

PATENT SPECIFICATION

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(54) PHOTOPOLYMERIZABLE COMPOSITIONS AND THEIR USE

(71) We, DYNACHEM CORPORATION, a corporation organised and existing under the Laws of the State of California, one of the United States of America, located at 13000 East Firestone Boulevard, Santa Fe Springs, State of California 90670, 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:—

This invention relates to a new and improved photo-polymerizable composition and a method for preparing and using the same. More particularly, the invention teaches a light-sensitive composition which can be readily developed by means of an alkaline aqueous solution to yield a product which is useful for printing plates and photoresists. These compositions are particularly useful for the manufacture of printed circuits because the resists formed therefrom are impervious to conventional plating solutions.

The desirability of forming light-sensitive compositions which can be developed without the need of the conventional organic solvents has long been recognized. Organic solvents are costly, hazardous with respect to toxicity and flammability, and pollute the air and water.

The advantages of such aqueous systems were noted as far back as 1956 in United States patent 2,760,863; however, no specific compositions were described and it may be speculated that the patentee was unable to find a satisfactory composition. Other references to such water soluble compositions are set forth in U.S. patent 2,927,022 and U.S. patent 2,893,868. Whatever may be the merits of the compositions disclosed in these patents, it appears that such compositions, to the extent they could be developed with aqueous alkaline solutions, were either not sufficiently insoluble in the exposed portions or

or were subject to attack by the conventional plating and etching solutions, where the photoresist was used for a printed circuit.

In accordance with this invention, it has now been discovered that photopolymerizable compositions can be produced which may be developed with aqueous alkaline solutions. Furthermore, the exposed portions of these compositions have outstanding resistance to the alkaline solutions, including the alkaline etchants and alkaline plating solutions frequently encountered in the fabrication of printed circuits and chemically machined parts.

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

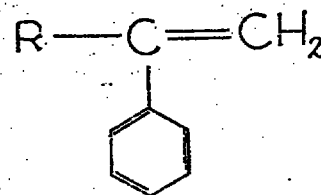
(A) from 10 to 60 parts by weight of an addition polymerizable material consisting essentially of one or more non-gaseous compounds having a boiling point above 100°C. at atmospheric pressure and containing at least two terminal ethylenic groups;

(B) from 0.001 to 10 parts by weight of a photo-initiated free-radical generating addition polymerizing initiating system;

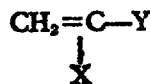
(C) from 0.001 to 5 parts by weight of a thermal-addition polymerizable inhibitor; and

(D) from 40 to 90 parts by weight of a preformed macromolecular polymeric binding agent which is a polymer of:

a first monomeric material which contains one or more non-acidic vinyl compounds selected from those having the general formula:



SPECIFICATION AMENDED: SEE ATTACHED SLIP



wherein R is hydrogen, an alkyl group having from 1 to 6 carbon atoms or a halo group and wherein X is hydrogen and Y is OOCR_1 , OR_1 , OCR_1 , COOR_1 , CN , $\text{CH}=\text{CH}_2$,



or Cl ; or X is methyl and Y is COOR_1 , CN , $\text{CH}=\text{CH}_2$, or



or X is chlorine and Y is Cl ; and wherein R_1 is an alkyl group having from 1 to 12 carbon atoms, a phenyl group or a benzyl group and R_3 and R_4 are the same or different and are hydrogen, an alkyl group having from 1 to 12 carbon atoms or a benzyl group; and

a second monomeric material which consists essentially of one or more alpha, beta-unsaturated carboxyl-containing monomers having from 3 to 15 carbon atoms;

wherein the ratio of the first monomeric material to the second monomeric material is sufficient to render the binding agent soluble in a dilute aqueous solution containing from 0.01 to 10% by weight of a water-soluble base.

The initiating system may consist of one or more initiators.

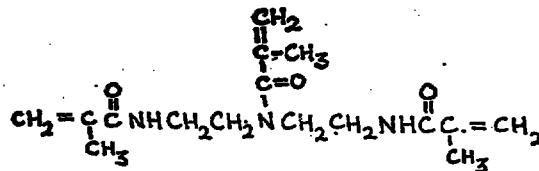
Compositions according to the invention may additionally contain suitable dyes and pigments and other additives, such as plasticizers and adhesion promoters, as may be necessary to enhance the physical and chemical properties of the photo-polymerizable composition.

The ethylenically unsaturated compound must be capable of forming a high polymer by free-radical photo-initiated, chain propagating addition polymerization. Examples of

such compounds are disclosed in U.S. patent 2,760,863.

Preferably, the ethylenically unsaturated compounds have a plasticizing action on the thermoplastic polymeric binder. Suitable compounds, which may be used alone or in combination, include an alkylene or a polyalkylene glycol diacrylate prepared from alkylene glycols having 2 to 15 carbons or polyalkylene ether glycols of 1 to 10 ether linkages.

