

Description

This invention concerns polymerizable compositions which have their primary utility in the area of coatings and sealants. The invention has particular utility in the area of conformal coatings for printed circuit boards and electronic components and will be described in connection with such utility, although other uses are contemplated.

Printed circuit boards and electronic components may be coated with a protective film to avoid or at least minimize degradation in electrical performance due to contamination. The most damaging, and usually the most prevalent contaminant generally is considered to be moisture or humidity. Excessive moisture or humidity will drastically lower insulation resistance between conductors, accelerate high-voltage breakdown and dendritic growth, and corrode conductors. Other contaminants which may damage printed circuit boards include various chemicals which may be residues of the manufacturing process such as fluxes, organic solvents, release agents, metal particles and marking inks, and contaminants which inadvertently may be deposited by human handling such as body greases, fingerprints, cosmetics and food stains. Ambient operating conditions may also contribute a variety of contaminants such as salt spray, dirt and dust, oil, fuel, acid, corrosive vapor and fungus. Although the list of possible contaminants is almost endless, in all but the most severe cases, their destructive action effectively can be eliminated by provision of a good conformal coating.

In addition to providing protection from contaminants, conformal coatings also provide a certain degree of protection to mechanical shock, vibration and tampering.

Various conformal coating systems are known in the art and are available commercially. Each has its advantages and disadvantages. One such prior art conformal coating system is based on acrylics. Acrylics are excellent coating systems from a production standpoint because they readily may be applied by spraying or brushing. Acrylic coatings have desirable electrical and physical properties and are fungus resistant. Additional advantages of acrylic coatings include long life, low or no exotherm during cure, and little or no shrinkage during cure. However, acrylic coatings typically are formed by solvent evaporation and reach optimum physical characteristics during cure typically in a matter of minutes. Conventional acrylic coatings are soluble in chlorinated solvents such as trichloroethane or methylene chloride.

Another prior art conformal coating system is based on polyurethanes. Polyurethanes are available as either single or two-component systems. Polyurethane coatings offer excellent humidity and chemical resistance and good dielectric properties. Single-component urethanes are relatively easy to apply and exhibit relatively long working pot life. However, single-component polyurethanes typically require a curing time of three to ten days at room temperature to reach optimum physical characteristics. Two-component polyurethanes typically achieve optimum cure at elevated temperatures within one to three hours, but exhibit relatively short working pot life. Also, surface preparation of substrate boards prior to application of polyurethane based coatings is important, since even minute quantities of moisture on a substrate board could produce blistering under humid conditions. Blisters, in turn, may lead to electrical failures and mandate costly rework. Polyurethane coatings are insoluble in most common solvents, which is a drawback to rework. Thus, replacement of a component on a polyurethane coated board requires a corrosive stripper to remove effectively all traces of the polyurethane film. However, extreme caution must be exercised when such a stripper is used, because the stripper also may corrode metallic surfaces on the board.

Epoxy resin systems also have been employed by the prior art for conformal coating printed circuit boards. Epoxy resins are available as two component systems only. Epoxy resin coatings provide good humidity resistance and high abrasive and chemical resistance. However, epoxy resins are virtually impossible to remove chemically for rework because any stripper that will attack the coating also will attack the epoxy coating of potted electronic components and the epoxy-glass of the printed circuit board as well. Thus, the only effective way to repair an epoxy resin coated board is to burn through the epoxy coating with a hot knife or soldering iron. However, burning introduces a cosmetic defect which is unacceptable to many consumers. Moreover, epoxy resins shrink somewhat during cure. Accordingly, a buffer material must be placed around fragile electronic components to prevent fracturing from shrinkage. Curing of epoxy systems can be accomplished in one to three hours at elevated temperature, or four to seven days at room temperature. Epoxy resins exhibit a relatively short working pot life which is an additional disadvantage.

Silicone resins also have been employed by the prior art for conformal coating circuit boards. Silicone resin coatings provide high humidity and corrosion resistance along with high temperature resistance which makes silicone resins preferred for coating printed circuit assemblies that contain high heat-dissipating components such as power resistors. However, silicone resins are relatively thick making them somewhat difficult to apply. Moreover, silicone resins require a relatively long cure, and repairability is difficult since silicone resins once cured are essentially insoluble, and cannot be vaporized with the heat of a soldering iron. Accordingly, the only effective way to repair a silicone resin coated circuit board is to mechanically remove the coating.

The prior art also has employed polyimides for conformal coating circuit boards. Polyimide coatings provide high-temperature, moisture and chemical resistance over extended periods of time. However, polyimide coatings require high temperature cure (one to three hours at 200 to 250°C) which could damage heat sensitive electronic components, and this requirement severely limits the use of polyimide coating

systems on most printed circuit board assemblies. Also, since polyimides are high-temperature, moisture and chemical resistant, the only effective way to repair a polyimide coated board is to mechanically remove the coating.

Diallyl phthalate varnishes also have been proposed by the prior art for conformal coating circuit boards and provide excellent high temperature and chemical resistance. However, diallyl phthalate varnishes require high temperature cure (approximately 150°C) which severely limits their use. And, diallyl phthalate coatings also typically must be mechanically removed to permit repair.

The preceding discussion of background in the art of conformal coating circuit boards is taken largely from *Printed Circuits Handbook*, Clyde F. Coombs, Jr., Editor, McGraw Hill Book Company, Second Edition (1979).

