

PHOTOIMAGEABLE COMPOSITIONS CONTAINING PHOTOPOLYMERIZABLE URETHANE OLIGOMERS AND LOW T_g BINDER POLYMERS

The present invention is directed to negative-acting photoimageable compositions such as those used as photoresists for forming printed circuit boards. The photoimageable compositions utilize a binder polymer having a low glass transition temperature (T_g) and contain, as at least a portion of a photopolymerizable component, a photopolymerizable urethane oligomer.

Background of the Invention

This invention is directed to negative-acting photoimageable compositions which are developable in alkaline aqueous solutions. The invention is particularly applicable to primary photoimaging resists, but is applicable, as well, to compositions that are hardenable so as to form solder masks and the like.

A variety of such photoimageable compositions are described. Essential components of compositions of the type to which the present invention is directed are A) a binder polymer; B) photopolymerizable α,β -ethylenically unsaturated compound(s), and C) a photoinitiator chemical system. The binder polymer A) has sufficient acid functionality, generally carboxylic acid functionality, that it is soluble in alkaline aqueous solution and thereby renders the photoimageable composition developable in alkaline aqueous solutions.

The photoimageable compositions of the present invention have particular advantages when applied as dry film. Such dry films conventionally comprise a relatively rigid support sheet, such as polyethylene terephthalate, a photoimageable composition layer, and a protective film, such as a polyethylene film. Such dry films are supplied as rolls. At the time of application to a blank for a printed circuit board (typically a copper-

clad/fiberglass-epoxy board), the film is removed, the photoimageable composition layer is laminated to the blank with heat and pressure, and the support sheet subsequently removed.

A common problem of dry film photoresist compositions is balancing the coldflow (edge fusion) of the film in roll form with the adhesion of the film to the substrate during processing. The typical prior art remedies for improved adhesion are combinations of low T_g polymers in compositions containing high levels of multifunctional polymerizable monomers. While improving adhesion, such compositions also promote undesirable coldflow and tend to degrade shelf lives of the dry films, often resulting in shelf lives less than a month. Attempts to increase shelf life has generally resulted in poor adhesion or reduced flexibility.

It is a general object of the present invention to provide a photoimageable composition, suitable as a photoresist for producing printed circuit boards, with the excellent adhesion to substrates afforded by low T_g polymers, but with minimal coldflow, good shelf life, and good flexibility.

Summary of the Invention

The negative-acting photoimageable composition comprises A) between about 29 and about 69 wt% based on total weight of A) plus B) plus C) of an organic polymeric binder having sufficient acid functionality to render the photoimageable composition developable in alkaline aqueous solution and having a glass transition temperature (T_g) between about 60°C and about 90°C, preferably between about 80°C and about 90°C, B) between about 30 and about 60 wt % (calculated relative to total weight of A) plus B) plus C)) of an addition-polymerizable component, component B) comprising a nongaseous ethylenically unsaturated compound or compounds capable of forming a polymer by free-radical initiated chain-propagating addition polymerization, and between about 0.5 and about 15 wt% of C) (calculated relative to total weight of A) plus B) plus C)) of an organic, radiation-sensitive free-radical generating system activatable by actinic radiation to initiate chain-propagating addition polymerization of the addition-polymerizable material

B). In accordance with the invention, component B) comprises an isocyanate trimer B') having tri- α,β -ethylenically unsaturated functionality, trimer B' comprising between about 2 and about 30 wt% relative to total weight of A) plus B) plus C); balance of B, i.e., up to 57 wt%, preferably at least about 5 wt%, relative to total weight of A) plus B) plus C) of B" comprising other α,β -ethylenically unsaturated monomers. In addition, compositions in accordance with the invention preferably contain between about 1 and about 8 wt%, preferably between about 2 and about 6 wt% (calculated relative to total weight of A) plus B) plus C)) of D) a dibenzoate plasticizer.

Detailed Description of Certain Preferred Embodiments

Herein, unless otherwise noted, all percentages are weight percentages. Component A) (the binder polymer), Component B) (the photoimageable compounds(s)) and Component C) (the photoinitiator chemical system) are herein considered to equal 100 wt%, and other components, such as plasticizer, are calculated as parts relative to 100 parts of A) plus B) plus C). Molecular weights of polymers and oligomer, unless otherwise stated, are weight average molecular weights (M_w).

The invention is directed to photoimageable compositions which are developable in alkaline aqueous solution and which therefore have substantial acid functionality. Such photoimageable compositions typically have a binder A) having acid functionality, typically an acid number of at least about 80, preferably at least about 100 and more preferably about 150 or more, up to about 250. The acid functionality is typically carboxylic acid functionality, but may also include, for example, sulfonic acid functionality or phosphoric acid functionality. Binder polymers for photoimageable compositions typically have weight average molecular weights between about 40,000 and about 200,000 preferably at least about 80,000.

