

Description

The present invention is directed to compositions which may be applied as a layer on a substrate, photoimaged, developed and cured to form a patterned, permanent layer, suitable as a solder mask for a printed circuit board.

Solder masks are patterned films or layers which are designed to permanently overlie the printed circuitry on a printed circuit board. Patterned openings in solder masks selectively permit solder to adhere to metal of the printed board. The solder mask also protects the circuitry against short-circuiting.

Because solder masks are designed to provide a permanent layer, hardness and durability of the layer are considered important features of a solder mask composition. Among the hardest and most durable of photomask compositions are those which are epoxy-based. Such compositions generally comprise an epoxy resin dissolved in a solvent. A major disadvantage of epoxy compositions is that they are imagewise screen printed, a primitive technology compared to much more desirable photoimaging.

Photoimageable compositions which may be used to form solder masks or the like typically contain a film-forming material, a photo-polymerizable monomer, e.g., an acrylate monomer, and a photoinitiator. Examples of such compositions are described in U.S. Patent No. 4,528,261. Although such compositions have the advantage of being photoimageable, they are not as strong or as durable as those based upon epoxy resins.

U.S. Patent No. 4,268,614, describes photoimageable compositions which include acrylic resins, acrylic monomers and epoxy resins. The photoimageable compositions described in this '614 patent may be applied as a solution in an organic solvent directly to a circuit board or applied as a solution to a base sheet so as to form a dry film. Compositions such as described in the '614 patent which form a film upon evaporation of an organic solvent are disadvantageous with respect to the use of high levels of organic solvents. In forming films from solutions, the organic solvent typically comprises about one-half of the solution volume. The cost of the solvent, including the shipping and storage of the same, is quite significant. Furthermore, organic solvents, which must be evaporated from the layered compositions, pose substantial health and environmental problems. A further disadvantage of the photoimageable compositions described in the '614 patent is that once photoimaged, the film is developed by washing away the unexposed areas with an organic solvent.

It is an object of the present invention to provide a photoimageable substance which at or near 100% solids may be formed into a film, exposed, developed with aqueous solution and thereafter cured to form a layer with hardness and permanency characteristics similar to films based entirely upon epoxy resins.

In accordance with the invention, there is provided a photoimageable composition comprising a homogeneous solution of (a) between 10 and 40 wt. percent of a flowable, film-forming polymeric binder which is soluble in aqueous or alkaline aqueous solution, (b) between 5 and 25 wt. percent of a cross-linking agent for said polymeric binder, selected from melamine-formaldehyde condensation products, urea-formaldehyde resins and phenolic resins, (c) between 15 and 35 wt. percent of a polymerizable acrylic substance, (d) between 0.01 and 15 wt. percent of a photosensitive, free radical-generating initiator chemical system which in the presence of actinic radiation initiates polymerization of said acrylic substance to form a three-dimensional chemical structure that renders actinic radiation-exposed portions of said photoimageable composition insoluble to aqueous or alkaline aqueous solutions, (e) between 20 and 50 wt. percent of an epoxy resin composition which is curable to harden said photoimageable composition subsequent to exposure to actinic radiation, and (f) between 0.01 and 5 wt. percent of a cure catalyst for said epoxy resin, said polymeric binder being sufficiently soluble in aqueous or alkaline aqueous solution and used at a sufficient level that said photoimageable composition as a whole is developable in aqueous or alkaline aqueous solution, said components (a)-(f) being selected to be mutually miscible and mixed together to form said homogeneous solution.

The composition is preferably substantially free of organic solvent, i.e. at or near 100% solids. The substrate may be a surface of a printed circuit board. Alternatively, the substrate may be a backing sheet or other layer of a dry-film laminate from which the photosensitive film is transferred to a printed circuit board or the like. The polymerizable acrylic substance and photosensitive, free-radical generating material provide the means of imaging the film by forming a polymer which insolubilizes those portions of the film which are exposed to actinic radiation. The epoxy resin, as promoted by its cure catalyst, hardens the film so as to be suitable as a solder mask or as a layer in totally additive plating. The binder is selected for its film-forming properties, whereby the photoimageable composition may be used, substantially in the absence of solvents, to form a layer on the substrate. Also, the binder is selected to have sufficient solubility in aqueous or alkaline aqueous solution that the photoimageable composition may be developed in either aqueous or alkaline aqueous solution. Upon sufficient reaction with the cross-linking agent, the binder will harden and become insoluble in aqueous or alkaline aqueous solution and thereby contribute to the permanency of the fully cured layer, e.g. a solder mask, which is eventually formed. However, as described in greater detail hereinafter, it is preferred that the binder and crosslinking agent be selected so that a partial cure may be effected under conditions which do

not substantially cure the epoxy resin. For example, compositions according to this invention may be "heat-bumped" under mild conditions of time and temperature to effect a partial cure of the binder that renders the photoimageable composition non-tacky, yet leaves a film of the photoimageable composition soluble in aqueous or alkaline aqueous solution.

Herein, unless otherwise stated, all percentages are by weight and are calculated relative to the homogeneous solution of components (a) - (f). Thus components (a) + (b) + (c) + (d) + (e) + (f) = 100 wt. percent. The amounts of any additional ingredients, such as fillers, solvents, etc. are calculated relative to the sum of (a)-(f).

At the outset, a photoimageable composition, in accordance with the invention, contains a substance (a) or substances capable of forming a film on a substrate. Because it is preferred that the photoimageable composition be substantially free of organic solvent, that is, approaching 100% solids, the film-forming binder material should be liquid at room temperature and preferably free-flowing at room temperature. In order that the photoimageable composition be developable in aqueous or alkaline aqueous solution, the film-forming material itself must be soluble in an aqueous solution, either water or a base-containing aqueous solution. Furthermore, the film-forming material must be compatible with the other components of the photoimageable composition.

One important class of film-forming materials useful as binders in forming photoimageable compositions in accordance with the present invention comprises polymers and copolymers of acrylic acids. These polymers and copolymers contain free carboxyl groups and are therefore soluble in alkaline aqueous solutions. These binders are selected for sufficient solubility in alkaline aqueous solution and are employed at a sufficient weight percent of the photoimageable composition that the photoimageable composition is likewise soluble in alkaline aqueous solutions (until exposure to actinic radiation) and hence developable in alkaline aqueous solution. Generally, the higher the acid number of the acrylic polymeric binder, the more soluble the photoimageable composition is in alkaline aqueous solution and the acrylic polymers and copolymers used in accordance with this invention generally have acid numbers greater than 100, preferably greater than 150 and most preferably greater than 200. To provide a high acid number, the polymeric binder material must be formed from one or more acrylic monomers having a free carboxylic acid group, e.g., acrylic acid and methacrylic acid.

The selection of binders which are sufficiently soluble in aqueous solution or alkaline aqueous solution and to an extent sufficient to render the entire photoimageable composition soluble and developable in aqueous or alkali aqueous solution contrasts sharply with the photoimageable compositions provided by above-referenced U. S. Patent No. 4,268,614 which must be developed in organic solvents. Although U. S. Patent No. 4,268,614 teaches the use of acrylic polymers in photoimageable compositions, the polymers described therein are of low acid number and, therefore, do not render the compositions soluble in alkaline aqueous solutions.

The polymeric binder may, and generally is, formed from additional comonomers, including esters of acrylic acids, such as methyl acrylate, methyl methacrylate, hydroxy ethyl acrylate, butyl methacrylate, octyl acrylate, 2-ethoxy ethyl methacrylate, t-butyl acrylate, 1,5-pentanediol diacrylate, N,N-diethylaminoethyl acrylate, ethylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, hexamethylene 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, trimethylolpropane triacrylate, pentaerythritol triacrylate, 2,2-di(p-hydroxy-phenyl)-propane diacrylate, pentaerythritol tetracrylate, 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.

Suitable non-acrylate co-monomers which may be incorporated in the binders include, but are not limited to, styrene, vinyl toluene, maleate esters such as dibutyl maleate, maleic anhydride, vinyl ethers, vinyl ketones, vinyl pyridines and allyl acetoacetates.