As thus is apparent from the above discussion, none of the currently available conformal coating systems are completely satisfactory since all prior art conformal coating systems at best are a tradeoff of preferred application characteristics (i.e., processing speed, ease of application, pot life and cure conditions), preferred physical characteristics, (i.e., electrical properties, temperature, chemical and moisture resistance), and repairability.

Compositions which cure under the influence of ultraviolet light are known and reference can be made to GB—A 2030584 and EP—A1—0000407 as disclosures of such compositions. GB—A 2030584 discloses a composition useful for application to printed circuit boards which comprises a photopolymerisable urethane resin (e.g. urethane-acrylate resin) a chain modifier and a photoinitiator. EP—A1—0000407 discloses a radiation curable coating composition based on a polyester resin esterified with acrylic acid and/or methacrylic acid, a vinyl compound and a photoinitiator.

It is thus a primary object of the present invention to provide an improved conformal coating system, i.e. method and materials which overcomes the aforesaid and other disadvantages of the prior art.

Other objects of the present invention are to provide an improved composition for conformal coating printed circuit board assemblies and the like which compositions demonstrate extended pot life and ease of application, rapid dry-to-touch cure, good electrical properties, superior adhesion and abrasion resistance, excellent high temperature, chemical and moisture resistance, and ease of repairability.

Generally, the foregoing and other objects of the invention are achieved by the provision of an ultraviolet (hereinafter "uv") curable polymerizable coating system having one or more secondary curing mechanisms built in. More specifically, in accordance with the invention the polymerizable system is a two component system comprising (1) a first component comprising at least one polyester-urethane-acrylate or methacrylate, a mono or polyfunctional reactive acrylate or methacrylate reactive diluent and a polymerization initiator of the photoinitiator type, and (2) a second part comprising a polyisocyanate adduct, at least one component of the first part containing unreacted hydroxyl groups, the composition having an equivalent weight excess of isocyanate groups in the second part to the hydroxyl groups in the first part of at least 2:1.

In accordance with another aspect of the invention, there is provided a method of forming a uv curing polymerizable conformal coating on a substrate wherein the substrate has one or more shadow areas, comprising the steps in sequence of:

(1) providing a two-part coating composition, the first part of which comprises at least one polyester-urethane-acrylate or polyester-urethane-methacrylate compound, a mono or polyfunctional acrylate or methacrylate reactive diluent and a polymerization initiator of the photo-initiator part, and a second part which comprises a polyisocyanate containing adduct, at least one component of the first part containing unreacted hydroxyl groups, the composition having an equivalent weight excess of isocyanate groups in the second part to the hydroxyl groups in the first part of at least 2:1;

(2) blending the first and second parts to form a coating composition;

(3) coating the substrate at least in part with the polymerizable composition;

(4) exposing the coated substrate to uv light of wave length and intensity to effect uv cure of exposed areas of the coating; and

(5) storing the coated substrate under conditions of temperature and humidity which promote curing of unexposed (shadow) areas of the coating through a built-in secondary moisture cure mechanism.

In yet other aspects of the invention, there are provided circuit boards and components coated with the polymerizable coating compositions as above described.

The coating system is uv curable, and also possesses at least one additional cure mechanism. A particular feature and advantage of the instant invention is that the uv radiation cure produces extremely rapid dry-to-the-touch cure of all exposed areas of the coating thereby permitting substantially immediate handling of the coated products and maintaining the shape of the coating which might otherwise sag and creep, while secondary cure mechanism(s) provide substantially complete cure of unexposed (shadow) areas of the coating under conditions of ambient temperature and humidity.

For a fuller understanding of the nature and objects of the present invention, reference should be made to the following detailed description of the invention taken in connection with the accompanying examples.

The terms "liquid", and "solid" or "dry-to-the-touch" are used herein with reference to physical properties of the materials, are to be understood as to be referring to such properties as they exist under conditions as may be specified. For example, the term "liquid" refers to a physical state wherein a material is readily flowable while the terms "solid" and "dry-to-the-touch" are to be understood as referring

respectively to physical states wherein a material is resistant to change in shape and is without free surface moisture or surface tackiness.

Detailed description of the invention

5 Part A (the monomer)

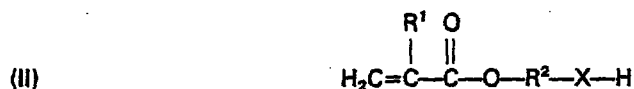
The urethane-acrylates or methacrylates employed in Part A of the two component system of the instant invention preferably comprise polyester-urethane-acrylates formed by reacting a polyester diol with a diisocyanate, and reacting the resulting product with a polymerizable acrylic or methacrylate acid ester. The preferred polyester diol is manufactured by the Inolex Company under the trade name Lexorez 10 1400—120. This polyester diol is formed by reaction of neopentyl glycol and 1,6-hexanediol with adipic acid. Other polyester diols useful are formed by the reaction of neopentyl glycol and a diol of more than 3 carbon atoms, e.g., 1,4-butanediol with adipic acid. Other polyesters found useful include adipates of 1,4 butane diol and 1,6 hexane diol as well as polycaprolactone diols of similar molecular weight. The preferred diisocyanate is toluene diisocyanate (TDI) although other relatively low molecular weight diisocyanates of 15 the general formula:



wherein R is a C_{2-20} alkylene, alkenylene or cycloalkylene radical or a C_{6-40} arylene, alkarylene or aralkylene are useful. 20

