

PATENT SPECIFICATION

(11) 1425 423

1425 423

- (21) Application No. 19010/73 (22) Filed 19 April 1973
 (31) Convention Application No. 247747 (32) Filed 26 April 1972 in
 (33) United States of America (US)
 (44) Complete Specification published 18 Feb. 1976
 (51) INT CL² C08F 2/50 G03C 1/68//C07C 103/66 69/90
 (52) Index at acceptance

C3P 8D2A 8D2B2 8D4 8D5 D1 P1C P1D P1F P1X P4C
 P5 P6C P6X
 C2C 200 220 227 22Y 230 234 240 263 26X 270 281 30Y
 342 34Y 360 362 364 366 367 368 36Y 491 498 500
 502 50Y 591 623 624 628 62X 633 638 648 652
 658 65X 662 668 66X BT KK KM
 G2C 1G1 C6



- (72) Inventors JOHN MICHAEL NOONAN
 RICHARD CALVIN SUTTON and
 ROBERT CHARLES McCONKEY

(54) PHOTOPOLYMERISABLE COMPOSITIONS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to photopolymerisable compositions, to photosensitive materials and to methods of forming relief images.

Photopolymerisable compositions are known and are employed, for example, in the production of printing plates and as photoresists for plating or etching processes. These compositions may be coated on a substrate and exposed imagewise to actinic radiation after which the less hardened areas are removed by development with a solvent. The solvent is usually organic which can involve hazards to operating personnel.

The present invention provides negative-working photopolymerisable compositions which may be developed in an aqueous alkaline solution and can show exceptionally clean developing characteristics.

According to the present invention there is provided a photopolymerisable composition comprising:

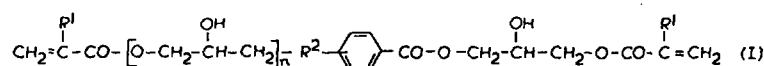
(a) a photopolymerisable monomer which contains two acyl groups of an α,β -ethylenically unsaturated carboxylic acid and a moiety derived from a *p*- or *m*-hydroxy or *p*- or *m*-amino-benzoic acid,

(b) a film-forming polymeric binder containing pendant carboxylic acid groups and
 (c) a photoactivatable polymerisation initiator.

The monomers (a) may be compounds which have attached through the carboxy group of the benzoic acid moiety, a substituent which is terminated by an α,β -ethylenically unsaturated acyl group, e.g. an acrylate, acrylamide, methacrylate or methacrylamide group, and which have attached *via* their *para* or *meta* hydroxy or amino group another α,β -ethylenically unsaturated acyl group or a substituent which is terminated thereby. Preferred monomers (a) are bismethacrylates and contain a moiety derived from *p*-hydroxy-benzoic acid.

The polymeric binder (b) is preferably selected so that the photopolymerisable composition is initially soluble in dilute aqueous alkaline solutions, but upon exposure to actinic radiation becomes insoluble therein. Such polymers may be vinyl addition polymers containing free carboxylic acid groups. Preferred polymeric binders are polymers of 30 to 94, preferably 61 to 94, mole percent of one or more alkyl acrylates and/or methacrylates and 70 to 6, preferably 39 to 6, mole percent of one or more α,β -ethylenically unsaturated carboxylic acids.

The monomer (a) may have the general formula:



wherein

R¹ is hydrogen or an alkyl group having 1—4 carbon atoms,

R² is —O— or —NH— attached to the benzene ring in the *p*- or *m*- position and

n is 0 or 1.

5

Examples of monomers of formula I are:

5

2-hydroxy-3-acryloyloxypropyl 4-acryloyloxybenzoate,

2-hydroxy-3-acryloyloxypropyl 3-acryloyloxybenzoate,

2-hydroxy-3-acryloyloxypropyl 4-acrylamidobenzoate,

2-hydroxy-3-acryloyloxypropyl 4-methacryloyloxybenzoate,

10

2-hydroxy-3-acryloyloxypropyl 3-methacryloyloxybenzoate,

10

2-hydroxy-3-acryloyloxypropyl 4-methacrylamidobenzoate,

2-hydroxy-3-acryloyloxypropyl 3-methacrylamidobenzoate,

2-hydroxy-3-acryloyloxypropyl 3-(2-hydroxy-3-acryloyloxypropoxy)benzoate,

2-hydroxy-3-acryloyloxypropyl 4-(2-hydroxy-3-acryloyloxypropylamino)benzoate,

15

2-hydroxy-3-acryloyloxypropyl 3-(2-hydroxy-3-methacryloyloxypropoxy)benzoate,

15

2-hydroxy-3-acryloyloxypropyl 4-(2-hydroxy-3-methacryloyloxypropoxy)benzoate,

2-hydroxy-3-acryloyloxypropyl 3-(2-hydroxy-3-methacryloyloxypropylamino)benzoate,

2-hydroxy-3-acryloyloxypropyl 4-(2-hydroxy-3-methacryloyloxypropylamino)benzoate,