It will be appreciated by those skill in the art that certain functional groups on the various components of the photoimageable composition will, to a greater or lesser degree, interact with epoxy groups of the epoxy resin, and thereby cause premature cross-linking of the epoxy resin. This is primarily a shelf-life problem, and the level of certain chemical functional groups may have to be limited to provide a desired shelf-life. However, shelf-life is not the only concern in formulating photoimageable compositions, and compositions according to the invention may be finally formulated near to the time of use. Generally, free amine groups cannot be used in the presence of epoxy resins if any degree of shelf-life is to be achieved. Carboxyl groups, hydroxyl groups and amide groups will also initiate epoxy polymerization, though the levels of these groups may be controlled to be consistent with reasonable shelf-life. Where shelf-life is important, e.g., in formulating dry films, it is es-

pecially desirable to control the level of epoxy-reactive groups, to the extent that is consistent with other desirable aspects of the photoimageable composition, e.g., providing requisite solubility in alkaline aqueous solution. Thus, for example, where shelf-life is to be extended, it is desirable that the acrylate binder contain few hydroxyl moieties, such as those found in N,N-diethylaminoethyl acrylate, glycerol diacrylate and pentaerythritol triacrylate.

The acrylate-containing polymers having high acid numbers are the preferred film formers or binders for compositions in accordance with this invention, particularly for use as a film on a printed circuit board which must pass IPC/ANSI SM-840A Class III tests. However, because of the large number of acidic groups in these polymers, there are limitations to long-term stability of compositions containing both acrylic film formers and the epoxy resins, which are another component of the photoimageable compositions. The acrylate-containing polymers are, however, compatible with epoxy resins for relatively short periods, and there is generally no urgency to apply these resins immediately after final formulation. Thus, compositions containing both acrylate polymers having free carboxylic acid groups and epoxide resins may be provided as one-part liquid compositions for application to printed circuit boards or even as partially cured (heat-bumped) layers of dry films. The shelf-life of such compositions depends upon the particular components of the system, e.g., the acid number of the particular acrylic binder which is used, and the temperature at which the composition is stored prior to use. The compatibility problems of epoxy resins in the presence of free carboxyl groups may, however, require liquid compositions or dry films formed therefrom to be used within a shorter period of time than is customary in the art. Because of the long-term compatibility problem of the acrylate-containing binder polymers and epoxy resins, a composition may be provided commercially as a two-part system, one part containing the acrylate-containing binder and the other part containing the epoxy resin. The remaining components are appropriately distributed among the two parts of the system, it being generally desirable in such two-part systems to keep curing agents separate from the corresponding polymerizable or cross-linkable materials.

Another type of material used as binders in photoimageable compositions in accordance with the present invention are styrene-maleic anhydride copolymers in which the mer units derived from maleic anhydride remain in the anhydride state. The polymers, while having no free hydroxyl or carboxylic acid groups, may be saponified in alkaline solution to the acid form. Styrene-maleic anhydride copolymers, which are saponifiable to acid numbers of 100 or more, are preferred, as they provide good solubility in aqueous solution.

A type of film-forming binder which is long-term compatible with epoxy resins is polyvinyl alcohols. Polyvinyl alcohols are substantially saponified poly-vinyl acetates, preferably being at least 80% hydrolyzed. Polyvinyl alcohols are available in a wide variety of viscosities, and viscosities are selected for the particular application.

Carboxylated polyvinyl alcohols are similar to polyvinyl alcohols, but between 1 and 5% of the per units contain free carboxyl groups. Carboxylated polyvinyl alcohols are formed by copolymerizing vinyl acetate and an alkyl ester of acrylic acid and then hydrolyzing the ester bonds of the polymer. Carboxylated polyvinyl alcohols are hydrolyzed to at least 75%. Because of the free carboxyl groups, this polymer is somewhat less compatible with epoxy resins.

Polyvinyl alcohols suitable for use in accordance with the invention are available from Air Products, Allentown, PA, under the tradenames Vinol 125, 165, 107, 325, 350, 425, WS-42, 205, 523, 540, 205S, 523S and 540S. Carboxylated polyvinyl alcohols suitable for use in the invention are sold by Air Products, e.g., under the trade name Vinol 118M. Polyvinyl alcohol and carboxylated polyvinyl alcohol, unlike the acrylate-containing polymers having high acid numbers, are soluble in water, generally regardless of the pH, and therefore do not require basic developers, that is, photoimageable compositions based upon these binder materials may be developed in water. Polyvinyl alcohol and carboxylated polyvinyl alcohols are considered less desirable binders as compared with acrylate binders with respect to hardness and water-susceptibility of the finally cured-film.

Novolac resins, such as those described in *Polymer Chemistry*, Malcolm P. Stevens, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, (1975) pp 324-327, are also suitable as binders. Novolac resins have relatively good stability with epoxy resins (an advantage in one part formulations) and can be used to form binders which pass Class III standards.

Other suitable film-forming resins for use in the invention include, but are not limited to, cellulose, and hydroxyethyl cellulose. Furthermore, mixtures of the several polymeric binders discussed above may be included in a photoimageable composition formulation.

The polymeric binder or mixture of polymeric binder materials comprises between 10 and 40% by weight of the homogeneous solution of components (a)-(f), preferably between 15 and 25% by weight.

The photoimageable composition is applied as a viscous, tacky, flowable liquid to a substrate, such as a printed circuit board or to a backing sheet to form a dry film. As explained in greater detail hereinafter, it is often desired that the photoimageable composition be partially curable to either partially harden or to insolubilize the film, and to this end, the photoimageable composition contains a cross-linking agent (b) which cross-

links the binder and may also cross-link certain other components of the photoimageable composition.

Desirably, the cross-linking agent acts primarily at temperatures somewhat above room temperature, e.g., above 35°C, whereby the photoimageable composition may be applied to a substrate at or near room temperature and subsequently heat-bumped to effect a controlled level of cross-linking. It is important for several applications that the controlled level of cross-linking be effected using relatively mild temperatures and in a relatively short period of time. By relatively mild temperatures and relatively short periods of time, is herein meant, in comparison to the substantially higher temperatures and/or longer periods of time required to finally cure the epoxy resins, as described hereinafter.

Preferred cross-linking agents are melamine-formaldehyde condensation products, such as those sold under the trademark Resimene by Monsanto, St. Louis, MO. or Cymel by American Cyanamide. The functional groups on the amino moieties react with complementary reactive groups, e.g., hydroxyl groups, on the resin, forming a three-dimensional thermoset polymer network. The other cross-linking agents which may be used are urea-formaldehyde resins and phenolic resols. The cross-linking agent comprises between 5 and 25% by weight of the homogeneous solution of components (a)-(f). Generally for photoimageable compositions which are to be applied as a liquid film, the amount of the cross-linking agent is toward the lower end of this range; in forming dry films, the amount of the cross-linking agent is toward the upper end of this range.

The photoimaging system is based upon the polymerizable acrylic substances (c). The polymerizable acrylic substances are generally monomers containing one or more acrylic moieties. They can, however, contain acrylic dimers or trimers. Any of the acrylic monomers listed above as components of an acrylic polymeric binder is suitable as a polymerizable acrylic substance for purpose of this invention. Mixtures of acrylates are also suitable. As in polyacrylate binder, the polymerizable acrylate substance(s) must be selected with the intended shelf-life of the photoimageable composition in mind, and levels of free carboxyl, hydroxyl, amide and other epoxy-reactive functional groups appropriately controlled. The polymerizable acrylic materials comprise between 15 and 35 wt. percent of homogeneous solutions (a)-(f) according to the invention and preferably from 18 to 25 wt. percent.

In some cases, it has been found to be advantageous to use an acrylic monomer that includes at least one free hydroxyl group, for example, hydroxy alkyl acrylates and methacrylates, such as pentaerythritol tetraacrylate, 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate and 2-ethoxy ethyl methacrylate. The free hydroxy groups are acted upon by the cross-linking agent during the heat-bump, chemically linking at least some of the polymerizable acrylates to the polymeric binder and thereby providing a more integrated cross-linked film structure.

Also required in conjunction with the polymerizable acrylate substance is a chemical initiator system which generates free radicals in the presence of actinic radiation and polymerizes the acrylic substance. Polymerization of acrylic monomer units into a three-dimensional structure insolubilizes the photoimageable composition by immobilizing the polymeric binder. The choice of the photosensitive, free radical-generating initiator system is not considered to be critical to the practice of the present invention, and a wide variety of such compounds may be successfully utilized in the practice of this invention. Examples of chemical photoinitiator systems include benzophenone, benzoin ether, benzil ketals and acetophenone and its derivatives. Other suitable initiator systems are described, for example, in U.S. Patent Nos. 3,469,982, 4,451,523 and 4,358,477.

