphenol-A, hydrogenated bisphenol-A, and alkoxyated bisphenol-A, poly(urethane) diol derived from di-carbonate and primary or secondary amines, trimethylolpropane and its alkoxyated and lactone modified polyol, glycerol and
its alkoxyated derivatives, pentaerythritol and its alkoxyated derivatives, dipentaerythritol and its alkoxyated derivatives.

25

11. Process according to claim 2 wherein compound (IV) is added to the reaction mixture in a ratio between 0 and 10 % by weight of the final product.

12. Process according to claim 2 wherein compound (IV) is methoxy propanol.

30

13. Process according to claim 2 wherein the reaction product of Compound (I),

(II), and (III), and optionally Compound (IV) is further reacted with an epoxy-containing unsaturated Compound (V).

14. Process according to claim 13 wherein Compound (V) is added in a ratio of
5 from 0.1 to 0.8 epoxy equivalent to each equivalent of carboxylic acid.

15. Process according to claim 13 wherein the Compound (V) is added in a ratio of at a maximum of 0.50 epoxy equivalent to each equivalent of carboxylic acid.

10 16. Process according to claim 13 wherein the further reaction is conducted at a temperature of 95 to 100°C until the epoxy content is less than 0.4% in the final product.

15 17. Process according to claim 13 wherein Compound (V) is glycidyl methacrylate and/or 4-hydroxybutyl acrylate glycidyl ether.

18. Process according to claim 2 wherein the ratio of Compound (I), Compound (II), and Compound (III) are such that based on number of carboxylic acid equivalents of the anhydride of Compound (II) and hydroxyl equivalents of
20 Compounds (I) and (III);

$$(i) \ 6 \leq (x + y + z) \leq 400,$$

$$(ii) \ y \geq 3,$$

$$(iii) \ x + z \geq y,$$

$$(iv) \ x/y \text{ is between } 0.2 \text{ and } 0.9, \text{ and}$$

25 $(v) \ z/y \text{ is between } 0.1 \text{ and } 0.8,$

where x, y and z are the number of equivalents of compounds (I), (II), and (III), respectively.

19. Radiation curable composition comprising:

- a) 50 to 100 parts by weight of the radiation curable polymer of Formula (θ),
- b) 0 to 100 parts by weight of COOH-functional acrylic polymer,
- c) 0 to 100 parts by weight of COOH-functional acrylated acrylic polymer,
- 5 d) 0 to 50 parts by weight of multifunctional monomer or (meth)acrylate diluent,
- e) 1-20 parts by weight of photo-polymerization initiator,
- f) 1-20 parts by weight of pigments or dye, and
- g) 0-50 parts by weight of epoxy-group containing resin.

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20. Composition according to claim 19 wherein the COOH-functional acrylic polymer is selected from any acrylic copolymer prepared from reaction of a carboxylic group bearing (meth)acrylate compound with any of alkyl (meth)acrylate, styrene and its derivatives, hydroxyl-containing (meth)acrylates, vinyl ether, butadiene, vinyl acetate or from those obtained from partial esterification of maleic anhydride copolymers selected from one of the following: styrene-maleic anhydride copolymers, alkylene-maleic anhydride copolymer, and poly(butadiene)-maleic anhydride copolymer with mono-alcohols.

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20 21. Composition according to claim 20 wherein the carboxylic group bearing (meth)acrylate compound is selected from (meth)acrylic acid or dimer of (meth)acrylic acid.

22. Composition according to claim 19 wherein the COOH-functional acrylic polymer has a weighted average molecular weight between 5000 and 200,000; acid number between 50 and 250 mg KOH/gm; and glass transition temperature higher than 60 degree Celsius.

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23. Composition according to claim 19 wherein the COOH-functional acrylated acyclic polymer is prepared from polymerization of (meth)acrylate monomers selected from any of these (meth)acrylic acid, alkyl (meth)acrylate, styrene and its derivatives, hydroxyl containing (meth)acrylates, vinyl ether, butadiene and vinyl acetate and epoxy- containing (meth)acrylates.

24. Composition according to claim 19 wherein the multifunctional (meth)acrylate monomer or meth(acrylate) diluent is hydroxyethyl methacrylate, hydroxypropyl acrylate and methacrylate, trimethylolpropane triacrylate and trimethacrylate, pentaerythritol triacrylate and tetraacrylate, dipentaerythritol hexaacrylate, or any mixture of these.

25. Composition according to claim 19 wherein the photo-polymerization initiator is selected from one of the following: 2-benzyl-2N,N-dimethylamino-1(4-morpholinophenyl)-1-butanone and 2-methyl-1(4-methylthiophenyl)-2-morpholino propan-1-one.

26. Composition according to claim 19 wherein the pigments are selected from one of the following: phthalocyanines, quinacridones, dioxanines, isoindolinones, perylenes, anthraquinones or their mixtures.

27. Composition according to claims 19 wherein the epoxy-group containing resin is bisphenol-A epoxy, its polymer with bisphenol-A, cycloaliphatic epoxy, epoxy phenol novolak, epoxy cresol novolak, triglycidyl of isocyanurate, triglycidyl ether of trimethylolpropane, bisphenol-A novolak, or epoxy containing (meth)acrylate resin.

28. Use of a composition according to any of claims 19 to 27 as an alkali-developable photosensitive formulation.

29. Use of a composition according to any claims 19 to 27 for fabrication of printed circuit boards or flat panel displays.