20

2-hydroxy-3-methacryloyloxypropyl 4-acryloyloxybenzoate,

20

2-hydroxy-3-methacryloyloxypropyl 3-acrylamidobenzoate,

2-hydroxy-3-methacryloyloxypropyl 4-methacryloyloxybenzoate,

2-hydroxy-3-methacryloyloxypropyl 3-methacryloyloxybenzoate,

2-hydroxy-3-methacryloyloxypropyl 4-methacrylamidobenzoate,

25

2-hydroxy-3-methacryloyloxypropyl 3-methacrylamidobenzoate,

25

2-hydroxy-3-methacryloyloxypropyl 4-(2-hydroxy-3-acryloyloxypropoxy)benzoate,

2-hydroxy-3-methacryloyloxypropyl 3-(2-hydroxy-3-acryloyloxypropylamino)benzoate,

2-hydroxy-3-methacryloyloxypropyl 4-(2-hydroxy-3-methacryloyloxypropoxy)benzoate,

2-hydroxy-3-methacryloyloxypropyl 3-(2-hydroxy-3-methacryloyloxypropoxy)benzoate,

30

2-hydroxy-3-methacryloyloxypropyl 4-(2-hydroxy-3-methacryloyloxypropylamino)benzoate, and

30

2-hydroxy-3-methacryloyloxypropyl 3-(2-hydroxy-3-methacryloyloxypropylamino)benzoate.

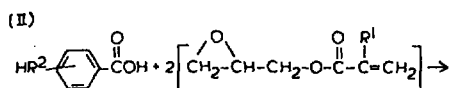
35

These photopolymerisable monomers may be prepared by condensing a *p*- or *m*-hydroxy or *p*- or *m*-aminobenzoic acid with an acrylate-type reactant or reactants using standard condensation techniques. When both the carboxy group and the hydroxy or amino group on the benzoic acid are to be substituted with the same unsaturated acyl group, a one step reaction is employed in which the benzoic acid is condensed with a reactant such as glycidyl acrylate. This is illustrated by reaction sequence II below. When the carboxy group and the hydroxy or amino group on the benzoic acid are to be substituted with different unsaturated acyl groups, a two-step reaction is employed in which the hydroxy or amino groups is first condensed with a reactant such as acryloyl chloride (which does not react with the carboxy group) and then the carboxy group is condensed with a reactant such as glycidyl acrylate. This is illustrated by reaction sequence III below.

35

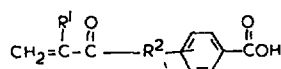
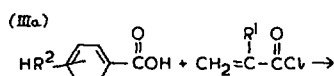
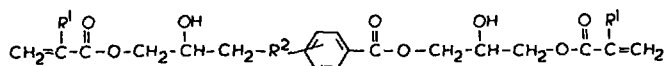
40

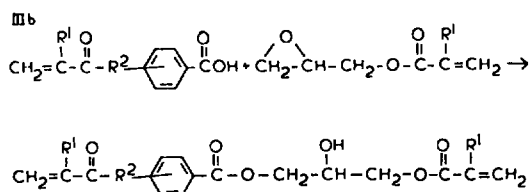
40



45

45





Typically, the one step reaction is carried out at elevated temperatures e.g. 50—100°C, in the presence of a thermal polymerisation inhibitor, e.g., *p*-methoxyphenol, quinone, hydroquinone, *m*-dinitrobenzene or phenothiazine, and a catalyst which will aid cleavage of the glycidyl ring, e.g., tetramethyl ammonium chloride, sodium chloride, sodium hydroxide, sodium bicarbonate or lithium acetate, and, optionally, in a solvent such as acetone, acetonitrile, tetrahydrofuran, *N,N*-dimethylformamide or dimethylsulphoxide. The first step of the two-step reaction is typically carried out at lowered temperatures, e.g., 0—10°C, in a solvent mixture such as a mixture of methylene chloride with water or pyridine, and in the presence of an acid acceptor such as sodium hydroxide, pyridine, trimethylamine or triethylamine. The second step of the two step reaction can be performed using the same materials and conditions as the one-step reaction.

Examples of alkyl acrylates and methacrylates for use in preparing the preferred polymeric binder (b) include methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate. Examples of α,β -ethylenically unsaturated carboxylic acids for use as comonomers include acrylic acid and methacrylic acid. The film-forming polymeric binders preferably have inherent viscosities of from 0.05 to 2.0 measured in *N,N*-dimethylformamide, at a concentration of 0.25 grams per decilitre of solution and at a temperature of 25°C. Particularly preferred are polymers having inherent viscosities of 0.1 to 0.4.