The amount of photoinitiator employed may vary over a wide range, depending upon the polymerizable acrylic substance(s), the particular photoinitiator system and the desired time of development. The photoinitiator chemical system comprises between 0.01 and 15 wt. % of the homogeneous solution (a)-(f).

The material which imparts the excellent hardness and durability to the film or layer after development and final curing is the epoxy resin or mixture of epoxy resins. The epoxy resin or resins comprise between 20 and 50 percent by weight of the homogeneous solution (a)-(f). At high temperatures and/or in the presence of a catalyst, the epoxy groups of the resin molecules open and react with other materials present. Primarily the epoxy resin molecules react with each other; however, to a certain extent, the epoxy molecules react during final curing with the cross-linking agent, and perhaps also with the acrylic binder material and the remaining polymerized and unpolymerized acrylate substances. The major consideration of selection of the epoxy resin or mixture of resins is that the epoxy resin composition be a liquid at about room temperature, whereupon the photoimageable composition can be applied as a liquid film to the substrate. Generally, lower molecular weight epoxies, e.g., having molecular weights between 240 and 260, tend to be liquid, and preferably at least 70% by weight of the epoxy resins comprises polyepoxy molecules having molecular weights below 260. It is permissible, however, to dissolve higher molecular weight, solid epoxies in the lower molecular weight, liquid epoxies, providing that the combination of epoxy resins is liquid. Higher molecular weight epoxies may be advantageously incorporated into a photoimageable composition to control viscosity of the photoimageable composition. The inclusion of some higher molecular weight epoxy resin dissolved in lower molecular weight epoxy resin may result in formation of a harder, more durable film.

A wide variety of epoxy resins are suitable for use in accordance with the present invention. Suitable epoxy resins are described, for example, in U.S. Patent No. 4,092,443. Preferred epoxy resins for purpose of the invention are cycloaliphatic epoxides, such as those sold under the trade names Cyanacure UVR-6100 and UVR-6110 by Union Carbide, Danbury, CT.

Epoxy resins are generally heat-curable; high temperatures open the epoxy groups, thereby causing them to react. Several applications of photoimageable compositions in accordance with the invention require that curing of the epoxy resin composition takes place at a higher temperature and/or is cured over a longer period of time than the temperature and time required for the heat-bump, during which the acrylic binder is cross-linked to a controlled extent. Although some degree of curing of the epoxy resins may take place continuously and even at a somewhat increased rate during the heat-bump, the epoxy resin composition in several applications must remain substantially uncured until after exposure to patterned actinic radiation and development. Once the epoxy resin composition cures to any appreciable extent, the photoimageable composition becomes insoluble in aqueous and alkaline aqueous solutions and therefore non-developable. Accordingly, the epoxy resin composition is further selected so as to be curable under harsher conditions of time and temperature than are required for the initial heat-bump.

The photoimageable composition includes a cure catalyst for the epoxy resin composition which promotes more rapid curing at the final heat cure temperature. Suitable heat-activated curing agents include polycarboxylic acid anhydrides, dicyandiamides, complexes of amines, such as solely tertiary amines, with boron trifluoride or boron trichloride, latent boron difluoride chelates, aromatic polyamines and imidazoles, such as 2-ethyl-4-methylimidazole. Other examples of epoxy cure catalysts are found in U.S. Patent No. 4,438,189. Preferred epoxy catalysts are blocked or latent catalysts, such as those sold under the trade name SA-102 by Air Products. Such catalysts have an epoxy-catalyzing group, e.g., an acid group or amine or amide group, appropriately blocked. At a threshold temperature, the catalyst releases its blocking group and catalyzes epoxy ring opening. The threshold activation temperature of such catalysts is particularly advantageous in a process which includes an initial, relatively low-temperature, relatively short-time heat-bump and a subsequent heat-cure under more vigorous temperature/time conditions. Epoxy cure catalysts are used at levels of from 0.01 to 5 wt. percent of the homogeneous solution (a)-(f).

The components of the photoimageable composition are selected to be mutually soluble to form a single-phase liquid composition. The liquid photoimageable composition may be applied to a substrate by a variety of application methods, including screen printing, curtain coating, roller coating and extrusion coating. Each application method has its own particularities, and photoimageable compositions in accordance with this invention may be formulated in accordance with the particular requirements of the particular method of application, e.g., to provide a suitable photoimageable composition viscosity.

It may be appreciated at this time that all of the components described above remain present in the final cured film which is formed, that is, the formulation supplies substantially 100% solids. This is an important advantage of the photoimageable compositions of the present invention, in contrast to films which are formed by solvent evaporation. It is contemplated, however, that the photoimageable composition may contain minor amounts of organic solvent, e.g., up to 20 parts by weight per 100 weight parts of the homogeneous solution (a)-(f) and preferably less than 2% by weight. Some solvent may be present only because certain of the components of the system may be commercially provided along with a volatile organic solvent.

In addition to the components described above which are essential to a photoimageable composition in accordance with the invention, the photoimageable composition may optionally contain additional components which are standard in the art. The photoimageable composition may contain organic or inorganic fillers at levels up to 35 weight parts per 100 weight parts of the homogeneous solution (a)-(f). Some examples of fillers are micro talc, ground polyethylene, clay, fumed silica and polyvinylidene fluoride. Also, relatively small amounts of flow-control agents, antioxidants, dyes, etc. may be added.

The compositions in accordance with the invention which provide a photoimaging reaction in combination with a two-stage cure are useful in several types of applications, and advantages of the compositions will become more fully appreciated as the use of these compositions is discussed with respect to several applications. It will be appreciated, that the exact formulation and treatment conditions for any formulation will depend upon the application to which it is to be put.

An important use of the compositions of the present invention is for direct application to a printed circuit board where contact printing is to be employed. The composition is applied as a layer on the surface of the board. Subsequent to application of the photoimageable composition to the surface, the photoimageable composition is heat-bumped for a controlled period of time so that the photoimageable composition forms a non-tacky layer, yet leaves the photoimageable composition soluble in an appropriate aqueous solution. The heat-bump takes place at a controlled temperature and for a controlled time period to achieve the non-tacky condition; however, care must be taken to avoid excess cross-linking of the several components which would ren-

der the photoimageable composition insoluble in aqueous or alkaline aqueous solutions. Heat-bump times and temperatures must be determined for each particular photoimageable composition. For any particular photoimageable composition, different temperatures may be used with different times. Typically, heat-bump temperatures range from 70-100°C at times of from 5 to 60 min.; however, it can easily be appreciated that lower temperatures with longer heat-bump times may be employed.

During the heat-bump, the primary reaction is between the cross-linking agent and the polymeric binder; however, minor reactions probably involve interactions between a number of components. Heat-bump reactions contribute to non-tackiness of the film. For applications where the film is to remain soluble and developable in an appropriate aqueous or alkaline aqueous solution, reactions which occur during the heat-bump must be consistent with continued solubility of the film.

For contact printing and dry film applications, the non-tacky, but developable film which forms after the heat-bump is ready for exposure to actinic radiation. For contact-printing, the artwork, e.g., diazo artwork, is laid directly on the film. The non-tacky nature of the film at this stage enables the artwork to be contacted with the film. As those with skill in the art readily appreciate, contact printing is generally preferred over remote exposure techniques for producing sharply defined images. Light intensities (which generally depends upon the unit used) and exposure times (which are generally determined by the operator) determine the light energy applied during exposure. Required light energies for exposure depends primarily on the polymerizable acrylic substances and the photoinitiator systems used and amounts thereof. Exposure must be determined for each photoimageable composition.

For non-contact printing, the film may be exposed either after a heat-bump, which leaves the film soluble in aqueous or alkali aqueous solution, or with the film in unaltered, tacky form.

Subsequent to exposure, the non-exposed portions are dissolved and washed away in aqueous or alkaline aqueous solution. Films based upon polyvinyl alcohol, carboxylated polyvinyl alcohol, cellulose or the like are soluble in water and may be developed in an aqueous solution, including water. Photoimageable compositions based upon acrylic binder-containing films having high acid numbers, on the other hand, must be developed in an alkaline aqueous solution. Typical alkaline developers contain from 0.5 to 3% by weight of a weak base, such as potassium carbonate, sodium carbonate or ammonium hydroxide or from 0.4% to 3% by weight of a strong base, such as sodium hydroxide or potassium hydroxide. Novolac-containing films are also developed in alkaline aqueous developers.

