

The invention concerns a method for producing heat-resistant structured layers by applying radiation-sensitive soluble polymers in the form of a layer or film on to a substrate, irradiating the layer or film through negative patterns with actinic light or by guiding a light, electron, laser or ion beam, removing the non-irradiated portions of the layer or film, and possibly by subsequent tempering, with the use of polyether-based photopolymers in the form of addition products of an olefinically-unsaturated monoisocyanate and a hydroxyl group-containing phenoxy resin, as well as the use of these structured layers.

Methods for the production of structured layers based on heat-resistant polymers are known, for example, from DE-PS 2 308 830 and from EP-PS 0 019 123 and EP-PS 0 026 820. In these processes, soluble photo-reactive precursors of highly heat resistant polymers are used for photo-lithographic structuring, and in a subsequent tempering step the structures produced therefrom are cyclized to highly heat resistant structures. For complete cyclization and removal of the cleavage products, temperatures up to 400 °C are needed. This requires substrates capable of high thermal load.

From US-PS 3 776 889 light-sensitive, film-forming polymers are known which are soluble in organic solvents and consist essentially of an allylcarbonyl ester of a hydroxyl group-containing polymer having a molecular weight of 500 to 115,000. Phenoxy resins, polyvinylalcohol, polyester, polyurethane resins and shellac serve as the hydroxyl group-containing polymers. These hydroxyl group-containing polymers are esterified with allylisocyanate, with the light-sensitive polymers resulting. The light-sensitive polymers come into use in photo-mechanical processes and in photo-lithography, that is to say, for the production of photographic resist images.

In circuit and transmission applications, for example in circuit-board technology, among other things epoxy-based substrates are used which can be subjected to a thermal load of up to approximately 150 °C per hour and which have to withstand temperatures of 260 °C, for a number of seconds only, in soldering processes for example. The so-called solder resists used here for partial printed conductor coverings must meet similar thermal requirements; that is to say, in this case, in order to cover the regions of the circuit surface which are not to come into contact with the solder metal, polymers of a medium thermal stability are needed. The epoxy and acrylate-based dry resists and screen printing lacquers which are still used for this purpose meet the requirements of a solder stop mask, yet they only partially fulfill the more

stringent requirements for dimensional accuracy in micro-conductor technology with structures of less than 100 μm , and at the required cycle strength. For this, photo-lithographic lacquer systems are needed.

5 There is already available a photo-structurable epoxy-based lacquer system which has chalcone groups incorporated in the polymer chain, and which provides sufficient dimensional accuracy. However, relatively
10 long exposure times, and particularly long developing times, are necessary for photo-structuring. Moreover, with the known lacquer system additional, lasting protection of the sensitive circuit surface against
15 noxious gas, as is often required, can only be obtained by using costly multiple coatings. Furthermore, because hardening times of several hours are required, the process is lengthy and expensive.

 It is an object of the invention to provide a method of the type mentioned at the start in which
20 polyether-based photopolymers are used, and so that it is possible to produce, in a single coating process, dimensionally exact, high-grade structured layers, for circuit surfaces in particular, which withstand the
25 extensive thermal and mechanical stresses of, for example, dip soldering, and which effectively and durably protect the circuit surface against moisture and corrosion. In particular, the process is to be
 shortened by a reduction in the exposure, developing, and tempering times, so that the method is made cost-efficient.