Because of their generally more rapid rate of insolubilization on exposure, presumably due to a relatively rapid establishment of a network polymer structure, an outstanding class of the low molecular weight addition polymerizable components are those having a plurality of addition polymerizable ethylenic linkages, of which at least two must be present as terminal linkages, and especially those wherein at least one and preferably most of such linkages are conjugated with a doubly bonded carbon, including carbon doubly bonded to carbon and to such heteroatoms as nitrogen, oxygen, and sulfur. Outstanding are such materials wherein the ethylenically unsaturated groups are conjugated with ester or amide structures. The following specific compounds are further illustrative of this class: unsaturated esters of polyols, particularly such esters of the α,β -unsaturated carboxylic acids, e.g., ethylene diacrylate; diethylene glycol diacrylate; glycerol diacrylate; glycerol triacrylate; ethylene dimethacrylate; 1,3-propylene di-methacrylate; 1,2,4-butane triol trimethacrylate; 1,4-benzene-diol dimethacrylate; pentaerythritol tetramethacrylate; mixed acrylate esters of pentaerythritol (commercially obtainable pentaerythritol tetraacrylate is a mixture of the tetraacrylate ester (70%) and triacrylate ester (30%); 1,3-propanediol diacrylate; 1,5-pentane-diol dimethacrylate; the bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200—500, and the like; unsaturated amides, particularly those of the α,β -unsaturated carboxylic acids, and especially those of alpha, omega-diamines and oxygen-interrupted alpha, omega-diamines, such as methylene bisacrylamide; methylene bis-methacrylamide; 1,6-hexamethylene bis-acrylamide; diethylene triamine tris-methacrylamide



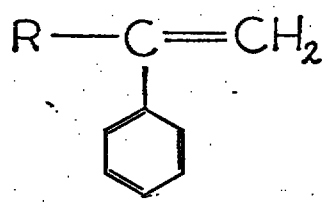
bis (methacrylamidopropoxy) ethane; β -methacrylamidoethyl methacrylate; vinyl esters such as divinyl succinate, divinyl

adipate, divinyl phthalate, divinyl terephthalate, divinyl benzene-1,3-disulfonate, and divinyl butane-1,4-disulfonate.

The addition polymerizable compound may be a combination of two or more of the above compounds such as an admixture of trimethylolpropane triacrylate and tetraethylene glycol diacrylate or an admixture of mixed acrylate esters of pentaerythritol and tetraethylene glycol diacrylate.

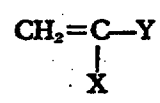
The amount of monomer added varies with the particular thermoplastic polymer.

The constituent of the polymeric binder having the general formula:



may be ring substituted with from 1 to 5 functional groups, such as nitro, alkoxy, acyl, carboxyl, sulpho, hydroxyl or halo. Preferably, the substituent is a single alkyl group such as a methyl or t-butyl group. More preferred of these compounds are styrene, alpha-methyl styrene, para-methyl styrene and para-t-butyl styrene.

Examples of vinyl monomers of the formula



are vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinylidene chloride, methyl methacrylate and methyl acrylate, acrylonitrile and methacrylonitrile, methacrylamide, N-alkyl substituted acrylamide, vinyl methyl ketone, vinyl propyl ketone, vinyl methyl ether, vinyl ethyl ether and vinyl hexyl ether.

The carboxyl containing constituent of the polymeric binder preferably contains from 3 to 6 carbon atoms. Most preferred compounds are acrylic acid and methacrylic acid. Other acids which may be used are cinnamic acid, crotonic acid, sorbic acid, itaconic acid, propiolic acid, maleic acid, and fumaric acid, or the half esters of the above mentioned dicarboxylic acids or, where possible, the corresponding anhydride. Mixtures of two or more of these compounds may also be used.

The ratio of the non-acidic monomer component to the acidic comonomer is selected so that the copolymer is soluble in a dilute aqueous solution containing from 0.01% to 10% by weight of a water soluble base. If the amount of the non-acidic vinyl monomer is too high, the unexposed portion of the binder will now be sufficiently soluble; on the other hand, if the amount of the non-acidic monomer is too low, the exposed area will be

tacky, swollen, or dissolved in the aqueous alkaline solution. As a convenient criterion, the binder copolymer should be such that a 40% by weight solution thereof in ketones or alcohols will have a viscosity of from 100 to 50,000 centipoises at 25°C.

Representative comonomer weight ratios are 70:30 to 85:15 for styrene-acrylic acid or methacrylic acid; 35:65 to 70:30 for styrene-monomethyl maleate and 70:30 to 95:5 for vinyl acetate-crotonic acid. The degree of polymerization of the binder copolymer is such that the binder forms a non-tacky continuous film after exposure and development. Broadly, the molecular weight is from 1,000 to 500,000. The ranges for the copolymer ratios and the degree of polymerization for the particular binders can be readily ascertained by testing the solubility of the copolymer in dilute alkaline solution of representative polymers.

As noted, the resist from the practice of this invention is resistant to the usual plating and etching solutions. Most surprising is its resistance to the copper pyrophosphate solution which is used in pattern plating and has an extremely high alkalinity. Other solutions which leave the resist unaffected include ferric chloride, ammonium persulfate and chromic-sulfuric acid solutions.

The photoinitiators used in the compositions are preferably those activatable by actinic light and thermally inactive at 185°C. or below. These include the substituted or unsubstituted polynuclear quinones such as 9,10-anthraquinone; 1-chloroanthraquinone; 2-chloroanthraquinone; 2-methylantraquinone; 2-ethylantraquinone; 2-tert-butylantraquinone; octamethylantraquinone; 1,4-naphthaquinone; 9,10-phenanthraquinone; 1,2-benzanthraquinone; 2,3-benzanthraquinone; 2-methyl-1,4-naphthaquinone; 2,3-dichloronaphthaquinone; 1,4-dimethylantraquinone; 2,3-dimethylantraquinone; 2-phenylantraquinone; 2,3-diphenylantraquinone; sodium salt of anthraquinone alpha-sulfonic acid; 3-chloro-2-methylantraquinone; retenequinone; 7,8,9,10-tetrahydronaphthacenequinone; 1,2,3,4-tetrahydrobenzo(a)anthracene-7,12-dione.

The following photoinitiators, described in U.S. Patent 2,760,863, some of which may be thermally active at temperatures as low as 85°C., are also useful: vicinal ketaldonyl compounds, such as, diacetyl and benzil; alpha-ketaldonyl alcohols, such as, benzoin and pivaloin; acyloin ethers, e.g., benzoin methyl and ethyl ethers; and alpha-hydrocarbon substituted aromatic acyloins such as alpha-methylbenzoin; alpha-allylbenzoin; and alpha-phenylbenzoin.

Silver persulfate is also useful as a free-radical generating initiator activatable by actinic radiation. Certain aromatic ketones,

e.g., benzophenone and 4,4' - bis - dialkyl-amino - benzophenones, are also useful.

Thermal polymerization inhibitors are also present in the compositions. These include p-methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, naphthylamines, beta-naphthol, cuprous chloride, 2,6 - di - tert - butyl p-cresol 2,2 - methylene - bis - (4 - ethyl - 6 - t - butylphenol), pheno-thiazine, pyridine, nitrobenzene, dinitrobenzene, p-toluquinone, chloranil, aryl phosphites, and aryl alkyl phosphites.

If desired, the compositions may contain dyes and pigments. Suitable colorants will be compatible with the photosensitive compositions and not interfere appreciably with the photosensitivity of the composition. The following specific compounds are illustrative:

20 Fuchsine (C.I. 42510); Auramine Base (C.I. 4100B); Calcocid Green S (C.I. 44090); Para Magenta (C.I. 42500); Tryparosan (C.I. 42505); New Magenta (C.I. 42520); Acid Violet RRH (C.I. 42425); Red Violet 5RS (C.I. 42690); Nile Blue 2B (C.I. 51185); New Methylene Blue GG (C.I. 51195); C.I. Basic Blue 20 (C.I. 42585); Iodone Green (C.I. 42556); Night Green B (C.I. 42115); C.I. Direct Yellow 9 (C.I. 19540); C.I. Acid Yellow 17 (C.I. 18965); C.I. Acid Yellow 29 (C.I. 18900); Tartrazine (C.I. 19140); Supramine Yellow G (C.I. 19300); Buffalo Black 10B (C.I. 27790); Naphthalene Black 12R (C.I. 20350); Fast Black L (C.I. 51215); Ethyl Violet (C.I. 42600); Pontacyl Wool Blue BL (C.I. 50315); Pontacyl Wood Blue GL (C.I. 52320). (Numbers obtained from the second edition of Color Index).

40 The present invention also provides a coated article comprising a metallic substrate coated with a composition of the invention. The photopolymerizable composition may be cast into a film onto the substrate from a solution. Alternatively, the composition may be laminated as a precast film onto the substrate.

The metallic substrate may be copper or a copper alloy.

50 The coated article may additionally be provided with an oxygen impervious layer covering the photopolymerizable layer. The oxygen impervious layer should, of course, be transparent to actinic radiation.

55 In order to enhance adhesion of a composition of the invention to a metallic substrate, the composition may contain up to 1% by weight of a triazole. Preferably, the triazole is benzotriazole, tolutriazole or naphthotriazole.

60 Photopolymerizable compositions of the invention may be exposed to a source of actinic radiation. Accordingly, the invention also provides a coated article comprising a metallic substrate coated with a composition

of the invention in which areas of the composition are insolubilized by imagewise exposure to actinic light. The exposure may be through a half-tone image or a process transparency, e.g., a process negative or positive, stencil, or a mask. The exposure may also be through a continuous tone, negative or positive image. The exposure may be by the contact or projection method, with or without a cover sheet over the photopolymerizable layer or by projection using a cover sheet. These procedures are well known to those skilled in the art.

Since free-radical generating addition-polymerization initiators activatable by actinic radiation generally exhibit their maximum sensitivity in the ultraviolet range, the radiation source should furnish an effective amount of this radiation. Both point or broad radiation sources are effective. Such sources include carbon arcs, mercury-vapor arcs, fluorescent lamps with ultraviolet radiation-emitting phosphors, argon glow lamps, electronic flash units and photographic flood lamps. Of these, the mercury-vapor arcs, particularly the sun lamps, are most suitable. In certain circumstances it may be advantageous to expose with visible light, using a photoinitiator sensitive in the visible region of the spectrum, e.g., 9,10-phenanthraquinone. In such cases, the radiation source should furnish an effective amount of visible radiation. Many of the radiation sources listed above furnish the required amount of visible light.

The photopolymerizable compositions after exposure can be developed, e.g., by impingement of spray jets, with agitated immersion brushing or scrubbing to desirable images with aqueous bases, i.e., aqueous solutions of water-soluble bases in concentrations generally in the range from 0.01% to 10% by weight.

Suitable bases for the development include the alkali metal hydroxides, e.g., lithium, sodium and potassium hydroxide, the base-reacting alkali metal salts of weak acids, e.g., lithium, sodium, and potassium carbonates and bicarbonates; amines having a base-ionization constant greater than about 1×10^{-4} , e.g., primary amines, such as, benzyl, butyl and allyl amines; secondary amines, e.g., dimethylamine and benzyl methyl amine; tertiary amines, e.g., trimethylamine, and triethylamine; primary, secondary, and tertiary hydroxyamines, e.g., propanol-, diethanol- and triethanol amines, and 2 - amino - 2 - hydroxymethyl - 1,3 - propanediol, hetero cyclic amines, e.g., morpholine, piperidine, piperazine, and pyridine; polyamines, such as hydrazine, ethylene and hexamethylene diamines; the water-soluble basic salts, e.g., the carbonates and bicarbonates of the above amines, ammonium hydroxide and tetra-substituted ammonium hydroxides, e.g., tetramethyl-, tetraethyl-, trimethylbenzyl-, and trimethylphenylammonium hydroxides,

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sulfonium hydroxides, e.g., trimethyl-, diethyl-methyl-, dimethylbenzylsulfonium hydroxides, and the basic soluble salts thereof, e.g., the carbonates, bicarbonates and sulfides; alkali metal phosphates and pyrophosphates, e.g. sodium and potassium triphosphates and sodium and potassium pyrophosphates; tetra-substituted (preferably wholly alkyl)phosphonium, arsonium, and stibonium hydroxide, e.g., tetramethyl-phosphonium hydroxide.

Thus, the present invention also provides a process for making a photoresist comprising preparing a supported photopolymerizable layer of a composition of the invention, image-wise exposing said photopolymerizable layer to actinic light and washing the layer with a dilute aqueous alkaline solution to dissolve the unexposed portions of the photopolymerizable layer.

The photopolymerized compositions can generally be removed by immersion in heated aqueous solutions of strong alkalis or, if desired, in proprietary stripping formulas well known in the art.

To further illustrate the invention attention is directed to the following examples. In the examples, percentages are by weight and viscosity values quoted are those at 25°C.

Example I

The following solution was coated onto a 1 mil thick polyester film, and dried in air. The dry thickness of the sensitized layer was about 0.001 inch. The dried layer was covered with a 1 mil thick polyethylene film.

35	Copolymer of 37% styrene and 63% mono-n-butyl maleate, average mol. wt. 20,000, viscosity of 10% aqueous solution of ammonium salt=150 cps.	67.0 g
40	Trimethylolpropane triacrylate	22.0 g
	tetraethylene glycol diacrylate	11.0 g
	Benzophenone	2.3 g
45	4,4'-bis-(dimethylamino)-benzophenone	0.3 g
	2,2'-methylene-bis (4-ethyl-6-tert-butyl phenol)	0.1 g
	Methyl violet 2B Base	0.07 g
50	Benzotriazole	0.20 g
	Methyl ethyl ketone	140.0 g

A piece of copper clad, epoxy-fiber glass board was cleaned by scouring with an abrasive cleaner, swabbing and thoroughly rinsing in water. It was then given a 20-second dip in a dilute hydrochloric acid solution (2 volumes water plus 1 volume conc. hydrochloric acid), a second rinse with water and then dried with air jets.

The polyethylene cover film was removed from a section of the sandwiched photopolymerizable element. The bared resist coating

with its polyester support was laminated to the clean copper surface of the above mentioned board with the surface of the photopolymerizable layer in contact with the copper surface. The lamination was carried out with the aid of rubber covered rollers operating at 250°F. with a pressure of 3 pounds per lineal inch at the nip at a rate of 2 feet per minute. The resulting sensitized copper clad board protected as it is by the polyester film, could be held for later use if need be. Actually it was exposed to light through a high-contrast transparency image in which the conducting pattern appeared as transparent areas on an opaque background. The exposure was carried out by placing the sensitized copper clad board (with its polyester film still intact) and the transparency into a photographic printing frame. The exposure was for a period of 45 seconds to a 400 watt, 50 ampere mercury vapor lamp at a distance of 12 inches. The polyethylene terephthalate support film was peeled off and the exposed resist layer developed by agitating the board in a tray containing 2% sodium carbonate in water for 3-1/2 minutes followed by a water rinse. The resulting board contained a dyed resist pattern of the clear areas of the exposing transparency.

The board was now etched with a 45° Baume solution of ferric chloride, then rinsed and dried. The resist was removed from the remaining copper by dipping for 2 minutes in a 3% solution of sodium hydroxide in water at 70°C. The result was a high quality printed circuit board.

Example II

The following solution was coated onto 1 mil thick polyester film and was allowed to dry at ambient conditions for 30 minutes.

	Copolymer of 75% styrene and 25% methacrylic acid, viscosity of a 40% solution in methyl ethyl ketone is 10,360 cps.	11.00 g
	Trimethylolpropane triacrylate	4.66 g
	Tetraethyleneglycol diacrylate	2.33 g
	Benzophenone	0.75 g
	4,4'-bis-(dimethylamino)-benzophenone	0.10 g
	2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol)	0.3 g
	Methyl Violet 2B Base	0.2 g
	Benzotriazole	0.07 g
	Methyl ethyl ketone	30.0 g

Dry thickness of the sensitized layer was about 1.35 mil. The coated material was then laminated onto a cleaned copper-clad board as in Example 1. Exposure was made through a transparency containing an opaque pattern of known area for 1-1/2 minutes with an exposure unit as described in Example I.

The polyester support film was peeled off and the exposed resist layer developed by agitating the board in a tray containing 2% trisodium phosphate in water for 2 minutes followed by a water rinse.

The surface of the exposed copper was further cleaned after development by dipping the board into a 20% ammonium persulfate bath for 30 seconds, washing copiously with water, dipping for 30 seconds in a 20% solution of hydrochloric acid in water, rinsing with water, then drying the board with jets of air. This cleaned board was then plated for 45 minutes at 30 amperes per square foot in a copper pyrophosphate plating bath at 55°C.

Example III

A copper clad piece of epoxy-fiber glass board was cleaned as described in Example I. The cleaned, dried board was sensitized by flowing the following solution over the surface of the board:

25	Copolymer of 37% styrene and 63% mono-n-butyl maleate, average mol. wt. 20,000, viscosity of 10% aqueous solution of ammonium salt=150 cps.	40.0 g
	Pentaerythritol tetraacrylate	23.0 g
30	Benzophenone	1.5 g
	4,4'-bis-(dimethylamino)-benzophenone	0.2 g
35	2,2'-methylene-bis-(4-ethyl-6-tertbutylphenol)	0.6 g
	Methyl Violet 2B Base	0.4 g
	Methyl Ethyl Ketone	100.0 g
	Benzotriazole	0.15 g

The excess solution is drained off the board at room temperature for 2 minutes. The coating was further dried by heating in a forced air oven at 60°C. for 5 minutes.

After cooling, the coated board was exposed as described in Example I. The resist was developed by agitating the board in a solution of 2% trisodium phosphate in water for 1 minute followed by a water rinse. The board was now etched in ferric chloride as described in Example I. After etching, the exposed resist was stripped from the protected copper by immersing the board in a 3% solution of sodium hydroxide in water at 50°C. for 2 minutes. The result is a high quality printed circuit board.

Example IV

The following solution was coated onto a 1 mill thick polyester film and dried in air.

60	Copolymer of 95% vinyl acetate and 5% crotonic acid, average mol. wt. 90,000, viscosity of 8.6% ethyl alcohol solution between 13 and 18 cps.	70.0 g
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Pentaerythritol tetraacrylate	30.0 g
Benzophenone	2.3 g
4,4'-bis'(dimethylamino)-benzophenone	0.3 g
2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol)	0.1 g
Methyl Violet 2B Base	0.07 g
Benzotriazole	0.20 g
Methyl ethyl ketone	150.0 g

The dry thickness of the sensitized layer was about 0.001 inch. A copper clad board was prepared, the resist coating laminated to it, and the resulting element exposed exactly as in Example I. The support film was peeled off and the exposed resist layer developed by agitating the board in a tray containing 2% trisodium phosphate solution for 2 minutes followed by a water rinse.

The board was now etched as in Example I to yield a high quality printed circuit board.

Example V

The photosensitive solution described in Example I is coated onto zinc, magnesium and copper printing plates. After drying in warm air to a dry thickness of about 0.001 inch, the photosensitive layer is coated with a dilute aqueous solution of polyvinyl alcohol and redried with warm air. The water-soluble polymer forms a thin protective barrier to oxygen. These pre-sensitized metal plates may be stored for extended periods.

Upon exposure to actinic light through a suitable photographic negative, the unexposed photosensitive layer and the water-soluble topcoat can be developed simultaneously, leaving the metal plate ready for etching. The photopolymerized image area then serves as an excellent resist for the deep-etching processes normally encountered in the fabrication of metal printing plates. These results are resistant to the common etchants, e.g., ferric chloride and nitric acid, filming agents, and banking agents commonly added to the etching mixture to control the geometry of the etch.

Example VI

The procedure of Example V is followed, except that a 0.001 inch thick film of polyester is used as a protective layer instead of the water-soluble polymer. Following exposure to actinic light, the protective layer is peeled off prior to developing in an aqueous alkaline solution. As in Example V, the photopolymerized image area serves as an excellent resist for the deep-etching of printing plates.

Example VII

The photosensitive solution as described in Example I is coated onto 0.001 inch thick polyester film, dried in air, and covered with a 0.001 inch thick polyethylene film. This three layer film sandwich can be stored in sheets or rolls in light-safe areas for indefinite

periods of time. Prior to use, the polyethylene cover film is peeled off, and the photosensitive layer is placed in contact with a metallic plate of the type described in Example V and backed by lamination. Upon exposure to actinic light, the protective polyester layer is peeled off and developed in aqueous alkaline solution. As in Example V, the photopolymerized image area is an excellent resist for the deep-etching of printing plates.

Example VIII

The photosensitive solution as described in Example I is coated onto thin aluminum plates as commonly used in offset lithography by procedures described in Examples V, VI, and VII. Following exposure to actinic light and development in aqueous alkaline solution, the photopolymerized image area serves as an excellent ink-receptor. It also has outstanding abrasion resistance. The resulting plates can be used with excellent results for off-set lithographic printing.

Example IX

The photosensitive solution as described in Example I is coated onto a woven, mesh-like substrate by procedures described in Examples V, VI, and VII. Following exposure to actinic light and development in aqueous alkaline solution, the photopolymerized image area serves as an excellent mask. This application has shown utility in silk-screen type printing.

WHAT WE CLAIM IS:—

1. A photopolymerizable composition comprising:

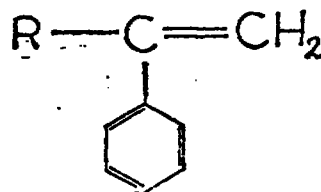
(A) from 10 to 60 parts by weight of an addition polymerizable material consisting essentially of one or more non-gaseous compounds having a boiling point above 100°C. at atmospheric pressure and containing at least two terminal ethylenic groups;

(B) from 0.001 to 10 parts by weight of a photo-initiated free-radical generating addition polymerizing initiating system;

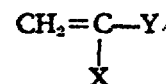
(C) from 0.001 to 5 parts by weight of a thermal-addition polymerizable inhibitor; and

(D) from 40 to 90 parts by weight of a preformed macromolecular polymeric binding agent which is a polymer of:

a first monomeric material which contains one or more non-acidic vinyl compounds selected from those having the general formula:



or



wherein R is hydrogen, an alkyl group having from 1 to 6 carbon atoms or a halo group and wherein X is hydrogen and Y is OOCR₁, OR₁, OCR₁, COOR₁, CN, CH=CH₂,



or Cl; or X is methyl and Y is COOR₁, CN, CH=CH₂, or



or X is chlorine and Y is Cl; and wherein R₁ is an alkyl group having from 1 to 12 carbon atoms, a phenyl group or a benzyl group and R₁ and R₂ are the same or different and are hydrogen, an alkyl group having from 1 to 12 carbon atoms or a benzyl group; and

a second monomeric material which consists essentially of one or more alpha, beta-unsaturated carboxyl-containing monomers having from 3 to 15 carbon atoms;

wherein the ratio of the first monomeric material to the second monomeric material is sufficient to render the binding agent soluble in a dilute aqueous solution containing from 0.01 to 10% by weight of a water-soluble base.

2. A composition according to claim 1 in which the binding agent is a copolymer of styrene and an unsaturated carboxyl-containing monomer.

3. A composition according to claim 1 in which the binding agent is a copolymer of vinyl acetate and an unsaturated carboxyl-containing monomer.

4. A composition according to any one of the preceding claims in which the unsaturated carboxyl-containing monomer is methacrylic acid.

5. A composition according to any of claims 1 to 3 in which the unsaturated carboxyl-containing monomer is acrylic acid.

6. A composition according to any of claims 1 to 3 in which the unsaturated carboxyl-containing monomer is maleic anhydride, maleic acid, a half-ester of maleic acid, or a mixture of two or more of these compounds.

7. A composition according to any one of the preceding claims in which the addition polymerizable compound is an admixture of trimethylolpropane triacrylate and tetraethylene glycol diacrylate.



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periods of time. Prior to use, the polyethylene cover film is peeled off, and the photosensitive layer is placed in contact with a metallic plate of the type described in Example V and backed by lamination. Upon exposure to actinic light, the protective polyester layer is peeled off and developed in aqueous alkaline solution. As in Example V, the photopolymerized image area is an excellent resist for the deep-etching of printing plates.

Example VIII

The photosensitive solution as described in Example I is coated onto thin aluminum plates as commonly used in offset lithography by procedures described in Examples V, VI, and VII. Following exposure to actinic light and development in aqueous alkaline solution, the photopolymerized image area serves as an excellent ink-receptor. It also has outstanding abrasion resistance. The resulting plates can be used with excellent results for off-set lithographic printing.

Example IX

The photosensitive solution as described in Example I is coated onto a woven, mesh-like substrate by procedures described in Examples V, VI, and VII. Following exposure to actinic light and development in aqueous alkaline solution, the photopolymerized image area serves as an excellent mask. This application has shown utility in silk-screen type printing.

WHAT WE CLAIM IS:—

1. A photopolymerizable composition comprising:

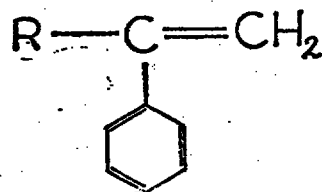
(A) from 10 to 60 parts by weight of an addition polymerizable material consisting essentially of one or more non-gaseous compounds having a boiling point above 100°C. at atmospheric pressure and containing at least two terminal ethylenic groups;

(B) from 0.001 to 10 parts by weight of a photo-initiated free-radical generating addition polymerizing initiating system;

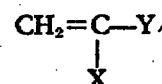
(C) from 0.001 to 5 parts by weight of a thermal-addition polymerizable inhibitor; and

(D) from 40 to 90 parts by weight of a preformed macromolecular polymeric binding agent which is a polymer of:

a first monomeric material which contains one or more non-acidic vinyl compounds selected from those having the general formula:



or



wherein R is hydrogen, an alkyl group having from 1 to 6 carbon atoms or a halo group and wherein X is hydrogen and Y is OOCR₁, OR₁, OCR₁, COOR₁, CN, CH=CH₂,



or Cl; or X is methyl and Y is COOR₁, CN, CH=CH₂, or



or X is chlorine and Y is Cl; and wherein R₁ is an alkyl group having from 1 to 12 carbon atoms, a phenyl group or a benzyl group and R₂ and R₃ are the same or different and are hydrogen, an alkyl group having from 1 to 12 carbon atoms or a benzyl group; and

a second monomeric material which consists essentially of one or more alpha, beta-unsaturated carboxyl-containing monomers having from 3 to 15 carbon atoms;

wherein the ratio of the first monomeric material to the second monomeric material is sufficient to render the binding agent soluble in a dilute aqueous solution containing from 0.01 to 10% by weight of a water-soluble base.

2. A composition according to claim 1 in which the binding agent is a copolymer of styrene and an unsaturated carboxyl-containing monomer.

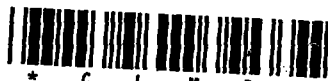
3. A composition according to claim 1 in which the binding agent is a copolymer of vinyl acetate and an unsaturated carboxyl-containing monomer.

4. A composition according to any one of the preceding claims in which the unsaturated carboxyl-containing monomer is methacrylic acid.

5. A composition according to any of claims 1 to 3 in which the unsaturated carboxyl-containing monomer is acrylic acid.

6. A composition according to any of claims 1 to 3 in which the unsaturated carboxyl-containing monomer is maleic anhydride, maleic acid, a half-ester of maleic acid, or a mixture of two or more of these compounds.

7. A composition according to any one of the preceding claims in which the addition polymerizable compound is an admixture of trimethylolpropane triacrylate and tetraethylene glycol diacrylate.



8. A composition according to any one of claims 1 to 6 in which the addition polymerizable compound is a mixed acrylate ester of pentaerythritol.
- 5 9. A composition according to any one of claims 1 to 6 in which the addition polymerizable compound is an admixture of mixed acrylate esters of pentaerythritol and tetraethylene glycol diacrylate.
- 10 10. A composition according to any one of the preceding claims in which the free-radical generating addition polymerization initiating system contains benzophenone, 4,4' - bis - (dimethylamino) - benzophenone, or a mixture thereof.
- 15 11. A composition according to any one of the preceding claims also containing up to 1% by weight of a triazole to enhance adhesion to metallic substrates.
- 20 12. A composition according to claim 11 in which the triazole is benzotriazole, toluotriazole, or naphthothiazole.
- 25 13. A photopolymerizable composition according to claim 1 and substantially as herein described.
- 30 14. A photopolymerizable composition substantially as described in any one of the foregoing Examples I to IV.
- 35 15. A coated article comprising a metallic substrate coated with a photopolymerizable composition according to any one of the preceding claims.
16. An article according to claim 15 in which the photopolymerizable composition is cast into a film onto the substrate from a solution.
17. An article according to claim 15 in which the photopolymerizable composition is laminated as a precast film onto the substrate.
18. An article according to any one of claims 15 to 17 in which areas of the photopolymerizable composition are insolubilized by imagewise exposure to actinic light.
19. An article according to any one of claims 15 to 18 in which the metallic substrate is copper or a copper alloy.
20. An article according to any one of claims 15 to 19 in which the photopolymerizable layer is covered by a cover layer impervious to oxygen and transparent to actinic radiation.
21. A coated article substantially as described in any one of the foregoing Examples.
22. A process for making a photoresist comprising preparing a supported photopolymerizable layer of a composition according to any one of claims 1 to 14; imagewise exposing said photopolymerizable layer to actinic light; and washing said layer with a dilute aqueous alkaline solution to dissolve the unexposed portions of the photopolymerizable layer.
23. A process according to claim 22 in which the photopolymerizable layer is supported on a metallic substrate.
24. A process according to claim 22 and substantially as described in any of the foregoing Examples.

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PATENTS ACT 1949

SPECIFICATION NO 1361298

In accordance with the Decision of the Principal Examiner, acting for the Comptroller-General, dated 18 November 1980 this Specification has been amended under Section 14 in the following manner:

Page 2, lines 25 to 27. Page 7 lines 81 to 83, *delete* dilute aqueous solution containing from 0.01 to 10% by weight of a water soluble base. *insert* 2% aqueous solution of trisodium phosphate in the absence of an organic solvent.

Page 3, lines 45 to 47, *delete* dilute aqueous solution containing from 0.01% to 10% by weight of a water soluble base. *insert* 2% aqueous solution of trisodium phosphate in the absence of organic solvent.

Page 3, line 13, *after* 5 *insert* non-acidic

Page 3, line 14, *after* acyl *delete* comma

Page 3, line 15, *delete* carboxyl, sulpho, hydroxyl

Page 3, line 50, *delete* binder will now *insert* photopolymerisable composition will not

8. A composition according to any one of claims 1 to 6 in which the addition polymerizable compound is a mixed acrylate ester of pentaerythritol.
- 5 9. A composition according to any one of claims 1 to 6 in which the addition polymerizable compound is an admixture of mixed acrylate esters of pentaerythritol and tetraethylene glycol diacrylate.
- 10 10. A composition according to any one of the preceding claims in which the free-radical generating addition polymerization initiating system contains benzophenone, 4,4' - bis - (dimethylamino) - benzophenone, or a mixture thereof.
- 15 11. A composition according to any one of the preceding claims also containing up to 1% by weight of a triazole to enhance adhesion to metallic substrates.
- 20 12. A composition according to claim 11 in which the triazole is benzotriazole, toluotriazole, or naphthothiazole.
13. A photopolymerizable composition according to claim 1 and substantially as herein described.
- 25 14. A photopolymerizable composition substantially as described in any one of the foregoing Examples I to IV.
15. A coated article comprising a metallic substrate coated with a photopolymerizable composition according to any one of the preceding claims.
- 30 16. An article according to claim 15 in which the photopolymerizable composition is cast into a film onto the substrate from a solution.
- 35 17. An article according to claim 15 in which the photopolymerizable composition is laminated as a precast film onto the substrate.
18. An article according to any one of claims 15 to 17 in which areas of the photopolymerizable composition are insolubilized by imagewise exposure to actinic light.
19. An article according to any one of claims 15 to 18 in which the metallic substrate is copper or a copper alloy.
20. An article according to any one of claims 15 to 19 in which the photopolymerizable layer is covered by a cover layer impervious to oxygen and transparent to actinic radiation.
21. A coated article substantially as described in any one of the foregoing Examples.
22. A process for making a photoresist comprising preparing a supported photopolymerizable layer of a composition according to any one of claims 1 to 14; imagewise exposing said photopolymerizable layer to actinic light; and washing said layer with a dilute aqueous alkaline solution to dissolve the unexposed portions of the photopolymerizable layer.
23. A process according to claim 22 in which the photopolymerizable layer is supported on a metallic substrate.
24. A process according to claim 22 and substantially as described in any of the foregoing Examples.

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THE PATENT OFFICE
13 February 1981

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