We have discovered quite unexpectedly that the use, as binder, of terpolymers of methyl methacrylate, ethyl acrylate and methacrylic acid in proportions of from 40% to 65%, 20% to 45% and 10% to 25%, respectively, on a molar basis, produces resist compositions according to our invention of exceptionally clean developing characteristics. Whereas photoresists heretofore known in the art have left microresidues after development, these terpolymer binders can be readily developed to produce areas substantially free of microresidues. These terpolymer binders when incorporated into the photoresist compositions of this invention have, in fact, been found to produce such clean developing characteristics that metal surfaces from which these photoresists have been removed by development with mildly alkaline solutions are satisfactory for subsequent metal plating without resort to any additional chemical or mechanical cleaning procedures. Usually when it is attempted to form metal layers directly onto a surface from which a photoresist has been removed by development and without any further surface treatment, the metal layer either immediately comes away from the surface or forms a very weak bond that can be readily broken. For example, metal layers deposited onto untreated areas formed by developing conventional photoresists can be expected to release readily when a piece of adhesive cellulose tape is applied and then pulled away.

The polymeric binders (b) may be prepared by any of the addition polymerisation techniques known to those skilled in the art, which include solution polymerisation, bulk polymerisation, bead polymerisation and emulsion polymerisation, in the presence of a free radical generating polymerisation initiator, such as peroxy compounds e.g., benzoyl peroxide, di(tertiary-amyl) peroxide, or diisopropylperoxy carbonate or azo initiators, e.g., 1,1'-azodicyclohexanecarbonitrile, 2,2'-azobis(2-methylpropionitrile).

The polymerisation reaction may be carried out in the presence of an inert solvent. Preferably, a low molecular weight alcohol which is a good chain transfer agent, e.g., ethyl alcohol, is used to promote formation of lower molecular weight polymers by a solution polymerisation technique. Molecular weight can also be controlled by varying the temperature (the higher the initial temperature, the lower the molecular weight) or by varying the amount of catalyst used (the more catalyst, the lower the molecular weight). Preferably, the polymerisation reaction is performed in an inert atmosphere, e.g. under a blanket of nitrogen. The polymerisation mixture is maintained at a temperature at which the polymerisation initiator generates free radicals. The exact temperature selected depends on the monomers being polymerised, the particular initiator being used, and the molecular weight desired. Temperatures ranging from room temperature or lower up to 100°C are suitable. It is usually desirable to carry the polymerisation reaction substantially to completion so that no unpolymerised monomers remain and

the proportions of each component in the final product are essentially those of the original monomer mixture.

The polymeric binder may be collected and purified by conventional techniques, such as precipitation into a non-solvent for the polymer followed by washing and drying.

The photoactivatable polymerisation initiators (c) in the compositions of the present invention may be any of the photopolymerisation initiators known and employed in the art. Preferably, these compounds are thermally inactive at temperatures encountered during storage and handling of the compositions and materials prepared therewith, i.e., temperatures below about 100°C.

Examples of initiators include aryldiazo sulphones such as those described in U.S. Patent 3,096,333, which also describes sensitizers for these initiators; polynuclear quinones, such as those described in U.S. Patent 3,046,127, e.g., 9,10-anthraquinone, 2 - t - butylanthraquinone, 1,4 - naphthaquinone, 9,10 - phenanthraquinone or 1,2-benzanthraquinone; vicinal polyketaldonyl compounds, such as are described in U.S. Patent 2,367,660, e.g., diacetyl or benzil, α -ketaldonyl alcohols, such as those described in U.S. Patents 2,367,661 and 2,367,670 e.g., benzoin or pivaloin; acyloin ethers, such as those described in U.S. Patent 2,448,828, e.g., 2-methoxy-2-phenylacetophenone or 2-ethoxy-2-phenylacetophenone; and α -hydrocarbon substituted aromatic acyloins, such as are described in U.S. Patent 2,722,512 e.g., α -methylbenzoin, α -allylbenzoin or α -phenylbenzoin. Particularly preferred are the synergistic mixtures of initiators described in U.S. Patent 3,427,161. Particularly preferred is the mixture of benzophenone with *p,p'*-dimethylaminobenzophenone, also known as Michler's ketone.

The compositions of the present invention may also contain thermal polymerisation inhibitors to prevent premature polymerisation of the composition during storage and handling. Examples of such inhibitors include *p*-methoxyphenol, hydroquinone, alkyl and aryl-substituted quinones and hydroquinones, *t*-butylcatechol, pyrogallol, copper, resinate, beta-naphthol, cuprous chloride, 2,6-di-*t*-butyl *p*-cresol, phenothiazine, pyridine, nitrobenzene, dinitrobenzene, *p*-toluquinone and chloranil.

The coating compositions also may include a variety of photographic addenda utilised for their known purpose, such as agents to modify the flexibility of the coating agents to modify its surface characteristics, dyes and pigments to impart colour to the coating, agents to modify the adhesivity of the coating to the support, antioxidants, preservatives, and a variety of other addenda known to those skilled in the art.