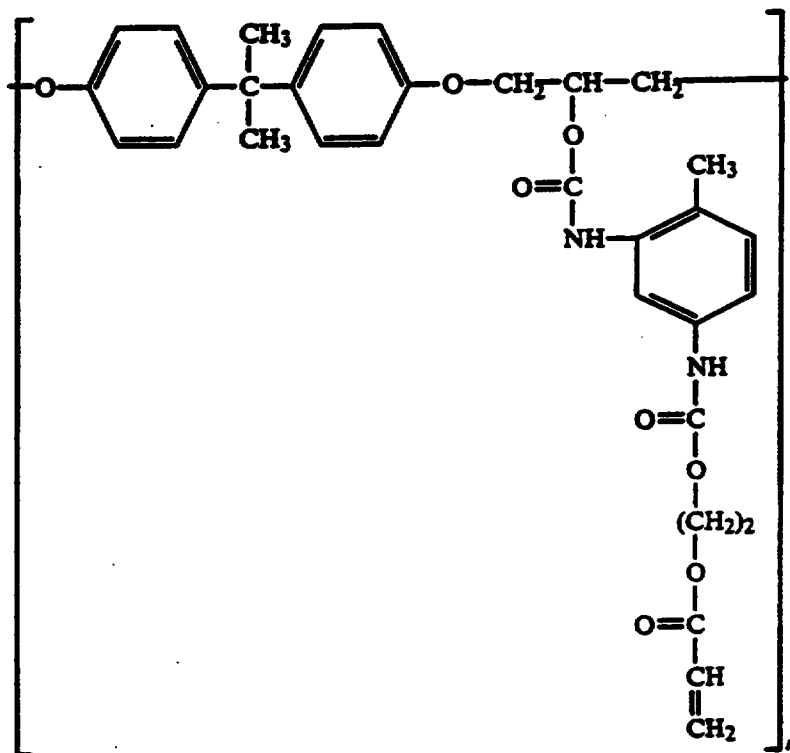
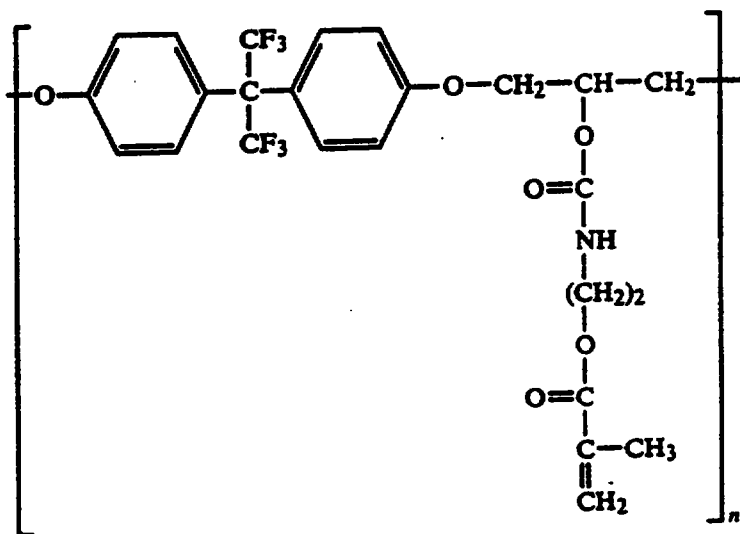
30 This is achieved according to the invention in that, with the polyether-based photopolymers which are present in the form of addition products of an olefinically-unsaturated monoisocyanate and a hydroxyl
35 group-containing phenoxy resin, a methacrylate group-containing isocyanate or an addition product of hydroxyethyl(meth)acrylate and 2,4-diisocyanatotoluene is used as the olefinically-unsaturated monoisocyanate.

 The method according to the invention provides for the cost-efficient production of finely structured
40 protective and insulating layers for semi-conductor and circuit applications, which effectively and durably protect the parts and circuits which are sensitive to corrosion. Especially advantageous is the fact that the developing process does not lead to undercutting;
45 therefore, solder bridges do not occur with the soldering process. Further, the method according to the invention not only fulfills the dimensional accuracy requirements of the structures produced, but it also permits a very high resolution in a wide range
50 of layer thicknesses with short developing times. Further, the method is also particularly cost-efficient because it produces, with a single application (with conventional equipment) - optionally after short tempering - photo-structured layers with a sufficient

level of heat resistance; even under solder bath conditions, these layers remain inherently stable and fissure-free, and are effective as a durable protection against moisture and corrosion. At the same time, good electrical characteristics are obtained which are not impaired, even in a humid climate.