The polymers are typically derived from a mixture of acid functional monomers and non-acid functional monomers. Some specific examples of suitable acid functional monomers are acrylic acid, methacrylic acid, maleic acid, fumaric acid, citraconic acid,

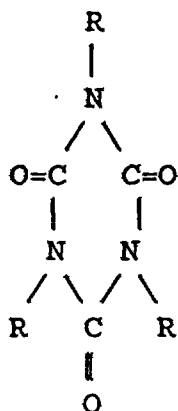
2-acrylamido-2-methylpropanesulfonic acid, 2-hydroxyethyl acryloyl phosphate, 2-hydroxypropyl acryloyl phosphate, 2-hydroxy-alpha-acryloyl phosphate, etc. One or more of such acid functional monomers may be used to form the binder polymer.

The acid functional monomers may be copolymerized with non-acid functional monomers, such as esters of acrylic acids, for example, methyl acrylate, methyl methacrylate, hydroxy ethyl acrylate, butyl methacrylate, octyl acrylate, 2-ethoxy ethyl methacrylate, t-butyl acrylate, n-butyl acrylate, 2-ethyl hexyl acrylate, n-hexyl acrylate, 1,5-pentanediol diacrylate, N,N-diethylaminoethyl acrylate, ethylene glycol diacrylate, 1,3-propanediol diacrylate, decamethylene glycol diacrylate, decamethylene glycol dimethacrylate, 1,4-cyclohexanediol diacrylate, 2,2-dimethylol propane diacrylate, glycerol diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, 2,2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate, polyoxyethyl-2,2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol dimethacrylate, polyoxypropyltrimethylol propane triacrylate, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 2,2,4-trimethyl-1,3-pentanediol dimethacrylate, pentaerythritol trimethacrylate, 1-phenyl ethylene-1,2-dimethacrylate, pentaerythritol tetramethacrylate, trimethylol propane trimethacrylate, 1,5-pentanediol dimethacrylate, and 1,4-benzenediol dimethacrylate; styrene and substituted styrene, such as 2-methyl styrene and vinyl toluene and vinyl esters, such as vinyl acrylate and vinyl methacrylate to provide the desired acid number.

The T_g of acrylic polymers is significantly dependent upon monomer content. In general, monomers providing hydrocarbon chains of meaningful length, either on the acrylate moiety or of an esterifying alcohol moiety, such as n-butyl acrylate, n-hexyl acrylate, and 2-ethyl hexyl acrylate tend to lower the T_g . Accordingly, the desired T_g can be obtained by appropriate selection of monomers used to form the binder polymer.

Examples of such polymers and photoimageable compositions using such polymers are found, in the following U.S. Patent Nos: 3,953,309, 4,003,877, 4,610,951, and 4,695,527 the teaching of each of which are incorporated herein by reference.

The photoimageable, acrylate functional, isocyanate trimer B') ("urethane oligomer") which comprises a portion of, and in some cases all of the photopolymerizable component B) has the general formula:



where R is $-(\text{CH}_2)_p-\text{NH}-\text{COO}-(\text{CHY}-\text{CHY}-\text{O})_m-\text{CO}-\text{CX}=\text{CH}_2$; where X is H or CH_3 , Y is H, CH_3 , or C_2H_5 , p is an integer from 1 to 36 and m is an integer from 1 to 14. Such trimers are described in European Patent Application EP 0 738 927 A2. When used in conjunction with low T_g polymers, the weight average molecular weight of the urethane oligomer should be at least about 1000, up to about 10,000. By using a relatively high molecular weight photopolymerizable component, i.e., the urethane oligomer, in conjunction with the low T_g binder polymer, satisfactory coldflow and shelf life are achieved without adversely affecting the adhesion and flexibility provided by the low T_g binder polymer. Intuitively, the adhesion should be adversely affected using a higher molecular weight photopolymerizable component because, on a mole for mole bases, monomer content is reduced. Surprisingly, using the urethane oligomer in accordance with the present invention, full advantage of using the low T_g binder polymer is realized.

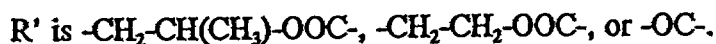
The balance of photopolymerizable component B), used at 0 to about 30 wt% of the photoimageable composition (calculated relative to total weight of A) plus B) plus C) is B"), typically a monomer, dimer or short chain oligomer having ethylenic unsaturation, particularly α,β -ethylenic unsaturation, including monofunctional compounds and compounds having α,β -ethylenic unsaturation functionality 2 or greater.. Suitable photopolymerizable compounds include, but are not limited to, the monomers recited above as suitable for forming binder polymers, particularly the non-acid functional compounds.