Coating compositions may be prepared by dispersing or dissolving the constituents of the present photopolymerisable compositions in a solvent or combination of solvents. Solvents that may be used to advantage are volatile organic solvents and include ketones such as 2-butanone, acetone, 4-methyl-2-pentanone, cyclohexanone, 2,4-pentanedione or 2,5-hexanedione; esters such as 4-butyrolactone, 2-ethoxyethyl acetate or 2-methoxyethyl acetate; ethers such as 2-methoxy ethanol, 2-ethoxy ethanol or tetrahydrofuran; and mixtures of these solvents. Typically, the photopolymerisable compound (a) and the film-forming binder (b) may each be employed in the coating composition in the range of from 1 to 40 percent by weight, based on the total weight of the coating composition. To produce coatings of exceptionally clean washing characteristics, i.e. capable of being developed in a substantially micro-residue free manner, it is preferred that the monomer (a) be present in the coating composition in a concentration of from 2.5 to 30 percent by weight based on the total weight of the composition and the binder be present in the coating composition in a concentration of from 5 to 40 percent by weight, based on the total weight of the composition. In the photopolymerisable layer which forms a material according to this invention it is preferred that the monomer (a) be present in a concentration of from 16 to 60 percent by weight based on the total weight of the layer while the binder (b) is present in the range of from 35 to 83 percent by weight based on the total weight of the layer. The preferred range of initiator concentration is 5 to 20 percent by weight, based on the weight of the photopolymerisable compound (a).

Photosensitive materials may be prepared by coating the photosensitive compositions from solvents onto supports in accordance with usual practices. Examples of support materials include fibre-base materials such as paper, polyethylene-coated paper, polypropylene-coated paper, parchment and cloth; sheets and foils of such metals as aluminium, copper, magnesium and zinc; glass and glass coated with such metals as chromium, chromium alloys, steel, silver, gold and platinum. synthetic polymeric materials such as polyethylene, polypropylene, poly(alkyl methacrylate), e.g., poly(methyl methacrylate), polyester film base, e.g., poly(ethylene terephthalate), poly(vinyl acetals), polyamides, e.g., nylon, cellulose ester film base, e.g., cellulose nitrate, cellulose acetate, cellulose acetate propionate and cellulose acetate butyrate. Preferred supports are those which bear the photopolymerisable layer on a metal surface, e.g. a copper

surface. The optimum coating thickness for a particular purpose will depend on such factors as the use to which the coating will be put, the particular light-sensitive composition employed, and the nature of other compounds which may be present. Typical coating thicknesses can be from 0.1 to 15 mil.

The coating composition may be coated directly on the support on which it is to be used in the preparation of, for example, a resist or a printing plate, or it may be coated on a temporary support and transferred, e.g., by thermal lamination, to the support where it is to be used, either uniformly or in an imagewise fashion. Such transfer techniques are described, for example, in U.S. Patents 3,060,023, 3,346,383, 3,469,982, 3,690,882 and 3,703,373.

Photomechanical or relief images may be prepared with photosensitive materials of this invention by imagewise exposing them to a source of actinic radiation for a period of time sufficient to polymerise and insolubilise material in exposed areas. Exposures of from several seconds to several minutes, or longer, e.g., ten seconds to fifteen minutes, may be required. Light sources that may be employed in exposing the materials include sources rich in visible radiation and sources rich in ultraviolet radiation, such as carbon arc lamps, xenon lamps, mercury vapour lamps, fluorescent lamps, tungsten lamps and certain lasers.

An image may be developed on the exposed material by such techniques as solvent washout of the unexposed, non-insolubilised areas, by thermal transfer of the unexposed, non-hardened areas, or by other techniques known to those skilled in the art. With solvent washoff techniques, although organic solvents such as those listed above as coating solvents, as well as others, may be employed, the developer solvent is preferably an aqueous alkaline solution. Examples of such developer solutions include aqueous solutions of an alkali metal carbonate, e.g., sodium carbonate; aqueous solutions of an alkali metal hydroxide, e.g., sodium hydroxide; mixtures thereof; and aqueous solutions of a lower alcohol, e.g., ethanol, isopropanol, with an alkanolamine, e.g., ethanolamine, propanolamine, or 2-diethylaminoethanol. The presence of a surfactant in the developer solution aids clean development. The alkaline strength of the developer solution is governed by the particular composition employed. The developer solution may also contain dyes and pigments. The developed image may be rinsed with distilled water, dried, and optionally postbaked.

The resulting image may be treated in any manner consistent with its intended use, such as treatment with desensitising etchants or plate lacquers when it is to be used as a printing plate or treatment with acidic etchants or plating baths when it is to be used as a resist. After the resist has served its intended purpose it can be readily removed with a strong alkali such as 10 percent sodium hydroxide.

The following Examples further illustrate the invention and the preparation of monomers and polymeric binders for use therein.