The reaction ratio of the equivalent weights of the polyester diol to the diisocyanate should generally be in the range of 1.0 of polyester diol to 1.7 to 2.2 of diisocyanate. The preferred reaction ratio is 1.0 equivalents of the polyester diol for every 1.9 equivalents of diisocyanate. This preferred reaction ratio is particularly important to the properties of the final composition. The 1:1.9 ratio yields a composition with a 25 chemical structure having a high degree of flexibility and stability. The copolymer formed is generally of a random copolymer structure. This copolymer product is then reacted with an hydroxyl-containing acrylate or methacrylate ester monomer, producing acrylate end-capping. The useful range of equivalents of the ester monomers is 0.9 to 3.0, the preferred being in the range of 1.6 to 2.0, and the most preferred being 1.8 equivalents.

The polymerizable acrylate and methacrylate ester monomers used to cap the polyester diisocyanate reaction product may be mono- or difunctional. Mono-functional monomers are preferred. Those monofunctional monomers found most effective are selected from the group consisting of hydroxyalkyl acrylates and methacrylates, amino alkyl acrylates and methacrylates. The most preferred polymerizable ester monomers are hydroxyethyl methacrylate and hydroxypropyl methacrylate. Additional 35 monofunctional polymerizable ester monomers deemed useful are represented by the following formula:



wherein X is —O— or 40



R^3 is hydrogen or lower alkyl of 1 to 7 carbon atoms;

R^1 is selected from the group consisting of hydrogen, chlorine and methyl and ethyl radicals; and R^2 is a divalent organic radical selected from the group consisting of lower alkylene of 1—8 carbon atoms, 50 phenylene and naphthylene.

Suitable hydroxy- or amine-containing materials are exemplified by, but not limited to, such materials as hydroxyethyl acrylate, hydroxyethyl methacrylate, aminoethyl methacrylate, 3-hydroxypropyl methacrylate, aminopropyl methacrylate, hydroxyhexyl acrylate, t-butylaminoethyl methacrylate, hydroxy-octyl methacrylate, and the monoacrylate or monomethacrylate esters of bisphenol-A, the fully 55 hydrogenated derivative of bisphenol-A, cyclohexyl diol, polyethyleneglycol methacrylate, and the like.

The end-capping reaction may be accomplished in the presence or absence of diluents. Diluents which include the hydrocarbons such as aliphatic, cycloaliphatic and aromatic hydrocarbons, for example, benzene, toluene, cyclohexane, hexane, heptane, and the like, may be employed, but other diluents, such as methyl isobutyl ketone and diamyl ketone, can also be utilized. Alternatively, the diluent may comprise a 60 mono or polyfunctional acrylate or methacrylate reactive diluent.

Ultraviolet ("uv") activated polymerization initiators are incorporated into Part A of the coating system. Many uv activated polymerization initiators are known in the art and may be incorporated directly into the urethane-acrylate monomer or methacrylate. For example, the uv activated initiators may be selected from metal carbonyls of the formula $M_x(CO)_y$, wherein M is a metal atom, x is 1 or 2, and y is an integer 65 determined by the total valence of the metal atoms, generally 4 to 10. The preferred uv activated initiators

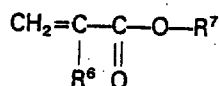
are selected from (a) C_{1-16} straight or branched chain alkyl diones; and (b) carbonyl compounds of the general formula $R^4(CO)R^5$ wherein R^4 is a C_{1-10} alkyl, aryl, aralkyl or alkaryl group, and R^5 is R^4 or hydrogen. In addition, R^4 or R^5 can contain any substituents which do not adversely affect the compound in serving its function. For example, R or R_1 can be alpha-substituted with an alkyl, aryl, alkaryl alkoxy or aryloxy radical, or with an amino or a mono- or dialkylamino derivative thereof, each of the above substituents containing up to about six carbon atoms. In addition, R^4 and R^5 taken together with carbonyl group form an aromatic or heterocyclic ketone containing up to about 16 carbon atoms.

The polymerization initiators are usually employed in amounts of about 1% to about 10% by weight of the urethane-acrylate or -methacrylate containing part (hereafter Part A) of the coating system.

As mentioned supra, also included in the first component (Part A) of the coating system is a mono or polyfunctional acrylate or methacrylate reactive diluent.

The mono or polyfunctional acrylate or methacrylate reactive diluents which may be used in the reactive diluent in the coating system of the present invention comprise allylic-bond containing acrylates or methacrylates of the formula:

(III)



in which R^6 is a radical selected from the group consisting of hydrogen and lower alkyl of 1 to 4 carbon atoms, and R^7 is an organic radical containing at least one allylic bond and does not contain any group which may adversely affect the coating system for purposes of disclosed herein. Preferably R^7 will consist of an allylic-bond containing aliphatic or substituted aliphatic carbon ring structure of which dicyclopentenyl is presently preferred. Other allylic-bond containing carbon ring structures such as dicyclopentenyl which is given as exemplary may also be advantageously employed.

This reactive diluent, which is usually employed in amounts of 30% to 70% by weight of Part A of the coating system may be added during the end-capping reaction step as previously described, or the proportions mentioned above made up at this time in the preparation.