The ability to be developed with aqueous or alkali aqueous solutions is considered to be an important advantage of the photoimageable composition of the present invention. Eliminating the need for solvent-based developers eliminates the cost of the solvents as well as health, environmental and recycling problems. Although the films formed in accordance with the invention are developable in aqueous solutions without any organic solvents, developers may include some organic solvents, providing that the added organic solvent does not solubilize the exposed portions of the film.

Following development, it is preferred to again expose the film to actinic radiation to effect a UV-cure. The UV-cure is optional, but is helpful in producing a stronger permanent film. Primarily, the UV-cure is believed to polymerize or cross-link any remaining polymerizable acrylic substance.

The primary cure of the exposed and developed film is the thermal cure which opens the epoxy groups of the epoxy resin molecules, resulting in cross-linking of the epoxy resin molecules with each other and with the other materials in the film. The thermal cure is generally carried out at temperatures ranging from 100°C to 200°C for a period of from 15 min. to 2 hrs. A typical cure would be 150°C for an hour. The actual cure time and cure temperature depends upon the epoxy resin used, the epoxy cure catalyst and the amounts of each. If a blocked or latent epoxy cure catalyst is used, curing is done at a temperature above that which deblocks the catalyst.

It is very often the case that a solder mask must be applied to two sides of a printed circuit board. Generally, for contact printing of a solder mask on both sides of a printed circuit board, the following modification of the above-described procedure is followed. The composition is applied to "side 1" of the board; the composition is heat-bumped to non-tackiness and the board is cooled. The composition is applied to "side 2" of the board; the composition is heat-bumped to non-tackiness and the board is cooled. The two sides are then contact-printed, and both sides of the board are developed simultaneously by washing the board in water or alkaline solution, as appropriate. Final curing is then effected. It may be appreciated that "side 1" is "heat-bumped" for a longer period of time than is "side 2". Careful control of the two heat-bumps is required so that "side 2" can be heat-bumped to non-tackiness while leaving "side 1" still soluble in the developer. The composition must therefore be formulated so as to provide a sufficiently wide "cure window" of heat-bump time which provides a non-tacky, yet developable film.

It is also contemplated that the photoimageable composition of the present invention be used for off-contact printing using highly collimated light for good resolution. Other considerations may apply when off-contact

printing is used. Particularly, it is not necessary that a non-tacky layer be provided prior to exposure, and even a film of viscous liquid may be exposed. Nevertheless, the two-stage cure provided by the compositions of the present invention is advantageous for off-contact printing.

5 A typical procedure for off-contact printing of two sides of a printed circuit board is as follows. The composition is applied as a film to "side 1" of the circuit board. The film is exposed to patterned actinic radiation. Resulting polymerization of the acrylic substance both hardens the exposed portions of the film and renders such portions insoluble to developer. The film is then developed in aqueous (or aqueous alkaline) solution. At this time, a heat-bump is employed to sufficiently harden and render non-tacky the portions of the film which remain so that these portions are not lost during subsequent handling of the board. This heat-bump further
10 insolubilizes the remaining portions of the film, protecting the film against treatment of "side 2". A film of composition is then applied to "side 2"; the film is exposed and the film on "side 2" is developed. At this point, the board is baked, resulting in cross-linking of the binder on "side 2" and curing of the epoxy resin on both sides of the board. It can be appreciated that the "window" of curing provided by the heat-bump in this procedure, where the heat-bump of side 1 follows exposure and development, may differ from that required in the contact printing procedure, described above, in which the heat-bump precedes exposure and development. In either case, the intermediate cure achieved during the "heat-bump", as provided by the acrylic binder, obviates the need to fully cure the epoxy resin of "side 1" before proceeding with treatment of "side 2".

15 In forming a dry film, the photoimageable composition is applied as a layer to the backing sheet and then heat-bumped to non-tackiness. The film is subsequently transferred from the backing sheet to a solid substrate, e.g., a printed circuit board, and then exposed, developed and cured as discussed above.

20 In forming a dry film, general considerations and techniques of dry film application apply. The film must be selectively adherent to the substrate as compared to its adherence to the backing sheet material, e.g., polyethyleneterephthalate. The backing sheet may be appropriately coated to provide such selective adherence. The dry film may also include other layers, such as an oxygen-impermeable membrane, e.g., polyethylene, which
25 remains on the film until just prior to or following exposure to radiation and which is then removed to allow development of the layer.

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

30 EXAMPLE 1

A photoimageable composition having the following composition was prepared:

35

40

45

50

55

	<u>Component</u>	<u>% Wt.</u>
5	acrylic resin (binder), acid no. 200	22.6
	1,8 diaza-bicyclo-(5,4,0)-undecene-7-phenol salt	1.2
10	equal wt. mixture of (a) hydroxyethyl methacrylate, (b) bisphenol A diacrylate, and (c) dipentaerithritol monohydroxy pentaacrylate	21.8
	2,2 dimethyl 2 phenyl-acetophenone	3.0
	liquid cycloaliphatic monoepoxy, epoxy equiv. 120-130	42.4
15	methyalted melamine	9.0
		100.0
	plus	
20	leveling agent	1.2
	pigment (phthalocyanine green CI#74260)	1.2
	Fillers	
25	fumed silica	1.8
	micro talc	14.4
	ground polyethylene	0.9

30 The photoimageable composition was applied as a .0381 mm thick layer on a printed circuit board. The photoimageable composition was heat-bumped at 80°C for 30 minutes, providing a non-tacky film. A diazo artwork was placed directly on the film, and the film was exposed to actinic radiation having an intensity of 200 mJ/cm² for 1 min. The film was then developed in a basic aqueous solution, i.e., 1% by weight sodium carbonate monohydrate. The film was UV-cured by exposure to actinic radiation having an intensity of 2 Joules for 2 min. Heat-curing was at 150°C for 1 hour.

35 The following additional compositions according to this invention are prepared and processed in accordance with Example 1.

40

45

50

55

EXAMPLE 2

<u>Components</u>	<u>% Wt.</u>
Acrylic resin with minimum acid number of two hundred	37.3
Hydroxyethyl acrylate	26.8
Hexamethylmelamine	10.9
Benzophenone	1.9
Liquid cycloaliphatic diepoxy	22.6
1,8 diaza-bicyclo-(5,4,0) undecene 7	0.5
	100.0
plus	
Leveling agent	1.2
Pigment (phthalocyanine green CI#74260)	1.2
Fillers	
polyvinylidene fluoride	9.3
micro talc	22.3

EXAMPLE 3

<u>Component</u>	<u>% Wt.</u>
Styrene maleic anhydride, acid no. 200, M.W. 10,000	22.2
Trimethylolpropane triacrylate	33.9
Butylated melamine	5.6
Isobutyl benzoin ether	0.9
Solid bisphenol-A epoxy, epoxy equiv. 525-1800	35.8
1,8 diaza-bicyclo-(5,4,0)-undecene-7-ethyl hexanoic acid salt	1.6
	100.0
plus	
Leveling agent - A	1.2
Pigment (phthalocyanine green CI#74260)	1.2
Fillers	
clay	3.6
micro talc	6.2
ground polyethylene	1.1

EXAMPLE 4

	<u>Component</u>	<u>% Wt.</u>
5	Styrene maleic anhydride, acid no. 200, - m.w. 10,000	28.8
	Ethoxylated trimethylolpropane triacrylate	16.7
10	Methyl-butyl melamine	22.3
	Isopropyl thioxanthone	2.5
	Solid multifunctional novalac epoxy	27.7
15	1,8 diaza-bicyclo-(5,4,0)-undecene-7-p-toluene sulfonic acid salt	1.0
	plus	<u>100.0</u>
20	Leveling agent	1.2
	Pigment (phthalocyanine green CI#74260)	1.2
25	Fillers	
	fumed silica	1.8
30	micro talc	14.4
	ground polyethylene	0.9
35		
40		
45		
50		
55		

EXAMPLE 5

<u>Component</u>	<u>% Wt.</u>
5 Acrylic resin with minimum acid number of two hundred	35.9
Diethyleneglycol diacrylate	15.7
10 Hexa-alkoxy methylol melamine resin	23.8
2 chlorothioxanthone	4.1
Liquid cycloaliphatic monoepoxy, epoxy equiv. 120-130	20.2
15 1,8 diaza-bicyclo-(5,4,0)-undecene-7-formic acid salt	0.3
	100.0
plus	
20 Leveling agent	1.2
Pigment (phthalocyanine green CI#74260)	1.2
25 Fillers	
fumed silica	1.8
micro talc	14.4
ground polyethylene	0.9