To initiate polymerization of the monomers upon exposure to actinic radiation, the photoimageable composition contains photoinitiator chemical system. Suitable photoinitiators include, for example, 9-phenyl acridine, benzoin ethers, benzil ketals, acetophenones, benzophenones and related compounds with amines. Also, suitable 9-phenyl acridine homologues, such as those described in U.S. Patent No. 5,217,845, the teachings of which are incorporated herein by reference, are useful photoinitiators.

In accordance with a preferred embodiment, flexibility, herein, is further improved through the use of dibenzoate plasticizers in conjunction with the isocyanate trimers. This combination further contributes to fine line adhesion and good stripping characteristics. Dibenzoate plasticizers in accordance with the invention have the general formula:



$\text{R} = \text{-CHX-CHX-O-}$ where one or both Xs are H or one X may be CH_3 and the other H; $n = 1$ to 10, and



Specific examples of suitable dibenzoates include, but are not limited to dipropylene glycol dibenzoate, diethylene glycol dibenzoate, polypropylene glycol dibenzoate, and polyethylene glycol dibenzoate. The dibenzoate plasticizer D) is used at levels of between about 1 and about 8 wt% relative to total weight of A) plus B) plus C), typically at between about 2 and about 6 wt%.

Compared to other plasticizers tested, the dibenzoates produced a significant improvement in tent strength. Coupled with improved flexibility, the combination of

dibenzoate plasticizer and the isocyanate trimer produces a fine line (less than 75 microns) resist sidewall that adheres better to the copper surface. It is believed that the addition of the dibenzoate contributes to a lower glass transition temperature (T_g) of the formulation. The lower T_g allows for better flow at lamination and better conformation to the copper surface. This property is particularly important on copper surfaces with nicks or scratches. Because the composition with the dibenzoate conforms better to the copper, more photoresist surface area is in contact with the copper surface. This results in more potential for chemical bonding to the copper surface and therefore, improved adhesion properties. Because the dibenzoate cannot be incorporated into the backbone of the exposed acrylic monomer system, the inclusion of the dibenzoate compounds results in less overall shrinkage of the composition. This reduced shrinkage probably produces less stress on the copper/photoresist interface, contributing to the improved adhesion. Less shrinkage is particularly observing if 9-phenyl acridine is used as the photoinitiator, as this initiator produces a high degree of cross-link density.

Additionally, the photoimageable compositions may contain a wide variety of additional components as are known in the art, including additional polymers, such as those which might be used to effect a final hardened cure of a solder mask, dyes, stabilizers, flexibilizing agents, fillers etc.

Processing of the photoimageable composition is in a conventional manner. In a typical procedure, a photoimageable composition layer, either formed from a liquid composition or transferred as a layer from a dry film, is applied to a copper surface of a copper-clad board. The photoimageable composition layer is exposed to actinic radiation through appropriate artwork. Exposure to actinic radiation polymerizes the monomer in the light-exposed areas, resulting in a cross-linked structure that is resistant to developer. Next, the composition is developed in dilute alkaline aqueous solution, such as a 1% sodium carbonate solution. The alkali solution causes salt formation with the carboxylic groups of the binder polymers, rendering them soluble and removable. After development, an etchant may be used to remove copper from those areas where the resist was removed,

thereby forming a printed circuit. The remaining resist is then removed using an appropriate stripper.

The invention will now be described in greater detail by way of specific examples.

Example A (comparative) and Example B (in accordance with the invention)

Photoimageable compositions "A" and "B" were formulated as in Table 1 below, each utilizing an acrylic binder polymer having a T_g of 85°C:

Table 1 - Base Ingredients and Monomer Changes

Ingredient	Formula "A" <i>monomer</i>	Formula "B" <i>oligomer</i>
Acrylic Polymer (23% methacrylic acid, 66% methylmethacrylate, 11% butyl acrylate)	40.0 grams	40.0 grams
Isocyanuric methane trimethacrylate		20.0 grams
Tetraethyleneglycol diacrylate	10.0 grams	10.0 grams
Ethoxylated (3 moles) Trimethylolpropane Triacrylate	20.0 grams	
9-phenylacridine	0.2 grams	0.2 grams
Dipropylene glycol dibenzoate	2.0 grams	2.0 grams
Michler's Ethyl Ketone	0.09 grams	0.09 grams
Nitrated Azo Dye (Euron Navy)	.075 grams	.075 grams
Methyl Hydroquinone	.045 grams	.045 grams
Triphenyl methane Dye (Flexoblite 650)	.025 grams	.025 grams

The compositions were prepared in 7:1 2-Butanone:2-Propanol at approximately 50% solids. The solutions were coated onto biaxially oriented 80 gauge polyester film and dried to approximately 1% or less retained solvent. The coated mixtures were then laminated onto mechanically scrubbed 1 oz./FR-4/1 oz. clad copper composite using a hot roll laminator at 110°C at 2 meters/minute and 3 bar pressure.

The laminated material was then imaged on a UV printer through an appropriate phototool with an adjusted exposure to obtain a copper step of 7 as measured with a Stouffer® 21 step wedge (approximately 20 mJ/cm²). The exposed panels were then developed in a 1% sodium carbonate monohydrate solution at 29°C using a conveyORIZED

spray developer at about 26 psi with residence time adjusted so that the break point occurred at 40% to 50% of the chamber length (unless otherwise noted in the specific example), followed by several spray rinses using tap water and the deionized water.

Etching was accomplished using a 2N cupric chloride/hydrochloric acid solution at 48°C in a conveyORIZED etcher equipped with multiple spray nozzles. The etched boards were then stripped of the imaged, developed and etched photo resist in a 3% sodium hydroxide solution at 54°C in a conveyORIZED stripping unit equipped with multiple spray nozzles followed by a spray rinse of tap water.

Process responses for the examples are cited at various points throughout the above procedure are given in Table 2 below.

Table 2 - Results of Monomer Change on Coldflow, Adhesion and Flexibility

Ingredient	Thickness	Break Point Time	Film Tack	Cross Hatch Adhesion	Tent Strength	Coldflow	Strip Time	Fine Line Adhesion
Formula "A"	38 μ m	20 seconds	moderate	75 % Intact	500 grams	severe	55 seconds	45 μ m
Formula "B"	38 μ m	19 seconds	slight	90 % Intact	750 grams	slight	53 seconds	40 μ m

Footnotes

Note 1 - The breakpoint time was recorded at the point the resist dissolved completely in 1% Na_2CO_3 at 30 °C.

Note 2 - Using a "razor blade like" tool, the developed photoresist is multiple cut in one direction than 90 ° to the previous cuts. This test measure brittleness and adhesion. The results are recorded as percent of resist left intact after all the blade cuts (100% = Best). The exposure was to a Stouffer 21 copper step 7 at a breakpoint in the developing chamber of 25%. Developing solution was 1% Na_2CO_3 at 30 °C.

Note 3 - A 0.25 inch hole laminated on both sides with the photoresist. The resist is then exposed and developed (The exposure was to a Stouffer 21 copper step 7 at a breakpoint in the developing chamber of 25%. Developing solution was 1% Na_2CO_3 at 30 °C). The flexibility of the resist over this "tenting" holes is then measured on a force gauge by pressing of the resist with a rounded probe. The force needed to break the tent is recorded in grams.

Note 4 - Coldflow was measured by the degree of resist deformation (orange peel) observed after 14 days at room temperature.

Note 5 -The resist is exposed to a Stouffer 21 copper step 7 at a breakpoint in the developing chamber of 25% with a developing solution of 1% Na_2CO_3 at 30 °C. The resist is then etched in cupric chloride at 130 of. After etching, the photoresist is stripped in 3% NaOH at 130 and the time is recorded in seconds.

Note 6 - Fine line adhesion measured after development. It is the smallest line left adhering with a 400 micron space. The exposure was to a Stouffer 21 copper step 7 at a breakpoint in the developing chamber of 25%. Developing solution was 1% $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ at 30 °C.



What is claimed is:

1. A photoimageable composition comprising

A) between about 29 and about 69 wt%, based on total weight of A) plus B) plus C), of an organic polymeric binder having sufficient acid functionality to render said photoimageable composition developable in alkaline aqueous solution, said binder polymer A) having a T_g between about 60°C and about 90°C,

B) between about 30 and about 60 wt%, based on total weight of A) plus B) plus C), of an addition polymerizable component comprising α,β -ethylenically unsaturated compounds, said component B) comprising

B') an isocyanate trimer having tri- α,β -ethylenically unsaturated functionality and a weight average molecular weight of at least about 1000, said trimer B') being present at between about 2 to about 30 wt% based on total weight of A) plus B) plus C), and B'') 0 to about 57 wt% based on total weight of A) plus B) plus C) of other α,β -ethylenically unsaturated compounds; and

C) between about 0.5 and about 15 wt%, based on total weight of A) plus B) plus C) of an organic, radiation-sensitive free-radical generating system.

2. The photoimageable composition according to Claim 1 wherein B'') is present in amounts of at least about 5 wt% relative to total weight of A) plus B) plus C).

3. The photoimageable composition according to Claim 1 wherein said free-radical generating system C) comprises 9-phenyl acridine.



4. The photoimageable composition of Claim 1 further comprising D) between about 1 and about 8 wt%, calculated relative to total weight of A) plus B) plus C) of a dibenzoate plasticizer.

5. The photoimageable composition of Claim 1 wherein the T_g of said binder polymer is between about 80°C and about 90°C.