Example 1

Preparation of 2-Hydroxy-3-methacryloyloxypropyl 4-methacryloyloxybenzoate Preparation of 4-Methacryloyloxybenzoic Acid

To 2170 ml of 2 Normal sodium hydroxide solution in a 5 litre, 3-necked round bottomed flask, fitted with a stirrer and condenser, is added 300 grams (2.17 moles) of *p*-hydroxybenzoic acid, with stirring until solution is effected. The flask is immersed in an ice bath, and the solution temperature reduced to 5°C. The mixture is diluted with 150 millilitres of dichloroethane and then treated dropwise with 226.5 grams (2.17 moles) of methacryloyl chloride while maintaining the temperature between 0–10°C. When the methacryloyl chloride addition is complete, another 150 millilitres of 1,2-dichloroethane is added rapidly and the ice bath is removed. After stirring 18 hours, the mixture is transferred to a separatory funnel, the aqueous layer removed and acidified by adding 2 litres of 4 percent hydrochloric acid, with stirring. The solid product is collected by filtration, washed on the filter with 2 litres of water, and dried under vacuum at room temperature. Melting point: 183–185°C. The nmr spectrum of the product is in agreement with the structure of 4-methacryloyloxybenzoic acid.

Preparation of Title Compound

A mixture of 329.3 grams (1.595 moles) of 4-methacryloyloxybenzoic acid, prepared as above, 500 grams (3.51 moles) of glycidyl methacrylate, 14.6 grams (0.133 mole) of tetramethylammonium chloride, and 1.4 grams (0.011 mole) of *p*-methoxyphenol is placed in a 2 litre, 2-necked flask fitted with a stirrer and condenser and immersed in an 80°C water bath, and stirred for 24 hours. The reaction mixture is cooled to room temperature, diluted with 500 millilitres of 1,2-dichloroethane, filtered

through diatomaceous earth, and the filtrate concentrated in a flash evaporator at 40°C. The title compound is obtained as an amber to yellow viscous liquid. The nmr spectrum of the product is consistent with that of the title compound.

Example 2

5 Preparation of 2-Hydroxy-3-Methacryloyloxypropyl 4-Methacrylamidobenzoate 5

Preparation of *p*-Methacrylamidobenzoic Acid

To a mixture of 20 grams (0.146 mols) of *p*-aminobenzoic acid, 146 millilitres of 2 Normal sodium hydroxide, and 200 millilitre of chloroform in a 1 litre round-bottomed flask cooled in an ice bath, is slowly added with vigorous stirring 16.7 grams (0.16 mols) of methacryloyl chloride while maintaining the temperature at 5 to 10°C. The mixture is stirred in the ice bath an additional 15 minutes, then stirred at room temperature for 30 minutes, and then allowed to stand about 16 hours. The solid is collected and dried. The yield is 26.1 grams of product melting at 222 to 224°C. The nmr spectrum of the product is consistent with the structure of *p*-methacrylamidobenzoic acid.

Preparation of Title Compound

A mixture of 205.2 grams (1.0 moles) of *p*-methacrylamidobenzoic acid, prepared as above, 284.3 grams (2.0 moles) of glycidyl methacrylate, 18.3 grams (0.168 mole) of tetramethylammonium chloride, and 2.05 grams of *p*-methoxyphenol is placed in a 3 litre, 3-necked round-bottomed flask fitted with a thermometer, a condenser, and a stirrer. The flask is immersed in a 60°C water bath and the mixture is stirred slowly to effect solution, then treated with an equal volume of water and stirred at 60°C for one hour. While still hot, the organic layer is separated, diluted with methylene chloride, dried over magnesium sulphate, treated with decolourizing carbon, and concentrated under vacuum at 40°C after removing the decolourizing carbon. The title compound is obtained as a dark amber oil (308 grams) which turns to an off-white waxy solid on standing. The structure of the title compound is confirmed by nmr spectroscopy.

Example 3

30 Preparation of 2-Hydroxy-3-Methacryloyloxypropyl *p*-(2-Hydroxy-3-methacryloyloxypropoxy)benzoate 30

In a 300 millilitre flask is mixed 25 grams (0.181 mole) of *p*-hydroxybenzoic acid, 54.0 grams (0.380 mole) of glycidyl methacrylate, 1.73 grams (0.0158 mole) of tetramethylammonium chloride, and 0.173 grams of *p*-methoxyphenol. The mixture is heated at 60°C for about 65 hours and extracted with methylene chloride until a clear solution results. The methylene chloride extracts are washed three times with 0.1 molar sodium hydroxide solution, three times with distilled water, and then dried over magnesium sulphate, the solvent removed by evaporation, and the title compound collected as a viscous oil weighing 36.8 grams. The structure is confirmed by nmr spectroscopy.

Example 4

40 Synthesis of Poly(methmethacrylate-co-ethyl acrylate-co-methacrylic acid) (59:25:16-mole(ratio)) 40

A flask, equipped with nitrogen inlet tube, stirrer, and reflux condenser, is charged with a solution containing 316 grams (3.156 mole) methyl methacrylate, 135.3 grams (1.351 mole) ethyl acrylate, 73.5 grams (0.8538 mole) methacrylic acid, 4725 millilitres ethyl alcohol, and 2.62 grams 2,2'-azobis(2-methylpropionitrile). The system is purged with nitrogen for 20 minutes before adding the catalyst. The flask is placed in an 80°C bath and allowed to heat, with stirring, under nitrogen for 17 hours. The resulting clear polymer solution is slightly viscous. The polymer is precipitated and washed by pouring the reaction mixture into cold water and then dried at 50°C under vacuum. Inherent viscosity is 0.20, measured in *N,N*-dimethylformamide (0.25 grams/decilitre solution at 25°C.).