EXAMPLE 6

<u>Components</u>	<u>% Wt.</u>
35 Styrene maleic anhydride, acid no. 200, -m.w. 10,000	17.3
Polyethyleneglycol diacrylate	20.1
40 Unsaturated acrylic melamine	20.4
Isobutyl benzoin ether	3.3
Solid multifunctional novalac epoxy	37.7
45 1,8 diaza-bicyclo-(5,4,0)-undecene-7-phenol salt	1.2
	100.0
50 plus	
Leveling agent	1.2
Pigment (phthalocyanine green CI#74260)	1.2
55 Filler	
clay	22.1

EXAMPLE 7

	<u>Components</u>	<u>% Wt.</u>
5	Acrylic resin with minimum acid number of two hundred	12.2
	Tetraethyleneglycol diacrylate	31.8
10	Butyl-esterified-phenol formaldehyde	5.7
	Diethoxy-2-methyl-1-phenylpropane-1-one	3.7
	Liquid cycloaliphatic monoepoxy	45.6
15	1,8 Diaza-bicyclo-(5,4,0)-undecene-7-ethyl-hexanoic acid salt	1.0
		100.0
	plus	
20	Leveling agent	1.2
	Pigment (phthalocyanine green CI#74260)	1.2
25	Fillers	
	fumed silica	1.8
	micro talc	14.4
	ground polyethylene	0.9

EXAMPLE 8

	<u>Components</u>	<u>% Wt.</u>
35	Acrylic resin with minimum acid number of two hundred	21.5
	Cyclohexyl acrylate	18.3
40	Butylated urea	14.9
	2,2 dimethyl-2-phenyl-acetophenone	2.2
	Solid bisphenol-A-epoxy, epoxy equiv. 525-1800	42.1
45	1,8 Diaza-bicyclo-(5,4,0)-undecene-7-phenol salt	1.0
		100.0
	plus	
50	Leveling agent	1.2
	Pigment (phthalocyanine green CI#74260)	1.2
55	Fillers	
	fumed silica	32.3

EXAMPLE 9

	Acrylic resin with minimum acid number of two hundred	30.3
5	Isodecylglycol triacrylate	16.2
	Methylated urea	14.3
10	2,2-dimethyl-2-phenyl-acetophenone	2.1
	Liquid cycloaliphatic diepoxy, epoxy equiv. 120-145	35.3
	1,8 diaza-bicyclo-(5,4,0)-undecene-7	1.8
15		100.0
	plus	
	Leveling agent	1.2
20	Pigment (phthalocyanine green CI#74260)	1.2
	Fillers	
25	fumed silica	1.8
	micro talc	14.4
	ground polyethylene	0.9

Claims

1. A photoimageable composition comprising a homogeneous solution of
 - (a) between 10 and 40 wt. percent of a flowable, film-forming polymeric binder which is soluble in aqueous or alkaline aqueous solution,
 - (b) between 5 and 25 wt. percent of a cross-linking agent for said polymeric binder, selected from melamine-formaldehyde condensation products, urea-formaldehyde resins and phenolic resols,
 - (c) between 15 and 35 wt. percent of a polymerizable acrylic substance,
 - (d) between 0.01 and 15 wt. percent of a photosensitive, free radical-generating initiator chemical system which in the presence of actinic radiation initiates polymerization of said acrylic substance to form a three-dimensional chemical structure that renders actinic radiation-exposed portions of said photoimageable composition insoluble to aqueous or alkaline aqueous solutions,
 - (e) between 20 and 50 wt. percent of an epoxy resin composition which is curable to harden said photoimageable composition subsequent to exposure to actinic radiation, and
 - (f) between 0.01 and 5 wt. percent of a cure catalyst for said epoxy resin, said polymeric binder being sufficiently soluble in aqueous or alkaline aqueous solution and used at a sufficient level that said photoimageable composition as a whole is developable in aqueous or alkaline aqueous solution, said components (a)-(f) being selected to be mutually miscible and mixed together to form said homogeneous solution.
2. A photoimageable composition according to claim 1 wherein said cross-linking agent is selected to react with said polymeric binder in controlled manner, whereby said photoimageable composition may be mildly heated to render said photoimageable composition non-tacky, yet developable in aqueous or alkaline aqueous solution, said epoxy resin being selected to be insufficiently cured under said mild heating conditions to render said photoimageable composition insoluble to aqueous or alkaline aqueous solution.
3. A photoimageable composition according to claim 1 or claim 2 wherein said cure catalyst is a latent catalyst

**EXAMPLE 9**

5	Acrylic resin with minimum acid number of two hundred	30.3
	Isodecylglycol triacrylate	16.2
	Methylated urea	14.3
10	2,2-dimethyl-2-phenyl-acetophenone	2.1
	Liquid cycloaliphatic diepoxy, epoxy equiv. 120-145	35.3
	1,8 diaza-bicyclo-(5,4,0)-undecene-7	1.8
15		100.0
	plus	
	Leveling agent	1.2
20	Pigment (phthalocyanine green CI#74260)	1.2
	Fillers	
25	fumed silica	1.8
	micro talc	14.4
	ground polyethylene	0.9

Claims

1. A photoimageable composition comprising a homogeneous solution of
 - (a) between 10 and 40 wt. percent of a flowable, film-forming polymeric binder which is soluble in aqueous or alkaline aqueous solution,
 - (b) between 5 and 25 wt. percent of a cross-linking agent for said polymeric binder, selected from melamine-formaldehyde condensation products, urea-formaldehyde resins and phenolic resols,
 - (c) between 15 and 35 wt. percent of a polymerizable acrylic substance,
 - (d) between 0.01 and 15 wt. percent of a photosensitive, free radical-generating initiator chemical system which in the presence of actinic radiation initiates polymerization of said acrylic substance to form a three-dimensional chemical structure that renders actinic radiation-exposed portions of said photoimageable composition insoluble to aqueous or alkaline aqueous solutions,
 - (e) between 20 and 50 wt. percent of an epoxy resin composition which is curable to harden said photoimageable composition subsequent to exposure to actinic radiation, and
 - (f) between 0.01 and 5 wt. percent of a cure catalyst for said epoxy resin, said polymeric binder being sufficiently soluble in aqueous or alkaline aqueous solution and used at a sufficient level that said photoimageable composition as a whole is developable in aqueous or alkaline aqueous solution, said components (a)-(f) being selected to be mutually miscible and mixed together to form said homogeneous solution.
2. A photoimageable composition according to claim 1 wherein said cross-linking agent is selected to react with said polymeric binder in controlled manner, whereby said photoimageable composition may be mildly heated to render said photoimageable composition non-tacky, yet developable in aqueous or alkaline aqueous solution, said epoxy resin being selected to be insufficiently cured under said mild heating conditions to render said photoimageable composition insoluble to aqueous or alkaline aqueous solution.
3. A photoimageable composition according to claim 1 or claim 2 wherein said cure catalyst is a latent catalyst



having blocking moieties, said catalyst becoming unblocked above a threshold temperature, whereupon cure of said epoxy resin is promoted above said threshold temperature.