It is useful, but not required to incorporate an adhesion promoter into Part A of the coating system. The adhesion promoter may be chosen from any of those commonly known to the person reasonably skilled in the art. Two types of promoters are preferred. The first type consists of mono- and dicarboxylic acids which are capable of copolymerizing with the acrylate or methacrylate ester monomer. The preferred species of these classes are methacrylic and acrylic acid. Such acids are used in proportion of 1—20% by weight of part one of the coating system, preferably in proportion of 1—15%. The second preferred type of adhesion promoter is of the well-known silane type, present in the composition in proportions of 1—10% by weight of part one of the coating system.

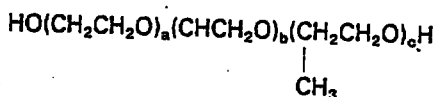
It is optional, but recommended, that chelators, cross-linking agents and inhibitors also be added to Part A of the coating system for optimum performance. Chelators and inhibitors are effective in amounts of about 0.1 to about 1% by weight of Part A of the coating system. Ethylenediamine tetra-acetic acid and its sodium salt (Na_4 EDTA), 1,1-ethylenebis-nitril methylidene dipyridine and the class of beta-diketones are generally the most effective and are preferred. Cross-linking agents, optionally present in amounts up to about 10% by weight of Part A of the coating system, include such compounds as copolymerizable dimethacrylates.

The inhibitor concentration left over in the monomers from manufacture is often high enough for good stability. However, to insure maximum shelf life, the proportions mentioned above (about 0.1 to about 1% by weight of Part A of the coating system) are recommended. Of those inhibitors which have been found of adequate utility is the group consisting of hydroquinones, benzoquinones, naphthoquinones, phenanthraquinones, anthraquinones, and substituted compounds of any of the foregoing. Additionally, various phenols can be employed as inhibitors, the preferred one being 1,6-di-tert-butyl-4-methyl phenol.

The amount of thickness, viscosity, or thixotropy desired can be varied in accordance with the particular application required. Thickeners, plasticizers, diluents, and various other agents common to the art can be employed in any reasonable manner to produce the desired characteristics.

It also is optional, but recommended, that surfactants be included in Part A of the adhesive composition for optimum performance. The preferred surfactants are non-ionic surfactants having pendant free hydroxyl groups. One such class of useful non-ionic surfactants is the ethoxylated alkyl (linear or branch) phenols. These typically have the formula

(IV)



wherein a, b and c are integers such that the molecular weight of the compound is in the range of about 500 to about 30,000, and units plus c comprise about 10 to 80 percent by weight of the final molecular weight. Such compounds are sold by BASF Wyandotte, Wyandotte, Michigan under the trademark "Pluronic."

Another example of this class on non-ionic surfactants are the polyoxyalkylene silicones sold by Union Carbide, New York, New York, under the trade name L-5320.

The above-mentioned surfactants all contain pendent free hydroxyl groups, which groups as will be explained in detail hereafter, are available to react with free isocyanate contained in Part B of the coating system. It will be appreciated that the above-mentioned surfactants are merely representative of useful surfactants available and are not intended to comprise an inclusive list. Selection of suitable surfactants is a matter of simple experimentation. Obviously the surfactant must be soluble in the monomer composition. This obviously can be quite readily determined for any concentration contemplated.

Surfactant concentration will depend in any given case upon the particular surfactant and monomer composition being used. Optimization will be a matter of routine experimentation within the skill of the art. Ordinarily, however, minimum concentration of about 0.25 percent surfactant by weight of Part A of the coating composition will be needed to achieve an acceptable degree of emulsifiability, and a concentration of at least about 0.5 percent by weight usually will be preferred. The maximum surfactant concentration will usually be about five percent by weight since above this level the surfactant may begin to interfere with the properties of the coating composition by adversely affecting, for example, its cure rate, stability or the cured products. As a practical matter, an upper concentration limit of about five percent, is usually satisfactory. For most surfactants or combinations of surfactants, the optimum concentration will probably fall in the range of about 1.0 to 2.5 percent by weight of the total coating composition.

20 The activator Part B (the activator)

The activator employed as Part B of the coating system of the present invention comprises a polyisocyanate adduct of aromatic or aliphatic isocyanates, or mixture thereof. The polyisocyanates which may be used as Part B may be generally represented by the formula $(O=C=N)_nQ$, in which n is an integer from 2 to about 20, preferably 2 to about 5, and Q is an organic radical having a molecular weight up to about 5000 and a bonding capacity equal to n. A preferred class of polyisocyanates are those of the formula:



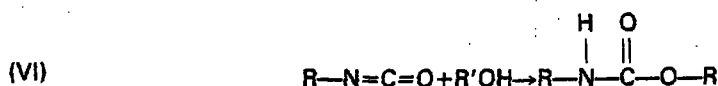
wherein n is 2 and R^6 is a C_{2-20} alkylene; alkenylene or cycloalkylene radical or a C_{6-40} arylene, alkarylene, aralkarylene, alkyloxyalkylene or aryloxyarylene radical which may be substituted by 1-4 chlorine atoms or by 1-3 amino or mono- or di- C_{1-3} -alkylamino or C_{1-3} alkoxy groups.

Typical examples of such polyisocyanates are toluene diisocyanate, 4,4'-diphenyl diisocyanate, 4,4'-diphenyl methane diisocyanate, dianisidine diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-diphenyl ether diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, ethylene diisocyanate, cyclohexylene diisocyanate, nonamethylene diisocyanate, octadecamethylene diisocyanate, 2-chloropropane diisocyanate, 2,2'-diethyl-ether diisocyanate, 2-(dimethylamino)pentane diisocyanate, tetrachlorophenylene-1,4-diisocyanate, 3-heptene diisocyanate and transvinylene diisocyanate. The preferred polyisocyanate adduct is manufactured by the Mobay Chemical Corporation under the trade name MONDUR CB-75. This polyisocyanate is an aromatic polyisocyanate dissolved in ethyl acetate having a solid content percent of about 75 percent, NCO content of approximately 12.5 to 13.5 percent, equivalent weight of 323 average and containing a maximum of about 0.7 percent free monomer based on resin solids.

The proportions in which the reactants, Part A and Part B, may be combined can be varied relatively widely; however, it is generally preferred to employ the reactants in proportions such that the polyisocyanate is in substantial chemical equivalent excess, e.g. at least 2:1 and up to 10:1 or more. The preferred range is 5:1 to 7:1, most particularly in excess of 6:1. (As used herein the expression "chemical equivalent amount" refers to the amount needed to furnish one isocyanate group per hydroxy group.)

As will be appreciated the coating system of the present invention is designed primarily as a uv curing product; however, due to the configuration of many circuit boards, there are areas that cannot be cured by a uv light. These areas, the so-called "shadow areas", are located on the board such that some other component, or a surface wire or connector interferes with the direct exposure to the uv source. To overcome this deficiency, the coating system of the present invention provides one or more additional built-in curing mechanisms. For example, in the case of the two-component coating system at least five additional curing mechanisms potentially are available to complete curing of the coating. These mechanisms are as follows:

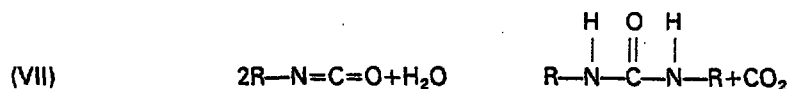
(1) The polyester urethane dimethacrylate of Part A of the system contains excess hydroxyethylmethacrylate (HEMA), the hydroxy functionality of which is available for reaction with the free isocyanates contained in the activator Part B thereby forming urethane linkages, i.e. according to the formula:



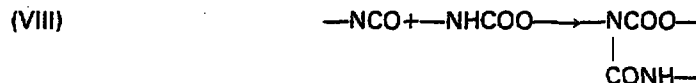
(13)

(2) Pendent free hydroxyl groups contained in the surfactant of Part A are available to react with free isocyanate in the activator Part B forming urethane linkages according to formula (IV), thereby chemically bonding the surface layer to the bulk of the coating.

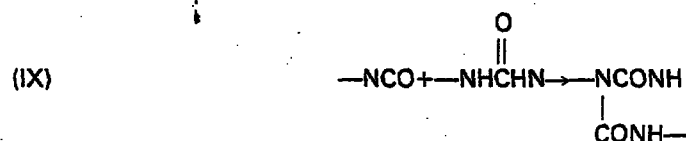
(3) Free isocyanate in the activator Part B can react with water, specifically atmospheric moisture, cross-linking through the formation of di-substituted ureas, i.e. according to the following formula:



(4) Free isocyanate in the activator Part B can react with previously formed urethane groups to form allophanates, thus increasing cross-linking density, i.e. according to the following formula:



(5) Free isocyanate in the activator can react with previously formed urea groups to form biurets, thus increasing cross-link density according to the following formula.



Additionally, all five of the aforesaid curing mechanisms are catalyzed by heat, and since most uv sources also generate intense I.R. waves, an excellent heat source is immediately available to help drive the secondary curing mechanisms. Therefore, in many instances, significant portions of the "shadow areas" will be cured during the uv exposure. Experiments have shown that areas that do not co-cure substantially immediately during uv exposure will dry hard and dry-to-the-touch within 2 to 24 hours under conditions of ambient temperature and average relative humidity.

To facilitate post-cure mechanism even further, a third curing mechanism is available with the two component system. More particularly, by selecting methacrylate monomers in Part A which contain not only a reactive methacrylate group, but a second point of unsaturation—the allyl bond, a significant level of cross-linking may occur when appropriate metal dryers are added to Part B of the system. Useful metal-dryers include salts of metals with a valence of two or greater and unsaturated organic acids. Amongst suitable compounds are mentioned the linoleates, naphthenates and resinates of cobalt, manganese, cerium, lead, chromium, iron nickel, uranium and zinc. The metal dryers are usually employed in concentrations of less than between about 0.01 and five percent by weight of Part B. In cases where the isocyanate related post-cure is hampered by the lack of heat or atmospheric moisture, cross-linking of the allyl bond on the monomer typically will provide a tack-free coating in twenty-four hours.

It is frequently desirable to add low levels, such as up to about 500 parts per million by weight, of a free-radical or uv stabilizer, many of which are known in the art, to prevent spurious polymerization of the composition prior to the time of its intended use. Suitable free-radical stabilizers are hydroquinone, p-benzoquinone, butylate of hydroxytoluene, and butylate of hydroxyanisole.

Example I

The invention will now be illustrated by the following description of a specific preferred embodiment thereof, given by way of example only.

Preparation Part A

A nitrogen-swept, four-necked uv shielded resin kettle equipped with a stainless steel stirrer, nitrogen inlet tube, thermometer, condensor, and entrance port, was heated to approximately 40°C., 165 grams of MOBAY TDI toluene diisocyanate added, and 460 grams of 1,6-hexanediol/neopentyl glycol adipate (Lexorez 1400—120 polyester, Inolex Company, Philadelphia, PA) was slowly added—460 grams over 20 minutes. At the completion of the polyester addition, heating was continued with stirring (40 to 45°C temperature) for one hour, followed by two hours heating with stirring at 100°C. Upon completion of the three hour reaction period, the bath temperature was lowered to 50°C, and 230 grams of hydroxyethyl-methacrylate was added. The reaction mixture was then heated, maintained at 50°C and stirred for two hours at that temperature. Six grams of isopropanol, 0.18 grams of sodium EDTA and 100 grams of Ciba-Geigy Irgacure 651 dimethoxy-2-phenyl acetophenol were added to the reaction mixture, the reaction mixture permitted to cool to room temperature and stirred for one-half hour at room temperature.

To the reaction mixture was then added, with stirring, 1378 grams of Rohm and Haas QM-657

dicyclopentenyl oxyethyl methacrylate, 146 grams of Rohm and Haas acrylic acid, 28 grams of Union Carbide 1—29 silane and 2.5 grams of Union Carbide L-5320 (Poly)oxyalkylene silicone surfactant.

The resulting solution contained approximately 34 percent concentration of polyester-urethane-methacrylate resin (PEUMA).

Part B

Part B of the coating system was prepared by dissolving 1757 grams of polyisocyanate adduct (MONDUR-CB-75) available from Mobay Chemical Corporation, Pittsburgh, PA. (the manufacturer describes this material as comprising an aromatic polyisocyanate adduct dissolved in ethyl acetate having 10 percent solid of about 75 percent solids, NCO content of approximately 12.5—13.5 percent, an average equivalent weight of 323 and containing a maximum of 0.7 percent free diisocyanate monomer based on resin solids) in 3262 grams of 1,1,1-trichloroethane.

Working Example

15 Blend solutions Part A and B prepared as above, and spray the resulting blend onto the top side surface (i.e. component side surface) of a printed circuit board. Cure of the coating was effected by exposing the boards to uv radiation (3650 angstroms, 60,000 microwatts per square centimeter). Those areas of the coating exposed to uv radiation were solid and dry to the touch within 10—45 seconds. Areas in the shadow of components, i.e. not receiving direct uv radiation, however, were observed to be wet to the touch, but found to be fully cured after standing at ambient temperature and humidity conditions for 24 hours. Circuit boards were sliced through shadow areas after 24 hours and the coating was found to be fully cured to the board.

Coated boards were placed on a rack in a stainless steel tank, and 500 grams of water added to the bottom of the tank. The tank was closed, sealed, and heated to a temperature of 115°C. After heating for 40 hours, the tank was allowed to cool, the tank was then opened and the boards removed and examined. No visible blistering or other evidence of coating failure was observed.

Example II

Example I was repeated except 1300 grams of Alcolac SIPOMER DCPM dicyclopentenyl methacrylate was used in Part A of the formulation in place of the dicyclopentenyl oxyethyl methacrylate. Similar results to Example I were obtained.

Example III

35 The procedure of Example I was repeated except 1400 grams of lauryl methacrylate was employed in place of the hydroxyethylmethacrylate of Part A of the formulation. Minor blistering of coating observed following 40 hours of heating in closed tank.

Example IV

40 The purpose of this Example is to show the effect of using a different reactive diluent. The procedure of Example I was repeated except 1600 grams of hydroxyethylmethacrylate was used in Part A of the formulation in place of the dicyclopentenyl oxyethyl methacrylate. Similar results to Example I were obtained. Minor blistering of coating observed following 40 hours of heating in closed tank.

Example V

45 Example I was repeated except 1600 grams of Mobay Chemical Corporation DESMODUR E-21 polyisocyanate (available as one hundred percent solids, NCO content of approximately 16, average equivalent weight of 262) was employed in place of the MONDUR—CB-75. Similar results to Example I were obtained.

50 As will be appreciated the foregoing invention provides novel and improved coating systems for conformal coating printing circuit boards and the like. The coating systems may be applied to a circuit board assembly by any convenient manner, for instance a spraying, brushing, dripping, rolling, dipping, etc. Moreover, the coating systems cure through multiple mechanisms including uv cure which permits fast fixture cure thereby achieving almost immediate dry-to-the-touch curing. However, unlike conventional uv cured products, the coating systems of the present invention do not require full area irradiation to achieve full cure due to their built-in secondary cure mechanisms. Moreover, the cured coatings have excellent adherence to plastics, metal, glass and wood, good abrasion resistance, and are hydrolytically stable and resistant to thermal cycling. The coatings also are repairable, i.e., can be removed by selective solvents such as methylethylketone, and then replaced by brush or spray, and uv cured.

60 The invention has been described particularly with application to conformal coating circuit board assemblies. However, one skilled in the art would appreciate that the coating systems may be applied to other electrical electronic components such as transformers or the like. Moreover, the coating composition is not limited to the use in the electronics field but may be employed in any industrial area where conformal protective coating is desired.



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Claims

1. A two-part coating composition, especially useful for conformal coating, characterised by comprising, in combination:

(1) a first part comprising at least one polyester-urethane-acrylate or polyester-urethane-methacrylate compound, a mono or polyfunctional acrylate or methacrylate reactive diluent and a polymerization initiator or the photo-initiator type; and

(2) a second part comprising a polyisocyanate containing adduct, at least one component of said first part containing unreacted hydroxyl groups, said composition having an equivalent weight excess of isocyanate groups in said second part to the hydroxyl groups in said first part of at least 2:1.

2. The composition of Claim 1, characterised in that the polyester portion of said polyester-urethane-methacrylate comprises a polyester diol.

3. The composition of Claim 2, wherein said polyester diol comprises the reaction product of neopentyl glycol and 1,6-hexandiol with adipic acid.

4. The composition of any of Claims 1 to 3, characterised by further comprising a non-ionic surfactant, said non-ionic surfactant preferably containing pendant free hydroxyl groups, said non-ionic surfactant more preferably comprising a polyoxyalkene silicone.

5. The composition of any of Claims 1 to 4, characterised in that said acrylate or methacrylate reactive diluent contains at least one reactive allylic bond.

6. The composition of any of Claims 1 to 5, characterized in that said reactive diluent comprises from 30% to 70% by weight of said first part.

7. The composition of any of Claims 1 to 6, characterized in that said polyisocyanate is present in equivalent weight excess in the range of 2:1 to 10:1, more preferably in equivalent weight range excess in the range of 5:1 to 7:1, most preferably in equivalent weight excess of 6:1.

8. A method of forming a uv curing polymerizable conformal coating on a substrate wherein said substrate has one or more shadow areas, characterized by the steps in sequence of:

(1) providing a two-part coating composition, the first part of which comprises at least one polyester-urethane-acrylate or polyester-urethane-methacrylate compound, a mono or polyfunctional acrylate or methacrylate reactive diluent and a polymerization initiator of the photo-initiator type, and a second part which comprises a polyisocyanate containing adduct, at least one component of said first part containing unreacted hydroxyl groups, said composition having an equivalent weight excess of isocyanate groups in said second part to the hydroxyl groups in said first part of at least 2:1;

(2) blending said first and second parts to form a coating composition;

(3) coating said substrate at least in part with said polymerizable composition;

(4) exposing the coated substrate to uv light of wave length and intensity to effect uv cure of exposed areas of said coating; and

(5) storing said coated substrate under conditions of temperature and humidity which promote curing of unexposed (shadow) areas of said coating through a built-in secondary moisture cure mechanism.

9. A method according to Claim 8, characterized in that said substrate comprises a circuit board, and wherein said circuit board has one or more components mounted thereon overshadowing areas of said first board.

10. An electrical or electronic component, if desired mounted on a printed circuit board, and covered at least in part with the composition of any of the claims 1 to 7 in cured form.

Patentansprüche

1. Zweiteilige Beschichtungszusammensetzung, besonders geeignet für konformes Beschichten, dadurch gekennzeichnet, dass sie in Kombination umfasst:

(1) einen ersten Teil, enthaltend wenigstens eine Polyester-Urethan-Acrylat- oder Polyester-Urethan-Methacrylat-Verbindung, ein reaktives mono- oder polyfunktionelles Acrylat- oder Methacrylat-Verdünnungsmittel und einen Polymerisationsinitiator vom Photo-Initiator-Typ; und

(2) einen zweiten Teil, enthaltend ein Polyisocyanat enthaltendes Addukt, wenigstens eine Komponente des ersten Teils, enthaltend unreaktierte Hydroxylgruppen, wobei die Zusammensetzung einen Äquivalentgewichtüberschuss an Isocyanatgruppen in dem zweiten Teil zu den Hydroxylgruppen in dem ersten Teil von wenigstens 2:1 aufweist.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, dass der Polyesteranteil des Polyester-Urethan-Methacrylats ein Polyesterdiol umfasst.

3. Zusammensetzung nach Anspruch 2, worin das Polyesterdiol das Reaktionsprodukt von Neopentylglykol und 1,6-Hexandiol mit Adipinsäure umfasst.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass sie weiterhin ein nicht-ionisches oberflächenaktives Mittel umfasst, wobei das nicht-ionische oberflächenaktive Mittel vorzugsweise angehängte freie Hydroxylgruppen enthält und wobei das nicht-ionische oberflächenaktive Mittel besonders bevorzugt ein Polyoxyalkensilikon enthält.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass das reaktive Acrylat- oder Methacrylat-Verdünnungsmittel wenigstens eine reaktive Allylbindung enthält.



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6. Zusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass das reaktive Verdünnungsmittel 30 bis 70 Gew.% des ersten Teils umfasst.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass das Polyisocyanat in einem Äquivalentgewichtüberschuss im Bereich von 2:1 bis 10:1, besonders bevorzugt in einem Äquivalentgewichtüberschuss im Bereich von 5:1 bis 7:1 und ganz besonders bevorzugt in einem Äquivalentgewichtüberschuss von 6:1 vorliegt.

8. Verfahren zur Bildung einer UV-härtenden polymerisierbaren konformen Beschichtung auf einem Substrat, worin das Substrat eine oder mehrere Schattenflächen aufweist, gekennzeichnet durch die Schrittsequenz:

(1) Bereitstellen einer zweiteiligen Beschichtungszusammensetzung, wobei deren erster Teil wenigstens eine Polyester-Urethan-Acrylat- oder Polyester-Urethan-Methacrylat-Verbindung, ein reaktives mono- oder polyfunktionelles Acrylat- oder Methacrylat-Verdünnungsmittel und einen Polymerisations-initiator vom Photo-Initiator-Typ umfasst, und der zweite Teil ein Polyisocyanat-enthaltendes Addukt, wenigstens eine Komponente des ersten Teils, enthaltend unreaktierte Hydroxylgruppen, wobei die Zusammensetzung einen Äquivalentgewichtüberschuss an Isocyanatgruppen in dem zweiten Teil zu den Hydroxylgruppen in dem ersten Teil von wenigstens 2:1 aufweist, umfasst;

(2) Vermischen des ersten und zweiten Teils unter Bildung einer Beschichtungszusammensetzung;

(3) Beschichten des Substrats zumindestens teilweise mit der polymerisierbaren Zusammensetzung;

(4) Belichten des beschichteten Substrats mit UV-Licht einer Wellenlänge und Intensität zur Bewirkung der UV-Härtung belichteter Flächen der Beschichtung; und

(5) Aufbewahren des beschichteten Substrats unter Temperatur- und Feuchtigkeitsbedingungen, welche die Aushärtung unbelichteter (Schatten) Flächen der Beschichtung durch einen eingebauten sekundären Feuchtigkeits-Härtungs-Mechanismus fördern.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, dass das Substrat eine Schaltungsplatte umfasst, wobei die Schaltungsplatte eine oder mehrere darauf montierte Komponenten aufweist, welche Flächen dieser Schaltungsplatte überschatten.

10. Elektrische oder elektronische Komponente, falls erwünscht, auf eine gedruckte Schaltungsplatte montiert und wenigstens teilweise mit der Zusammensetzung nach einem der Ansprüche 1 bis 7 in ausgehärteter Form bedeckt.

Revendications

1. Composition en deux parties pour revêtement, spécialement utilisable pour un revêtement épousant les formes, caractérisée en ce qu'elle comprend en combinaison:

(1) une première partie comprenant au moins un composé polyester-uréthane-acrylate ou polyester-uréthane-méthacrylate, un diluant réactif mono- ou polyfonctionnel d'acrylate ou de méthacrylate, et un initiateur de polymérisation du type photo-initiateur; et

(2) une seconde partie comprenant un produit d'addition contenant un polyisocyanate, au moins un composant de ladite première partie contenant des groupes hydroxyles inaltérés, ladite composition présentant un excédent pondéral équivalent de groupes isocyanates dans ladite seconde partie d'au moins 2:1 par rapport aux groupes hydroxyles dans ladite première partie.

2. Composition selon la revendication 1, caractérisée en ce que la portion polyester dudit composé polyester-uréthane-méthacrylate comprend un polyester diol.

3. Composition selon la revendication 2, dans laquelle ledit polyester diol comprend le produit de réaction du glycol néopentyle et du 1,6-hexandiol avec l'acide adipique.

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en qu'elle comporte en outre un surfactant non ionique, ledit surfactant non ionique contenant de préférence des groupes hydroxyles libres pendants, ledit surfactant non ionique comprenant de préférence un silicone polyoxy-alkène.

5. Composition selon l'une quelconque des revendications 1 à 4, caractérisée en ce que ledit diluant réactif d'acrylate ou de méthacrylate contient au moins une liaison allylique réactive.

6. Composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce que ledit diluant réactif constitue entre 30% et 70% en poids de ladite première partie.

7. Composition selon l'une quelconque des revendications 1 à 6, caractérisée en ce que ledit polyisocyanate figure en excédent pondéral équivalent compris entre 2:1 et 10:1, et de préférence compris entre 5:1 et 7:1, et encore de préférence égal à 6:1.

8. Procédé pour former un revêtement polymérisable durcissant aux ultraviolets et épousant les formes sur un substrat, ledit substrat présentant une ou plusieurs zones d'ombre, caractérisé par les étapes successives suivantes:

(1) utiliser une composition en deux parties pour revêtement, dont la première partie comprend au moins un composé polyester-uréthane-acrylate ou polyester-uréthane-méthacrylate, et un initiateur de polymérisation du type photo-initiateur, et une seconde partie qui comprend un produit d'addition contenant un polyisocyanate, au moins un composant de ladite première partie contenant des groupes hydroxyles inaltérés, ladite composition présentant un excédent pondéral équivalent de groupes



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isocyanates dans ladite seconde partie d'au moins 2:1 par rapport aux groupes hydroxyles dans ladite première partie;

(2) mélanger lesdites première et seconde parties pour former une composition de revêtement;

(3) revêtir ledit substrat au moins partiellement de ladite composition polymérisable;

5 (4) exposer le substrat revêtu à une lumière ultraviolette de longueur d'onde et d'intensité propres à produire un durcissement des zones exposées du revêtement; et

(5) stocker le substrat revêtu dans des conditions de température et d'humidité qui activent le durcissement des zones non exposées (zones d'ombre) du revêtement par un mécanisme secondaire incorporé de durcissement à l'humidité.

10 9. Procédé selon la revendication 8, caractérisée en ce que ledit substrat comprend une carte à circuits imprimés, et dans lequel ladite carte est pourvue d'un ou plusieurs composants montés sur elle et portant ombre sur des zones de cette carte.

15 10. Composant électrique ou électronique, monté le cas échéant sur une carte à circuits imprimés et recouvert au moins partiellement de la composition selon l'une quelconque des revendications 1 à 7 sous forme durcie.

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