Anal. Calcd. for $C_{256}H_{389}O_{106}$: C, 59.39; H, 7.91
Found: C, 59.6; H, 8.1

Example 5

55 Synthesis of Poly(Methyl methacrylate-co-ethyl acrylate-co-methacrylic acid) (27.3:63.5:9.2-mole ratio) 55

The procedure of Example 4 is followed except that the solution contained 13.8 grams (0.138 mole) methyl methacrylate, 32.2 grams (0.32 mole) ethyl acrylate, 4.0

grams (0.047 mole) methacrylic acid, 450 millilitres ethanol, and 0.25 gram 2,2'-azobis-(2-methylpropionitrile).

Example 6

Synthesis of Poly(ethyl acrylate-co-acrylic acid) (32.5:67.5—mole ratio)

5 The procedure of Example 4 is followed except the solution contains 40 grams (0.4 mole) ethyl acrylate, 60 grams (0.83 mole) acrylic acid, 500 millilitres acetone and 0.25 grams 2,2'-azobis-(2-methylpropionitrile). The reaction is operated at a temperature of 60°C for 16 hours. The polymer is isolated as in Example 4. 5

Example 7

Synthesis of Poly(n-butyl acrylate-co-acrylic acid) (86:14—mole ratio)

10 The procedure of Example 4 is followed except that the solution contains 90 grams (0.79 mole) n-butyl acrylate, 10 grams (0.14 mole) acrylic acid, 300 millilitres acetone and 0.5 gram 2,2'-azobis(2-methylpropionitrile). 10

Example 8

15 Synthesis of Five Poly(Methyl Methacrylate-co-Ethyl Acrylate-co-Methacrylic Acid) Terpolymers 15

A mixture of 439.2 g of methyl methacrylate, 284.4 g of ethyl acrylate, 116.4 g of methacrylic acid and 7500 ml of ethanol is placed in a 12 litre flask, degassed for one hour with nitrogen gas and immersed in a constant temperature bath at 80°C. With stirring, a solution of 4.2 g of 2,2'-azobis(2-methyl-propionitrile) in about 340 ml of ethanol is added in 3 portions, each portion followed by a rinse of 40 ml of ethanol. 20

The mixture is stirred at reflux for 20 hours. The volume is reduced to half by distillation of solvent, and the concentrated solution is poured into 25 to 30 gallons of water. The liquid is then decanted, and the solid is washed once with water, collected by filtration, and dried in a polyethylene bag under vacuum for 4 days with a nitrogen gas bleed at 40°C, then in a vacuum for 3 days. The resulting polymer, identified as Terpolymer C in Table I, was obtained in a yield of 700 g with an inherent viscosity of 0.20 in N,N-dimethylformamide measured in a concentration of 0.25 g per decilitre at 25°C. Terpolymer C consists essentially of 50% methyl methacrylate, 34% ethyl acrylate and 16% methacrylic acid, based on mole percentages. The terpolymers A, B, D and E also set forth in Table I were similarly prepared, but with differing proportions of methyl methacrylate and ethyl acrylate monomers as indicated. 25 30

TABLE I

35	Terpolymer	Mole % Monomer		Inherent Viscosity	35
		Methyl Methacrylate	Ethyl acrylate		
	A	34	50	0.14	
	B	42	42	0.20	
	C	50	34	0.20	
40	D	59	25	0.21	40
	E	67	17	0.22	

Example 9

Photopolymerisable Composition

A composition is prepared from the following components:

45 1 gram of the polymeric binder prepared in Example 4, 45
1 gram of the monomer, 2-hydroxy-3-methacryloyloxypropyl 4-methacryloyloxybenzoate, prepared in Example 1
0.1 gram of benzophenone
0.1 gram of Michler's ketone
50 5 millilitres of tetrahydrofuran. 50

The above composition is applied to a 2.5 mil copperclad epoxy board at a wet-thickness of 10 ml. The coating is air-dried for 5 minutes and baked at 90°C for 15 minutes. The coating is imagewise exposed to a xenon light source, and a resist image is developed by spraying with a 4 percent sodium carbonate solution for 60 seconds, followed by a water rinse and air drying. The circuit board is etched for 60 minutes with a ferric chloride etchant, and at the end of this time the resist image has not broken down. This demonstrates the suitability of the photoresist in forming structures 55

such as printed circuits and the like. By withstanding the ferric chloride etchant the photoresist protects the copper which it overlies. The remaining copper is removed by the etchant. After etching the circuit board is washed with water and the resist is stripped from the board with 10 percent sodium hydroxide. The copper cladding is left intact in those areas covered by the photoresist before removal by the sodium hydroxide. The copper cladding remaining could, for example, form conductive paths for a printed circuit.

Similar compositions are prepared from the monomers of Examples 2 and 3 and the binders of Examples 9 to 11. These compositions are used to prepare resist images, by development in dilute alkali, which stand up well in acidic etchants.