- 5 4. A photoimageable composition according to any preceding claim, wherein said binder is formed at least in part from acrylic monomers having free carboxylic acid groups, said binder having an acid number of at least 100.
- 10 5. A photoimageable composition according to any preceding claim, wherein said binder material is formed at least in part from one or more of polyvinyl alcohol, carboxylated polyvinyl alcohol, cellulose, hydroxy ethyl cellulose, styrene maleic anhydride copolymer, and Novolac resins.
- 15 6. A photoimageable composition according to any preceding claim, wherein said homogeneous solution is combined with a dispersible organic or inorganic filler at a level of up to 35 weight parts per 100 weight parts of said components (a)-(f).
- 20 7. A photoimageable composition according to any preceding claim, wherein said epoxy resin composition is liquid at room temperature.
- 25 8. A photoimageable composition in accordance with any preceding claim having no more than 20 parts by weight of organic solvents per 100 parts by weight of said homogeneous solution of components (a)-(f).
- 30 9. A photoimageable composition in accordance with claim 8 having no more than 2 parts by weight of organic solvents per 100 parts by weight of said homogeneous solution of components (a)-(f).
- 35 10. A photoimageable composition in accordance with claim 9 which is free of organic solvents.
- 40 11. A two-parts solution comprising components (a)-(f) in the amounts defined in claim 1, the two parts of which are miscible homogeneously to form a composition in accordance with any preceding claim, one said part containing said binder (a) and the other part containing said epoxy resin composition (e).
- 45 12. A substrate coated with a layer of a photoimageable composition in accordance with any one of claims 1 to 10.
- 50 13. A coated substrate in accordance with Claim 12 wherein said substrate is a printed circuit board, said layer of photoimageable composition being processable to provide a solder mask.
- 55 14. A coated substrate in accordance with Claim 12 wherein said substrate is a flexible backing sheet, said backing sheet and said photoimageable composition layer being partially curable by cross-linking of said binder to form a dry film which is developable in aqueous or alkaline aqueous solution.
15. A method of forming a hard, permanent, patterned film on a solid substrate comprising
 - (1) providing a photoimageable composition according to any one of claims 1 to 10,
 - (2) coating a film of said photoimageable composition on a surface of said substrate,
 - (3) heating said film of photoimageable composition for such time and temperature as to sufficiently cross-link said binder to render said film non-tacky yet still soluble in aqueous or alkaline aqueous solution,
 - (4) exposing said film to patterned actinic radiation so as to polymerize said acrylic substance and render exposed portions of said film insoluble to aqueous or alkaline aqueous solution,
 - (5) developing said film in aqueous or alkaline aqueous solution to remove non-exposed portions of said film, and
 - (6) curing said epoxy resin in said photoimageable composition at such time and temperature as to render said film hard and permanent.
16. A method according to Claim 15 which includes the step of UV-curing said exposed, developed film.
17. A method according to Claim 15 of forming a hard, permanent, patterned film on each of a first side and a second side of a solid substrate comprising providing said photoimageable composition according to step (1), preparing said first side according to steps (2) and (3), preparing said second side according to steps (2) and (3), exposing each of said sides according to step (4), developing said sides according to step (5), and then curing said epoxy resin in said films of photoimageable composition according to step



(6).

- 5 18. A method of forming a hard, permanent, patterned film on a solid substrate comprising
- (1) providing a photoimageable composition according to any one of claims 1 to 10,
 - (2) applying said photoimageable composition as a film on a backing sheet,
 - (3) heating said film of photoimageable composition for such time and temperature as to sufficiently cross-link said binder to render said film non-tacky yet still soluble in aqueous or alkaline aqueous solution,
 - (4) transferring said non-tacky film from said backing sheet to a solid substrate,
 - 10 (5) exposing said transferred film to patterned actinic radiation so as to polymerize said acrylic substance and render exposed portions of said film insoluble to aqueous or alkaline aqueous solution,
 - (6) developing said film in aqueous or alkaline aqueous solution to remove non-exposed portions of said layer, and
 - (7) curing said epoxy resin at such time and temperature as to render said film hard and permanent.
- 15 19. A method of preparing a dry film comprising
- (1) providing a photoimageable composition according to any one of claims 1 to 10,
 - (2) applying said photoimageable composition as a film on a backing sheet, and
 - (3) heating said film of photoimageable composition for such time and temperature as to sufficiently cross-link said binder to render said film non-tacky yet et still soluble in aqueous or alkaline aqueous solution.
- 20 20. A method of forming a hard, permanent, patterned film on each of a first side and a second side of a solid substrate, the method comprising
- (1) providing photoimageable composition according to any one of claims 1 to 10,
 - (2) coating a film of said photoimageable compositions on said first side,
 - (3) exposing said film to patterned actinic radiation so as to polymerize said acrylic substance and render exposed portions of said film insoluble to aqueous or alkaline aqueous solution,
 - (4) developing said film in aqueous or alkaline aqueous solution to remove non-exposed portions of said film,
 - 25 (5) heating said film of photoimageable composition for such time and temperature as to cross-link said polymeric binder,
 - (6) repeating steps (2) through (4) on said second side, and
 - (7) heating said films on said first and said second side to cross-link said polymeric binder of said film on said second side and to cure said epoxy resin of said films on said first and second sides.
- 30 35

Patentansprüche

- 40 1. Zusammensetzung für Photoaufzeichnung, die eine homogene Lösung von
- a) zwischen 10 und 40 Gew.-% eines fließfähigen, filmbildenden polymeren Bindemittels, das in wäßriger oder alkalisch-wäßriger Lösung löslich ist,
 - b) zwischen 5 und 25 Gew.-% eines Vernetzungsmittels für dieses polymere Bindemittel, ausgewählt unter Melamin-Formaldehyd-Kondensationsprodukten, Harnstoff-Formaldehydharzen und Phenolsolen,
 - 45 c) zwischen 15 und 35 Gew.-% einer polymerisierbaren Acrylsubstanz,
 - d) zwischen 0,01 und 15 Gew.-% eines lichtempfindlichen, freie Radikale erzeugenden chemischen Initiatorsystems, das in Gegenwart von aktinischer Strahlung eine Polymerisation der Acrylsubstanz unter Bildung einer dreidimensionalen chemischen Struktur einleitet, die aktinischer Strahlung ausgesetzte Bereiche der Zusammensetzung für Photoaufzeichnung in wäßrigen oder alkalischwäßrigen Lösungen unlöslich macht,
 - 50 e) zwischen 20 und 50 Gew.-% einer Epoxyharzzusammensetzung, die unter Härtung der Zusammensetzung zur Photoaufzeichnung nach dem Belichten mit aktinischer Strahlung härtbar ist, und
 - f) zwischen 0,01 und 5 Gew.-% eines Härtungskatalysators für das Epoxyharz umfaßt, wobei das polymere Bindemittel genügend löslich in wäßriger oder alkalisch-wäßriger Lösung ist und in ausreichender Menge verwendet wird, damit die Zusammensetzung für Photoaufzeichnung als Ganzes in wäßriger oder alkalisch-wäßriger Lösung entwickelbar ist, und wobei die Komponenten (a) bis (f) so ausgewählt sind, daß sie unter Bildung der homogenen Lösung wechselseitig miteinander mischbar und
- 55



miteinander vermischt sind.

- 5 2. Zusammensetzung zur Photoaufzeichnung nach Anspruch 1, bei der das Vernetzungsmittel so ausgewählt ist, daß es mit dem polymeren Bindemittel in gesteuerter Weise reagiert, wobei die Zusammensetzung für Photoaufzeichnung mild erwärmt werden kann, um die Zusammensetzung für Photoaufzeichnung nicht-klebrig zu machen, während sie noch in wäßriger oder alkalisch-wäßriger Lösung entwickelbar ist, und wobei das Epoxyharz so ausgewählt ist, daß es unter den milden Erwärmungsbedingungen ungenügend gehärtet wird, um die Zusammensetzung für Photoaufzeichnung in wäßriger oder alkalisch-wäßriger Lösung unlöslich zu machen.
- 10 3. Zusammensetzung für Photoaufzeichnung nach Anspruch 1 oder Anspruch 2, in der der Härtungskatalysator ein latenter Katalysator mit blockierenden Resten ist, wobei der Katalysator oberhalb einer Schwellentemperatur entblockiert wird, worauf die Härtung des Epoxyharzes oberhalb dieser Schwellentemperatur gefördert wird.
- 15 4. Zusammensetzung für Photoaufzeichnung nach einem der vorausgehenden Ansprüche, in der das Bindemittel wenigstens teilweise aus Acrylmonomeren mit freien Carbonsäuregruppen gebildet wird, wobei das Bindemittel eine Säurezahl von wenigstens 100 hat.
- 20 5. Zusammensetzung zur Photoaufzeichnung nach einem der vorausgehenden Ansprüche, in der das Bindemittelmateriale wenigstens teilweise aus einem oder mehreren der Materialien Polyvinylalkohol, carboxylierter Polyvinylalkohol, Cellulose, Hydroxyethylcellulose, Styrol-Maleinsäureanhydrid-Copolymer und Novolakharze gebildet ist.
- 25 6. Zusammensetzung für Photoaufzeichnung nach einem der vorausgehenden Ansprüche, in der die homogene Lösung mit einem dispergierbaren organischen oder anorganischen Füllstoff in einer Menge bis zu 30 Gewichtsteilen je 100 Gewichtsteile der Komponenten (a) bis (f) vereinigt ist.
- 30 7. Zusammensetzung für Photoaufzeichnung nach einem der vorausgehenden Ansprüche, in der die Epoxyharzzusammensetzung bei Raumtemperatur flüssig ist.
- 35 8. Zusammensetzung für Photoaufzeichnung nach einem der vorausgehenden Ansprüche mit nicht mehr als 20 Gewichtsteilen organischer Lösungsmittel je 100 Gewichtsteile der homogenen Lösung der Komponenten (a) bis (f).
- 40 9. Zusammensetzung für Photoaufzeichnung nach Anspruch 8 mit nicht mehr als 2 Gewichtsteilen organischer Lösungsmittel je 100 Gewichtsteile der homogenen Lösung der Komponenten (a) bis (f).
- 45 10. Zusammensetzung für Photoaufzeichnung nach Anspruch 9, die frei von organischen Lösungsmitteln ist.
- 50 11. Zweiteilige Lösung mit Komponenten (a) bis (f) in den in Anspruch 1 definierten Mengen, deren zwei Teile homogen unter Bildung einer Zusammensetzung gemäß einem der vorausgehenden Ansprüche mischbar sind, wobei einer der Teile das Bindemittel (a) enthält und der andere Teil die Epoxyharzzusammensetzung (e) enthält.
- 55 12. Mit einer Schicht einer Zusammensetzung für Photoaufzeichnung nach einem der Ansprüche 1 bis 10 überzogenes Substrat.
13. Überzogenes Substrat nach Anspruch 12, bei dem das Substrat eine Platte für eine gedruckte Schaltung ist, wobei die Schicht der Zusammensetzung für Photoaufzeichnung verarbeitbar ist, um eine Lötmaske zu liefern.
14. Überzogenes Substrat nach Anspruch 12, bei dem das Substrat ein flexibler Rückseitenbogen ist, wobei dieser Rückseitenbogen und die Zusammensetzungsschicht für Photoaufzeichnung durch Vernetzung des Bindemittels teilweise härtbar sind, um einen Trockenfilm zu bilden, der in wäßriger oder alkalisch-wäßriger Lösung entwickelbar ist.
15. Verfahren zur Herstellung eines harten, permanenten, mit Aufzeichnung versehenen Filmes auf einem festen Substrat, bei dem man:
 - (1) eine Zusammensetzung zur Photoaufzeichnung nach einem der Ansprüche 1 bis 10 vorsieht,



- (2) einen Film dieser Zusammensetzung für Photoaufzeichnung auf einer Oberfläche des Substrates als Überzug aufbringt,
(3) diesen Film der Zusammensetzung für Photoaufzeichnung so lange und auf solche Temperatur erwärmt, um das Bindemittel ausreichend zu vernetzen, um den Film nicht-klebrig, aber noch löslich in wäßriger oder alkalisch-wäßriger Lösung zu machen,
(4) den Film aufzeichnungsweise aktinischer Strahlung aussetzt, um die Acrylschubstanz zu polymerisieren und belichtete Bereiche des Filmes in wäßriger oder alkalisch-wäßriger Lösung unlöslich zu machen,
(5) den Film in wäßriger oder alkalisch-wäßriger Lösung entwickelt, um nicht belichtete Bereiche des Filmes zu entfernen, und
(6) das Epoxyharz in der Zusammensetzung für Photoaufzeichnung so lange und bei solcher Temperatur härtet, daß der Film hart und permanent gemacht wird.
16. Verfahren nach Anspruch 15, das die Stufe einer UV-Härtung des belichteten entwickelten Filmes einschließt.
17. Verfahren nach Anspruch 15 zur Bildung eines harten, permanenten, mit Aufzeichnung versehenen Filmes jeweils auf einer ersten und einer zweiten Seite eines festen Substrates, bei dem man die Zusammensetzung für Photoaufzeichnung nach der Stufe (1) vorsieht, die erste Seite nach den Stufen (2) und (3) vorbereitet, die zweite nach den Stufen (2) und (3) vorbereitet, jede der Seiten nach der Stufe (4) belichtet, die Seiten nach der Stufe (5) entwickelt und dann das Epoxyharz in den Filmen der Zusammensetzung für Photoaufzeichnung nach der Stufe (6) härtet.
18. Verfahren zur Bildung eines harten, permanenten, mit Aufzeichnung versehenen Filmes auf einem festen Substrat, bei dem man
(1) eine Zusammensetzung für Photoaufzeichnung nach einem der Ansprüche 1 bis 10 vorsieht,
(2) diese Zusammensetzung für Photoaufzeichnung als einen Film auf einem Rückseitenbogen aufbringt,
(3) diesen Film der Zusammensetzung für Photoaufzeichnung so lange und auf solche Temperatur erwärmt, daß das Bindemittel genügend vernetzt wird, um den Film nicht-klebrig, aber noch löslich in wäßriger oder alkalisch-wäßriger Lösung zu machen,
(4) den nicht-klebrigen Film von dem Rückseitenbogen auf ein festes Substrat überträgt,
(5) den übertragenen Film aufzeichnungsweise aktinischer Strahlung derart aussetzt, daß die Acrylschubstanz polymerisiert und belichtete Bereiche des Filmes unlöslich in wäßriger oder alkalisch-wäßriger Lösung gemacht werden,
(6) den Film in wäßriger oder alkalisch-wäßriger Lösung entwickelt, um nicht belichtete Bereiche der Schicht zu entfernen, und
(7) das Epoxyharz so lange und bei solcher Temperatur härtet, daß der Film hart und permanent gemacht wird.
19. Verfahren zur Herstellung eines Trockenfilmes, bei dem man
(1) eine Zusammensetzung für Photoaufzeichnung nach einem der Ansprüche 1 bis 10 vorsieht,
(2) diese Zusammensetzung für Photoaufzeichnung als einen Film auf einen Rückseitenbogen aufbringt und
(3) diesen Film der Zusammensetzung für Photoaufzeichnung so lange und auf solche Temperatur erwärmt, daß das Bindemittel genügend vernetzt wird, um den Film nicht-klebrig, aber noch löslich in wäßriger oder alkalisch-wäßriger Lösung zu machen.
20. Verfahren zur Bildung eines harten, permanenten, mit Aufzeichnung versehenen Filmes jeweils auf einer ersten Seite und einer zweiten Seite eines festen Substrates, bei dem man
(1) eine Zusammensetzung für Photoaufzeichnung nach einem der Ansprüche 1 bis 10 vorsieht,
(2) einen Film dieser Zusammensetzung für Photoaufzeichnung auf der ersten Seite als Überzug aufbringt,
(3) diesen Film aufzeichnungsweise aktinischer Strahlung aussetzt, um so die Acrylschubstanz zu polymerisieren und belichtete Bereiche des Filmes in wäßriger oder alkalisch-wäßriger Lösung unlöslich zu machen,
(4) den Film in wäßriger oder alkalisch-wäßriger Lösung entwickelt, um nicht belichtete Bereiche des Filmes zu entfernen,



(5) den Film der Zusammensetzung für Photoaufzeichnung so lange und auf solche Temperatur erwärmt, um das polymere Bindemittel zu vernetzen,
(6) die Stufen (2) bis (4) auf der zweiten Seite wiederholt und
(7) die Filme auf der ersten Seite und auf der zweiten Seite erwärmt, um das polymere Bindemittel des Filmes auf der zweiten Seite zu vernetzen und das Epoxyharz der Filme auf der ersten und zweiten Seite zu härten.