In the method according to the invention, the photopolymers can be used advantageously together with light- or radiation-sensitive compounds capable of copolymerisation. Preferably, compounds containing acrylate and/or methacrylate groups are used, in particular trimethylol propane triacrylate and trimethacrylate, and/or 1,4-butanediol dimethacrylate. Alternatively, allyl group-containing compounds can be used, for example, diallyl and triallyl cyanurates, as well as N-substituted maleinimides. In addition, photo initiators and or sensitizers can be used (cf.: "Industrie Chimique Belge," Vol. 24, 1959, pages 739 to 764; and J. Kosar, "Light-Sensitive Systems", John Wiley & Sons Inc., New York 1965, pages 143 to 146 and 160 to 188). Especially suitable are alpha-halogen acetophenones, dialkoxyacetophenones such as dimethoxyacetophenone and diethoxyacetophenone, benzoylphosphine oxides which can possibly be substituted, and Michler's ketone. Benzoin ether, 4,4'-bis(diethylamino)-benzophenone, 2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone, thioxanthenes such as isopropyl thioxanthone, and acetophenone are also suitable as photo-initiators or sensitizers. Bonding agents can also be used advantageously in the method according to the invention. These are preferably silanes, such as vinyltriethoxysilane, vinyl-tris(beta-methoxyethoxy)-silane, gamma-methacryloxypropyl-trimethoxysilane, gamma-glycidoxypropyl-trimethoxysilane and gamma-aminopropyl-triethoxysilane.

The photopolymers used in the method according to the invention are described in EP-OS 0 206 158. Photopolymers preferably used are addition products of isocyanatoethyl methacrylate and phenoxy resins, optionally having fluorinated isopropyl groups, or addition products of phenoxy resins and olefinically-unsaturated monoisocyanates in the form of addition products of 2,4-diisocyanatotoluene and hydroxyethyl acrylate or hydroxyethyl methacrylate. Such photopolymers are illustrated by way of examples in the following formulae:



where $n \geq 50$.

The phenoxy resins used preferably have a molecular weight of between 15,000 and 30,000.

As mentioned above, the structured layers according to the invention are produced by applying the photopolymer in the form of a layer or film on to a substrate, and exposing it to actinic light through a mask, or irradiating it by guiding a light, electron, laser, or ion beam. Subsequently, the unexposed or non-irradiated layer or film portions are dissolved or pulled off, and the resulting structured layers or relief structures are optionally tempered.

Advantageously, the photopolymer is applied to the substrate dissolved in an organic solvent. The concentration of the photo resist solution in common solvents, such as cyclohexanone, gamma-butyrolactone, N-methylpyrrolidone and mixtures thereof, can be adjusted so that, with known coating methods such as centrifuging, dipping, spraying, pouring, knifing, brushing or rolling, layer thicknesses of 0.01 to approximately 500 μm can be produced. To obtain a uniform and good surface quality on substrates having smooth surfaces, pouring (such a method is known, for example, from EP-PS 0 002 040), knifing and, in particular, electrostatic spray coating and centrifugal coating at 300 to 10,000 revolutions per minute, are advantageous. On uneven surfaces, such as circuit boards with copper conductors on the surface, centrifugal speeds of 300 to 1,500 are preferred. The viscosity range of the lacquer solutions used for the knifing, spraying, and pouring methods is advantageously between 200 and 1,500 mPa.s at 23 °C.

The photo resist layer applied to the substrate, which consists preferably of circuit-board material, glass, metal, plastic or semiconductors, can be separated from the solvent at room temperature, preferably at temperatures of 50 to 80 °C, in a current of nitrogen or air; the operation can take place under a vacuum, or drying can be carried out with infrared lamps or on a heated plate.