Example 10

Comparison of Photopolymerisable Compositions for Microresidue Free Development Characteristics

Bright copper supports are surface deoxidized by immersion in a 3 percent by volume sulphuric acid solution. The supports are then rinsed and dried. The Terpolymers A, B, C, D, and E set forth in Table I of Example 8 are incorporated in photoresist compositions otherwise identical to that set forth in the first paragraph of Example 9. Five separate photoresist compositions are prepared each incorporating a different terpolymer binder. After air drying for 5 minutes at room temperature the coated supports are baked for 5 minutes at 90°C. Each resist coating is exposed through a Kodak (trade mark) Control Scale T-14, which is a 14 step density scale ranging from a density of 0.04 (step 1) to 2.05 (step 14) at 0.15 increments. The resist image is developed by spraying with a 4 percent sodium carbonate solution for 60 seconds, followed by water rinse and air drying. To ensure that no oxides are present on the copper surfaces exposed during development these exposed areas are washed with a 3 percent sulphuric acid solution and rinsed with water. Since sulphuric acid does not etch copper, no metal is removed during this step nor are microresidues of photoresist, if present, removed. Copper is plated onto the exposed areas of the supports using a copper sulphuric plating bath. Properties of the processed supports are summarized in Table II.

TABLE II

Terpolymer	Speed	Development	Cleanout
A	8	Excellent	Excellent
B	8	Excellent	Excellent
C	8	Excellent	Excellent
D	7	Very good	Excellent
E	7	Very poor	Very poor

The supports coated with Terpolymers, A, B, C and D all give acceptable development properties. The support coated with Terpolymer D needed somewhat longer contact with the developer to obtain equivalent removal of the resist coating. For this reason the spraying of the support coating containing Terpolymer D is extended 30 seconds. The supports coated with Terpolymers A, B, C and D and developed as indicated are all substantially free of microresidues, that interfere with plated copper adhesion. In each of the materials the plated copper tenaciously adheres to the cleaned surface without etching. In the case of the support coated with Terpolymer E, spraying does not achieve development of the photoresist. Development can be achieved, however, by swabbing. Thus, the Terpolymer E coating is considered a useful resist coating, but not a preferred resist coating, since swabbing can damage the image definition and is impractical for very intricate or fine patterns. The coating containing Terpolymer A exhibits very high speed together with excellent development and cleanout properties. This terpolymer is not preferred, however, since it exhibits a somewhat lower degree of solidity after exposure as compared to the remaining coatings. The preferred coatings all exhibited excellent speed characteristics. The speed is reported in terms of the number of steps which developed.

WHAT WE CLAIM IS:—

1. A photopolymerisable composition comprising:

- (a) a photopolymerisable monomer which contains two acyl groups of an α,β -ethylenically unsaturated carboxylic acid and a moiety derived from a *p*- or *m*-hydroxy- or *p*- or *m*-amino-benzoic acid,
- (b) a film-forming polymeric binder containing pendant carboxylic acid groups and

such as printed circuits and the like. By withstanding the ferric chloride etchant the photoresist protects the copper which it overlies. The remaining copper is removed by the etchant. After etching the circuit board is washed with water and the resist is stripped from the board with 10 percent sodium hydroxide. The copper cladding is left intact in those areas covered by the photoresist before removal by the sodium hydroxide. The copper cladding remaining could, for example, form conductive paths for a printed circuit.

Similar compositions are prepared from the monomers of Examples 2 and 3 and the binders of Examples 9 to 11. These compositions are used to prepare resist images, by development in dilute alkali, which stand up well in acidic etchants.

Example 10

Comparison of Photopolymerisable Compositions for Microresidue Free Development Characteristics

Bright copper supports are surface deoxidized by immersion in a 3 percent by volume sulphuric acid solution. The supports are then rinsed and dried. The Terpolymers A, B, C, D, and E set forth in Table I of Example 8 are incorporated in photoresist compositions otherwise identical to that set forth in the first paragraph of Example 9. Five separate photoresist compositions are prepared each incorporating a different terpolymer binder. After air drying for 5 minutes at room temperature the coated supports are baked for 5 minutes at 90°C. Each resist coating is exposed through a Kodak (trade mark) Control Scale T—14, which is a 14 step density scale ranging from a density of 0.04 (step 1) to 2.05 (step 14) at 0.15 increments. The resist image is developed by spraying with a 4 percent sodium carbonate solution for 60 seconds, followed by water rinse and air drying. To ensure that no oxides are present on the copper surfaces exposed during development these exposed areas are washed with a 3 percent sulphuric acid solution and rinsed with water. Since sulphuric acid does not etch copper, no metal is removed during this step nor are microresidues of photoresist, if present, removed. Copper is plated onto the exposed areas of the supports using a copper sulphuric plating bath. Properties of the processed supports are summarized in Table II.