Revendications

1. Composition photosensible de production d'images comprenant une solution homogène de
 - (a) entre 10 et 40% en poids d'un liant polymère filmogène coulable qui est soluble en solution aqueuse ou aqueuse alcaline,
 - (b) entre 5 et 25% en poids d'un agent réticulant dudit liant polymère, choisi parmi les produits de condensation mélamine-formaldéhyde, les résines urée-formaldéhyde et les résols phénoliques,
 - (c) entre 15 et 35% en poids d'une substance acrylique polymérisable,
 - (d) entre 0,01 et 15% en poids d'un système chimique initiateur générateur de radicaux libres qui, en présence d'une radiation actinique, amorce la polymérisation de ladite substance acrylique pour former une structure chimique tridimensionnelle qui rend insolubles dans les solutions aqueuses ou aqueuses alcalines les portions exposées à la radiation actinique de ladite composition photosensible de production d'images,
 - (e) entre 20 et 50% en poids d'une composition de résine époxy qui est vulcanisable pour durcir ladite composition photosensible de production d'images après l'exposition à la radiation actinique et
 - (f) entre 0,01 et 5% en poids d'un catalyseur de vulcanisation de ladite résine époxy, ledit liant polymère étant suffisamment soluble en solution aqueuse ou aqueuse alcaline et utilisé à un degré suffisant pour que ladite composition photosensible de production d'images dans son ensemble soit développable en solution aqueuse ou aqueuse alcaline, lesdits composants (a)-(f) étant choisis pour être mutuellement miscibles et mélangés ensemble pour former ladite solution homogène.
2. Composition photosensible de production d'images selon la revendication 1, dans laquelle ledit agent réticulant est choisi pour réagir avec ledit liant polymère de manière contrôlée, de sorte que ladite composition photosensible de production d'images puisse être chauffée doucement pour rendre ladite composition photosensible de production d'images non collante, mais développable en solution aqueuse ou aqueuse alcaline, ladite résine époxy étant choisie pour être insuffisamment vulcanisée dans lesdites conditions de chauffage doux pour rendre insoluble en solution aqueuse ou aqueuse alcaline ladite composition photosensible de production d'images.
3. Composition photosensible de production d'images selon la revendication 1 ou 2, dans laquelle ledit catalyseur de vulcanisation est un catalyseur latent ayant des restes de blocage, ledit catalyseur devenant débloqué au-dessus d'une température de seuil, après quoi la vulcanisation de ladite résine époxy est activée au-dessus de ladite température de seuil.
4. Composition photosensible de production d'images selon l'une quelconque des revendications précédentes, dans laquelle ledit liant est formé au moins en partie de monomères acryliques ayant des groupes acides carboxyliques libres, ledit liant ayant un indice d'acide d'au moins 100.
5. Composition photosensible de production d'images selon l'une quelconque des revendications précédentes, dans laquelle ledit liant est formé au moins en partie d'un ou plusieurs ingrédients choisis parmi l'alcool polyvinylique, l'alcool polyvinylique carboxylé, la cellulose, l'hydroxyéthylcellulose, les copolymères styrène-anhydride maléique et les résines Novolac.
6. Composition photosensible de production d'images selon l'une quelconque des revendications précédentes, dans laquelle ladite solution homogène est combinée avec une charge organique ou inorganique dispersable à une teneur allant jusqu'à 35 parties en poids pour 100 parties en poids desdits composants (a)-(f).
7. Composition photosensible de production d'images selon l'une quelconque des revendications précédentes, dans laquelle ladite composition de résine époxy est liquide à la température ambiante.



8. Composition photosensible de production d'images selon l'une quelconque des revendications précédentes, n'ayant pas plus de 20 parties en poids de solvants organiques par 100 parties en poids de ladite solution homogène des composants (a)-(f).
- 5 9. Composition photosensible de production d'images selon la revendication 8, n'ayant pas plus de 2 parties en poids de solvants organiques par 100 parties en poids de ladite solution homogène des composants (a)-(f).
- 10 10. Composition photosensible de production d'images selon la revendication 9, qui est exempte de solvants organiques.
11. Solution en deux parties comprenant les composants (a)-(f) dans les quantités définies à la revendication 1, dont les deux parties sont miscibles de manière homogène pour former une composition selon l'une quelconque des revendications précédentes, l'une desdites parties contenant ledit liant (a) et l'autre partie contenant ladite composition de résine époxy (e).
- 15 12. Support revêtu d'une couche d'une composition photosensible de production d'images selon l'une quelconque des revendications 1 à 10.
- 20 13. Support revêtu selon la revendication 12, dans lequel ledit support est une plaquette de circuit imprimé, ladite couche de composition photosensible de production d'images étant apte au traitement pour donner un masque de soudure.
- 25 14. Support revêtu selon la revendication 12, dans lequel ledit support est une feuille dorsale flexible, ladite feuille dorsale et ladite couche de composition photosensible de production d'images étant partiellement vulcanisables par réticulation dudit liant pour former un film sec qui est développable en solution aqueuse ou aqueuse alcaline.
- 30 15. Procédé de formation d'un film permanent dur portant un motif sur un support solide comprenant les étapes suivantes:
(1) on produit une composition photosensible de production d'images selon l'une quelconque revendications 1 à 10,
(2) on applique un film de ladite composition photosensible de production d'images sur une face dudit support,
(3) on chauffe ledit film de la composition photosensible de production d'images pendant une durée et à une température aptes à réticuler suffisamment ledit liant pour rendre ledit film non collant, mais encore soluble en solution aqueuse ou aqueuse alcaline,
35 (4) on expose ledit film à une radiation actinique suivant un motif pour polymériser ladite substance acrylique et rendre les portions exposées dudit film insolubles en solution aqueuse ou aqueuse alcaline,
40 (5) on développe ledit film en solution aqueuse ou aqueuse alcaline pour séparer les portions non exposées dudit film et
(6) on vulcanise ladite résine époxy dans ladite composition photosensible de production d'images pendant une durée et à une température telles que ledit film soit durci et rendu permanent.
- 45 16. Procédé selon la revendication 15, qui comprend l'étape de vulcanisation par les UV dudit film exposé, développé.
- 50 17. Procédé selon la revendication 15, de formation d'un film dessiné permanent dur sur chacune d'une première face et d'une seconde face d'un support solide qui consiste à produire ladite composition photosensible de production d'images selon l'étape (1), à préparer ladite première face selon les étapes (2) et (3), à préparer ladite seconde face selon les étapes (2) et (3), à exposer chacune desdites faces selon l'étape (4), à développer lesdites faces selon l'étape (5) et ensuite à vulcaniser ladite résine époxy dans lesdits films de la composition photosensible de production d'images selon l'étape (6).
- 55 18. Procédé de formation d'un film permanent dur portant un motif sur un support solide comprenant les étapes suivantes
(1) on produit une composition photosensible de production d'images selon l'une quelconque des revendications 1 à 10,



- (2) on applique ladite composition photosensible de production d'images en un film sur une feuille dorsale,
- (3) on chauffe ledit film de la composition photosensible de production d'images pendant une durée et à une température aptes à réticuler suffisamment ledit liant pour rendre ledit film non collant, mais encore soluble en solution aqueuse ou aqueuse alcaline,
- (4) on transfère ledit film non collant de ladite feuille dorsale sur un support solide,
- (5) on expose ledit film transféré à une radiation actinique suivant un motif pour polymériser ladite substance acrylique et rendre les portions exposées dudit film insolubles en solution aqueuse ou aqueuse alcaline,
- (6) on développe ledit film en solution aqueuse ou aqueuse alcaline pour séparer les portions non exposées dudit film et
- (7) on vulcanise ladite résine époxy dans ladite composition photosensible de production d'images pendant une durée et à une température telles que ledit film soit durci et rendu permanent.
19. Procédé de préparation d'un film sec, comprenant les étapes suivantes
- (1) on produit une composition photosensible de production d'images selon l'une quelconque revendications 1 à 10,
- (2) on applique un film de ladite composition photosensible de production d'images sur une feuille dorsale,
- (3) on chauffe ledit film de la composition photosensible de production d'images pendant une durée et à une température aptes à réticuler suffisamment ledit liant pour rendre ledit film non collant, mais encore soluble en solution aqueuse ou aqueuse alcaline.
20. Procédé de formation d'un film permanent dur portant un motif sur chacune d'une première face et d'une seconde face d'un support solide, le procédé comprenant les étapes suivantes
- (1) on produit une composition photosensible de production d'images selon l'une quelconque revendications 1 à 10,
- (2) on applique un film de ladite composition photosensible de production d'images sur ladite première face,
- (3) on expose ledit film à une radiation actinique suivant un motif pour polymériser ladite substance acrylique et rendre les portions exposées dudit film insolubles en solution aqueuse ou aqueuse alcaline,
- (4) on développe ledit film en solution aqueuse ou aqueuse alcaline pour séparer les portions non exposées dudit film et
- (5) on chauffe ledit film de la composition photosensible de production d'images pendant une durée et à une température propres à réticuler ledit liant polymère,
- (6) on répète les étapes (2) à (4) sur ladite seconde face et
- (7) on chauffe lesdits films sur ladite première face et ladite seconde face pour réticuler ledit liant polymère dudit film sur ladite seconde face et pour vulcaniser ladite résine époxy desdits films sur lesdites première et seconde faces.