To obtain an acceptable difference in solubility between the irradiated and the non-irradiated layer or film portions, when using a 350 W superpressure mercury lamp in connection with the method according to the invention, exposure times between 5 and 400 seconds are sufficient, depending on the composition and on the layer thickness. After exposure, and an optional second drying process, the unexposed portions are dissolved away with organic solvents.

The structured layers or relief structures produced by the method according to the invention are distinguished by edge sharpness, high resolution, fissure-free homogeneous surfaces and thermal dimensional stability which withstands even the thermal and mechanical strains of dip soldering processes. The adhesion on the solder is very low so that, as is desired, no solder beads stick to the polymer layer.

5 The structured layers produced according to the invention are elastic enough to pass cycle tests between -65 and +125 °C without the formation of fissures. Circuit surfaces covered with the structured layers show no conductor corrosion in climate tests at 40 °C, with 92 % air humidity, and a voltage of 100 V. Such layers are therefore suitable not only as solder resist masks; they are also suitable as effective and durable protective layers against the action of

10 moisture and noxious gases.
The structured layers according to the invention are also suitable, because of the high level of purity demanded by their manufacture, for the production of passivation layers on semi-conductor elements, thin and
15 thick film circuits, solder protection layers on multi-layer circuits, and insulating layers which are components of film circuits; the layers can also be used as miniaturised protective and insulating layers on electrically conducting and/or semi-conducting
20 and/or insulating base materials, and generally for the fine structuring of substrates, and for structure transfer processes, such as wet or dry etching processes, zero-current or electroplating metal deposition and evaporation methods, and also as masks
25 for ion implantation. Moreover, these layers are suitable as insulating and protective layers in electrical engineering and in micro-electronics, and further as damping substances for surface wave filters, in particular, television intermediate frequency
30 filters, and as alpha-ray protectors on the cell fields of memory components, and as orientation layers in liquid crystal displays.

The invention will be described in further detail with reference to exemplary embodiments.

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EXAMPLE 1

40 40 parts by weight pure 2,4-diisocyanatotoluene are added in drops to 69 parts by weight dried dichloromethane in the absence of moisture; 29.2 parts by weight 2-hydroxyethyl acrylate are then slowly added in drops at room temperature with stirring to the solution thus obtained. After standing for 24 hours, the conversion of the isocyanate groups is determined to be 99 % by titration. The photo-reactive isocyanate is then extracted from the reaction solution with 250
45 parts by weight petroleum spirit; after removal of the extraction medium, it is isolated as a clear viscous liquid, with a yield of 64.5 g, or 93 % of the theoretical value.

50 At room temperature and with stirring, 140 parts by weight dry gamma-butyrolactone, 137 parts by weight dry N-methyl pyrrolidone, 50 parts by weight of the pure, photo-reactive monoisocyanate isolated in the manner described above, and 0.1 parts by weight dibutyl

tin dilaurate are added to 35 parts by weight of the phenoxy resin Rütapox 0717 (Rütapox^R is a trademark of Rütgerswerke AG). After stirring of the mixture for 48 hours, 7 parts by weight ethanol are added to the reaction solution. After another 24 hours, isocyanate groups are no longer detectable.

0.65 parts by weight benzoin isopropyl ether, 0.08 parts by weight Michler's ketone, 1.65 parts by weight trimethylol propane triacrylate and 0.3 parts by weight vinyl-tris(beta-methoxyethoxy)-silane are added to 100 parts by weight of the photo-reactive phenoxy resin produced in the manner described above (as a 23 % resin solution). The solution is then pressure filtered through a 5 μ m filter. The viscosity of the resulting solution is 830 mPa.s at 23 °C.

By centrifuging the solution at 800 rpm on to a silicone disk coated with a bonding agent, followed by drying for 30 minutes at 60 °C in a circulating air oven, 23 μ m-thick, homogeneous layers are obtained; after exposure for 40 seconds through a mask with 350 W superpressure mercury lamp, the layers are developed with gamma-butyrolactone/xylene (volumetric ratio 1:2) and then rinsed with xylene in a spraying process to produce structured layers having sharp contours. The edge formations and the surface quality of these layers are not impaired by tempering for one hour at 150 °C. The resolution quality of the structures is $\leq$ 20 μ m.

A photo-structured layer produced as described above and treated with known commercial fluxes exhibits a homogeneous, fissure-free surface after being tested in a solder bath at 260 °C with an immersion time of 20 seconds. The solder runs easily off the lacquer surface in beads.

EXAMPLE 2

33 parts by weight pure isocyanatoethyl methacrylate and 0.1 parts by weight dibutyl tin dilaurate are added to a solution of 110 parts by weight Rütapox 0723 (50 % solution in cyclohexanone/ethylglycol acetate) in 114 parts by weight gamma-butyrolactone; the mixture is then stirred for 30 hours at room temperature. After this, 9 parts by weight 2-hydroxyethyl methacrylate are added to the reaction solution. After another 24 hours, 0.6 parts by weight dichloroacetophenone, 0.3 parts by weight diethoxyacetophenone, 0.3 parts by weight Michler's ketone and 0.3 parts by weight vinyl-tris-(beta-methoxyethoxy)-silane are added to 100 parts by weight of the resin solution. Subsequently, the solution is pressure-filtered through a 5 μ m filter.

The filtered solution of the photo-reactive phenoxy resin is centrifuged at 400 rpm on to a circuit-board test plate with copper conductors on the surface, and then dried in a circulating air oven for

1/2 hour at 70 °C. The thickness of the lacquer film is then 50 µm. Next, the film is exposed with a 350 W superpressure mercury lamp through a mask for 10 seconds and subjected to a 30-minute second drying at 70 °C in a circulating air oven. After developing for 35 seconds with cyclohexanone, using water for stopping, sharp-edged structured layers, the surface qualities of which are not impaired even by 100 cycles between -65 and +125 °C, are obtained. These layers withstand both undamaged flow and dip soldering processes at 260 °C; the solder runs off the surface in beads. Moisture tests at 40 °C, with 92 % air humidity, and a voltage of 100 V, reveal no corrosion in the conductor regions covered with lacquer.

EXAMPLE 3

62 parts by weight 2,4-diisocyanatotoluene are added in drops in the absence of moisture to 113.2 parts by weight dried dichloromethane. After this, at room temperature and with stirring, 51.2 parts by weight 2-hydroxyethyl methacrylate are slowly added in drops. After a reaction time of 24 hours at room temperature, the isocyanate conversion is determined by titration to be 99 %. Upon addition of 450 parts by weight petroleum spirit, a precipitate of white crystals is obtained. The yield of pure photo-reactive monoisocyanate is 105 parts by weight, or 93 % of the theoretical value.

125.2 parts by weight phenoxy resin solution (Rütapox 0723) are added, in the absence of moisture, to a solution of 95 parts by weight of photo-reactive monoisocyanate, produced in the manner described above, in a mixture of 140 parts by weight gamma-butyrolactone, 105 parts by weight N-methyl pyrrolidone and 0.01 parts by weight dibutyl tin dilaurate, and caused to react for 12 hours at 50 °C with stirring. After this, 8 parts by weight 2-hydroxyethyl methacrylate are first added to the reaction solution at this temperature and then, after an additional 5 hours, 4 parts by weight ethanol are added. After 24 hours the resin solution has a viscosity of 330 mPa.s at 23 °C.

0.66 parts by weight isopropyl thioxanthone, 0.08 parts by weight Michler's ketone, 1.65 parts by weight trimethylol propane triacrylate and 0.3 parts by weight vinyltriethoxysilane are added to 100 parts by weight of the solution described above. After filtering through a 5 µm filter at a pressure of 5 bar, the mixture is poured on to substrates to produce 20 µm-thick lacquer layers, which are irradiated with a 350 W superpressure mercury lamp for 30 seconds through a mask. After this, the exposed layer is dried again in a circulating air oven for 5 min at 90 °C. The structuring (duration: 10 seconds) occurs by means of a

developer mixture of gamma-butyrolactone and xylene (volumetric ratio 1:2), stopping being carried out with xylene. The structural layer produced in this manner is resistant to solder bath.

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EXAMPLE 4

10 A mixture of 23.6 parts by weight pure 2-hydroxyethyl acrylate and 24.8 parts by weight pure 2-hydroxyethyl methacrylate is slowly added, in drops at room temperature with stirring and in the absence of moisture, to a solution of 66.8 parts by weight pure 2,4-diisocyanatotoluene in 115.3 parts by weight dichloromethane. After reaction at room temperature for 40 hours, isocyanate conversion is determined to be 98 % by titration.

15 The resulting solution of the photo-reactive monoisocyanate is combined with a solution of 107 parts by weight Rütapox 0717 in 397 parts by weight gamma-butyrolactone, and with 0.22 parts by weight dibutyl tin dilaurate. After reaction at room temperature for 20 25 hours, 15 parts by weight ethanol are added to the reaction solution. After another 24 hours, the solution is ready to be used for coatings.

25 To 100 parts by weight of the polyether solution produced in the manner described there are added 1.2 parts by weight 2,4,6-trimethyl benzoylphosphine oxide, 0.3 parts by weight Michler's ketone and 0.3 parts by weight vinyltriethoxysilane. After filtering through a 5 µm filter at a pressure of 5 bar, the mixture is 30 poured on to copper substrates to produce 30 µm-thick lacquer layers, which are irradiated through a mask for 30 seconds with a 350 W superpressure mercury lamp. After developing with the developer according to Example 2 for 35 seconds, structures with a smooth fissure-free surface, which are stable under solder 35 bath conditions even at 260 °C, are obtained; the solder does not adhere to the lacquer surface, but runs off in beads.



Claims

1. Process for the production of heat-resistant, structured layers by means of the application of radiation-sensitive, soluble polymers in the form of a layer or film on a substrate, the irradiation of the layer or film through negative patterns with actinic light or by guiding a light, electron, laser or ion beam, the removal of the non-irradiated portions of the layer or film, and possibly by means of subsequent tempering, with the use of polyether-based photopolymers in the form of addition products of an olefinically-unsaturated monoisocyanate and a hydroxyl group-containing phenoxy resin, characterised in that a methacrylate group-containing isocyanate, or an addition product of hydroxyethyl(meth)acrylate and 2,4-diisocyanatotoluene is used as the olefinically-unsaturated monoisocyanate.
2. Process according to claim 1, characterised in that the photopolymers are used together with light- or radiation-sensitive compounds capable of copolymerisation, in particular compounds containing acrylate or methacrylate groups.
3. Process according to claim 1 or 2, characterised in that the photopolymers are used together with photo initiators and/or photo sensitizers, in particular alpha-halogen acetophenones, dialkoxy acetophenones, benzoylphosphine oxides and Michler's ketone.
4. Process according to one of claims 1 to 3, characterised in that phenoxy resins with a molecular weight between 15,000 and 30,000 are used.
5. Heat-resistant structured layer, produced according to one or several of claims 1 to 4.
6. Use of the structured layer according to claim 5 as a solder resist and insulation layer providing lasting protection in micro-conductor technology.
7. Use of the structured layer according to claim 5 as a resist providing intermediate protection in structure transfer processes carried out by galvanising, wet and dry etching, and ion implantation.
8. Use of the structured layer according to claim 5 as a protective and insulating material in electrical engineering, in particular in semiconductor technology.
9. Use of the structured layer according to claim 5 as a damping substance for surface wave filters.
10. Use of the structured layer according to claim 5 as alpha-ray protection on the cell fields of memory components.
11. Use of the structured layer according to claim 5 as an orientation layer in liquid crystal displays.