TABLE II

Terpolymer	Speed	Development	Cleanout
A	8	Excellent	Excellent
B	8	Excellent	Excellent
C	8	Excellent	Excellent
D	7	Very good	Excellent
E	7	Very poor	Very poor

The supports coated with Terpolymers, A, B, C and D all give acceptable development properties. The support coated with Terpolymer D needed somewhat longer contact with the developer to obtain equivalent removal of the resist coating. For this reason the spraying of the support coating containing Terpolymer D is extended 30 seconds. The supports coated with Terpolymers A, B, C and D and developed as indicated are all substantially free of microresidues, that interfere with plated copper adhesion. In each of the materials the plated copper tenaciously adheres to the cleaned surface without etching. In the case of the support coated with Terpolymer E, spraying does not achieve development of the photoresist. Development can be achieved, however, by swabbing. Thus, the Terpolymer E coating is considered a useful resist coating, but not a preferred resist coating, since swabbing can damage the image definition and is impractical for very intricate or fine patterns. The coating containing Terpolymer A exhibits very high speed together with excellent development and cleanout properties. This terpolymer is not preferred, however, since it exhibits a somewhat lower degree of solidity after exposure as compared to the remaining coatings. The preferred coatings all exhibited excellent speed characteristics. The speed is reported in terms of the number of steps which developed.

WHAT WE CLAIM IS:—

1. A photopolymerisable composition comprising:
 - (a) a photopolymerisable monomer which contains two acyl groups of an α,β -ethylenically unsaturated carboxylic acid and a moiety derived from a *p*- or *m*-hydroxy- or *p*- or *m*-amino-benzoic acid,
 - (b) a film-forming polymeric binder containing pendant carboxylic acid groups and

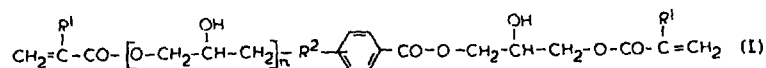


(c) a photoactivatable polymerisation initiator.

2. A composition as claimed in Claim 1 in which the polymeric binder (b) is a copolymer of 30—94 mole percent of one or more alkyl acrylates and/or methacrylates and 70—6 mole percent of one or more α,β -ethylenically unsaturated carboxylic acids.

3. A composition as claimed in Claim 1 or 2 in which the monomer (a) is a bis-methacrylate and contains a moiety derived from *p*-hydroxybenzoic acid.

4. A composition as claimed in Claim 1 or 2 in which the monomer (a) has the general formula:



wherein

R^1 is hydrogen or an alkyl group having 1—4 carbon atoms,

R^2 is —O— or —NH— attached to the benzene ring in the *p*- or *m*-position and n is 0 or 1.

5. A composition as claimed in any of Claims 1—4 in which monomer (a) is 2-hydroxy-3-methacryloyloxypropyl *p*-methacryloyloxybenzoate or 2-hydroxy-3-methacryloyloxypropyl *p*-(2-hydroxy-3-methacryloyloxypropoxy)benzoate.

6. A composition as claimed in any of Claims 1—5 in which binder (b) is a terpolymer of methyl methacrylate, ethyl acrylate and methacrylic acid.

7. A composition as claimed in Claim 6 in which the terpolymer comprises

40—65 mole percent methyl methacrylate,
20—45 „ „ ethyl acrylate and
10—25 „ „ methacrylic acid.

8. A composition as claimed in any of Claims 1—7 which contains an organic solvent and the components (a), (b) and (c) in the following amounts:

(a) 1—40 percent by weight of the total composition weight,
(b) 1—40 percent by weight of the total composition weight, and
(c) 5—20 percent by weight based on the weight of (a).

9. A composition as claimed in any of Claims 1—8 which contains an organic solvent and the components (a), (b) and (c) in the following amounts:

(a) 2.5—30 percent by weight of the total composition weight,
(b) 5—40 percent by weight of the total composition weight and
(c) 5—20 percent by weight based on the weight of (a).

10. A composition as claimed in any of Claims 1—9 in which the polymerisation initiator (c) is a mixture of benzophenone and Michler's ketone.

11. A photopolymerisable composition substantially as described herein and with reference to Examples 9 and 10.

12. A photosensitive material comprising a support bearing a layer of a solid composition according to any of Claims 1—7, 10 or 11.

13. A photosensitive material as claimed in Claim 12 in which the surface of the support which bears the photopolymerisable layer consists of a metal.

14. A photosensitive material as claimed in Claim 13 in which the metal is copper.

15. A photosensitive material as claimed in any of Claims 12—14 which contains components (a), (b) and (c) in the following amounts:

(a) 16—60 percent by weight of the photopolymerisable layer solids,
(b) 35—83 percent by weight of the photopolymerisable layer solids, and
(c) 5—20 percent by weight based on the weight of (a).

16. A method of preparing a relief image which comprises imagewise exposing a material according to any of Claims 12—15 to actinic radiation to polymerise the exposed areas of the photopolymerisable layer and then removing the unexposed areas by development with an aqueous alkaline solution to leave the relief image comprising the exposed areas.

L. A. TRANGMAR, B.Sc., C.P.A.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *