

Description

This invention relates to compositions comprising polymerisable material and photo-initiator systems for the polymerisation thereof, and particularly to such compositions for use as dry film resists.

Dry or tack-free film resists are known in the electronics art, for example as disclosed in US Patent Specification 3469982. Typically, such resists are formed from a solid photopolymerisable layer supported on a thin flexible polymeric support film and covered by a protective or cover film.

Recently so-called permanent or non-strippable dry film resists have been developed in which the cured photopolymerisable layer is able to withstand the harsh environments to which resists are subjected during the production of printed circuit boards. Use of permanent dry film resists eliminates one step in the production of printed circuit boards, namely removal of cured resist.

We have now found that certain oligomers in admixture with a suitable photoinitiator system may be used to form dry film resists and particularly permanent dry film resists.

According to the present invention there is provided a polymerisable composition comprising

(a) at least one polymerisable olefinically unsaturated oligomer which

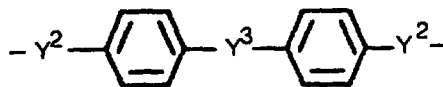
(i) comprises the repeating unit ($\text{Ar}^1\text{—CHR}^1$) wherein Ar^1 is an aromatic group or a suitable substituted derivative thereof, each of which aromatic groups may be the same or different; and R^1 , each of which groups in the oligomer backbone may be the same or different is hydrogen or a hydrocarbyl group; and

(ii) has pendant and/or terminal acyloxymethyl groups in which the acyl group is derived from an olefinically unsaturated carboxylic acid (hereinafter referred to for convenience as "aromatic/aldehyde oligomer");

(b) one or more polymeric binders which has a molecular weight of between 10,000 and 1,000,000; and

(c) a photoinitiator system for initiating polymerisation of the at least one aromatic/aldehyde oligomer.

The aromatic groups Ar^1 may be mono-nuclear, e.g. as in phenylene; fused polynuclear, e.g. as in naphthalene or anthracene; or preferably have the structure $\text{—O—Y}^1\text{—O—}$. In $\text{—O—Y}^1\text{—O—}$, O is the phenylene group and Y^1 is a direct link between the two phenylene groups; a divalent residue which contains one or more in-chain atoms, each of which atoms may be carbon or a hetero atom and may have one or more atoms appendant thereto, e.g. —O— , —S— , or $\text{—CH}_2\text{—}$ or a substituted derivative of $\text{—CH}_2\text{—}$, e.g. $\text{—C(CH}_3)_2\text{—}$; $\text{—CH}_2\text{CH}_2\text{—}$; or



where Y^2 each of which may be the same or different, is a group which activates the aromatic nucleus to electrophilic attack, e.g. —O— and —S— , and Y^3 is a group which deactivates the aromatic nucleus to electrophilic attack, e.g. $\text{—SO}_2\text{—}$ and —CO— .

Substituents which may be present on the aromatic groups include *inter alia* lower alkyl groups having up to five carbon atoms, e.g. methyl and ethyl; lower alkoxy groups e.g. methoxy; and halo groups, e.g. chloro.

R^1 in the repeating unit $\text{—(Ar}^1\text{—CHR}^1\text{)—}$ is preferably hydrogen. We do not exclude the possibility, however, that it may be an aryl group, e.g. phenyl; an alkaryl group, e.g. tolyl; an aralkyl group, e.g. benzyl; or an alkyl group having up to six carbon atoms.

Aromatic/aldehyde oligomers for use in the present invention preferably have functionalities between 2 and 6 and more preferably between 3 and 4. At functionalities less than 2 curing of the polymerisable composition is too slow; at functionalities more than 6 the cured product is often too brittle.

By "functionality" we mean the average number of pendant and terminal groups on each aromatic/aldehyde oligomer molecule.

In aromatic/aldehyde oligomers for use in the present invention in which the aromatic group Ar^1 has the structure $\text{—O—Y}^1\text{—O—}$, it is preferred that the ratio of *para-para* linkages to *ortho-para* linkages is between 5:1 and 2:1.

By "*para-para* linkage" we mean a linkage in which $\text{—CHR}^1\text{—}$ groups are attached to both phenylene groups in the residue $\text{—O—Y}^1\text{—O—}$ at positions which are *para* to the linkage joining the $\text{—Y}^1\text{—}$ residue to the phenylene groups.

By "*ortho-para* linkage" we mean a linkage in which a $\text{—CHR}^1\text{—}$ group is attached to a first phenylene group in the residue $\text{—O—Y}^1\text{—O—}$ at a position which is *ortho* to the position at which the $\text{—Y}^1\text{—}$ residue is attached to that first phenylene group and a $\text{—CHR}^1\text{—}$ group is attached to a second phenylene group in the residue $\text{—O—Y}^1\text{—O—}$ at a position which is *para* to the position at which the $\text{—Y}^1\text{—}$ residue is attached to the second phenylene group.

Aromatic/aldehyde oligomers for use in the present invention preferably have viscosities such that when they are mixed with polymeric binders as hereinafter defined and in the ratios as hereinafter described compositions are obtained which are tack-free and do not flow on storage at room temperature during their useful life.

Aromatic/aldehyde oligomers for use in the present invention preferably have number average molecular weights of between 900 and 1100 and weight average molecular weights of between 1900 and 2500.

Aromatic/aldehyde oligomers for use in the present invention may be prepared under the conditions which are more fully described in our copending European Patent Specification No. 0,112,650A.

Polymeric binders for use in the present invention are thermoplastics which on addition to solutions of the at least one aromatic/aldehyde oligomer in suitable solvents increase the viscosity of such solutions and tend to reduce the tackiness of solid layers deposited therefrom. They have molecular weights of between 10,000 and 1,000,000, preferably between 20,000 and 100,000.

It will be appreciated that polymeric binders, for use in the present invention will have Tg's above 20°C, preferably between 50°C and 120°C, and more preferably about 90°C, good thermal stability and should not unduly adversely affect the rate of polymerisation of the polymerisable composition. Use of polymeric binders having Tg's of about 90°C often gives polymerisable compositions which flow to form better laminates in the production of three-layer elements as hereinafter described under conventional production conditions of temperature, about 100°C, and rate of throughput.

As examples of suitable polymeric binders may be mentioned *inter alia* polystyrene, polymethyl methacrylate, poly-vinyl acetate, polyvinyl butyral, 'Haloflex', 'Alloprene' and polyvinyl pyrrolidone. Preferred polymeric binders include polymethyl methacrylate or preferably copolymers of methyl methacrylate and lower alkyl having up to 6 carbon atoms, e.g. ethyl and butyl, methacrylates or preferably acrylates, typically in a molar ratio of about 9:1.

Polymeric binders typically provide between 10 and 30% w/w and preferably between 15 and 20% w/w of the polymerisable composition.

The amount of polymeric binder used in polymerisable compositions according to the present invention and the Tg thereof will be chosen in the light of the conditions under which a three-layer element is prepared from the polymerisable composition as hereinafter described. Use of too much polymeric binder tends to lead to a flaky layer of the polymerisable composition in the three-layer element.

Polymerisable compositions according to the present invention may contain one or more substances which bear one or more polymerisable olefinically unsaturated groups and which is (are) copolymerisable with the at least one aromatic/aldehyde copolymer. Such substances are hereinafter referred to for convenience as "comonomers".

As examples of comonomers which may be present in polymerisable compositions according to the present invention and which contain one polymerisable olefinically unsaturated group may be mentioned readily available monomers selected from the classes including *inter alia* hydrocarbons, e.g. styrene; ethers, e.g. vinyl ethyl ether; esters, e.g. vinyl acetate, methyl methacrylate, ethyl acrylate, butyl methacrylate and 2-ethylhexyl methacrylate; and amides, e.g. N-vinyl pyrrolidone, and N-alkyl acrylamides.

As examples of comonomers which may be present in polymerisable compositions according to the present invention and which contain a plurality of polymerisable olefinically unsaturated groups may be mentioned polymerisable prepolymers. As examples of such prepolymers may be mentioned vinyl urethanes, for example those described in United Kingdom Patent Specification Nos. 1,352,063, 1,465,897 and 1,498,421 and German Offenlegungsschrift 2,419,887; and the reaction products of a diol, particularly a bisphenol, with a glycidyl alkacrylate, for example those described in United States Patent Specification Nos. 3066112 and 4131729. The disclosure in the aforementioned specifications are incorporated herein by way of reference.

Preferably, however, comonomers, where present in polymerisable compositions according to the present invention, are low viscosity compounds containing a plurality of polymerisable olefinically unsaturated groups. As examples of such compounds may be mentioned (alk)acrylic acid esters of polyhydroxy compounds, for example, diethylene glycol, trimethylolpropane and pentaerythritol, e.g. triethylene glycol dimethylacrylate and trimethylolpropane trimethacrylate.

The photoinitiator system for use in the present invention may comprise any of the known photoinitiator systems which are used to initiate polymerisation of polymerisable olefinically unsaturated monomers. As examples of such systems can be mentioned *inter alia* (a) mixtures of Michler's ketone and benzil or preferably benzophenone, typically in a weight ratio of about 1:4; (b) mixtures of amines and ketones as disclosed in EP 90493A, e.g. camphorquinone or fluorenone and N,N-dimethylaminoethyl methacrylate, typically in a weight ratio of about 1:1 (c) the coumarin-based photoinitiator systems described in US 4,289,844, (d) combinations of hexaarylbiimidazoles and leuco dyes, (e) cyclohexadienone-leuco dye systems described in US 4,241,869, or preferably (f) systems based on dimethoxyphenyl-acetophenone (benzil dimethyl ketal) and/or diethoxyacetophenone.

The concentration of the photoinitiator system used in the polymerisable composition of the present invention is typically up to about 10% w/w.

We do not exclude the possibility that polymerisable compositions according to the present invention may contain a peroxy initiator, but this is not preferred.

Optionally polymerisable compositions according to the present invention on exposure to actinic radiation of a wavelength which is absorbed by the photo-initiator system interact therewith such that a contrast between exposed and unexposed regions of the polymerisable composition is generated. For

example, where the polymerisable composition is colourless a colour may be generated in the exposed region thereof, or preferably, where the polymerisable composition is coloured, the colour disappears or changes in the exposed region thereof. For the generation of such a contrast, the polymerisable composition preferably contains a light-sensitive system which absorbs the aforesaid actinic radiation. As examples of such light sensitive systems may be mentioned *inter alia* leuco dyes, e.g. crystal violet; fluoran and a compound which generates an acid on exposure to suitable actinic radiation e.g. $\text{Ph}_3\text{S}^+\text{PF}_6^-$; and a combination of a light-fast dye, typically blue in colour, and a light-unstable dye, typically yellow in colour.

Polymerisable compositions according to the present invention may contain a pigment, for example a phthalocyanine green.

Polymerisable compositions according to the present invention typically contain processing aids. As examples of processing aids may be mentioned *inter alia* agents which act as at least one of the following: surfactant, flow modifier or anti-blocking agent. Suitable such agents are well known in the art and include *inter alia* $\text{CF}_3(\text{CF}_2\text{CF}_2)_{17}\text{CH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_{16}\text{CH}_3$ or preferably a silicone acrylate or more preferably a silicone diacrylate.

Polymerisable compositions according to the present invention may contain a particulate filler, e.g. a silica. It will be appreciated that where a particulate filler is present it does not unduly adversely affect the properties of the polymerisable composition. However, the presence of a particulate filler is not preferred.

Polymerisable compositions according to the present invention typically contain a suitable thermal polymerisation inhibitor. As examples of such inhibitors may be mentioned *inter alia* p-methoxyphenol, hydroquinone, alkyl- and aryl- substituted hydroquinones and quinones, and t-butyl catechol. Such inhibitors are used in a concentration of up to a few weight% of the polymerisable composition.

In a preferred embodiment of the present invention, the polymerisable composition comprises (a) 55—85% w/w of one or more aromatic/aldehyde oligomers, (b) 10—30% w/w of one or more methacrylate homo- or copolymers, (c) a photo-initiator system for initiating polymerisation of the polymerisable composition, and optionally (d) various additives as hereinbefore defined, the combined weight percentages of components (a), (b), (c) and (d) amounting to 100%.

Conveniently polymerisable compositions according to the present invention are used in the form of a three-layer element in which a layer of the polymerisable composition, preferably in the form of a solid or tack-free layer, is sandwiched between a support film and cover film. However we do not exclude the possibility that a suitable substrate, as hereinafter described, may be coated directly with the polymerisable composition for example by deposition from a suitable solvent.

As examples of suitable polymers of which support films used in the preparation of permanent dry film resists may be comprised may be mentioned *inter alia* polyamides, polyolefins, vinyl polymers, cellulose or preferably polyesters, more preferably polyethylene terephthalate. Preferably the support film transmits actinic radiation of a wavelength which is to be used to cure the photopolymerisable composition. Preferably the support film is substantially impermeable to oxygen. The thickness of the support film may be between 5 μm and 200 μm , and typically is between 10 μm and 50 μm .

Cover films used in the preparation of permanent dry film resists may be made from a polymer which has hereinbefore been indicated as suitable for preparation of the support film. Preferably the cover film comprises a polyolefin, and more preferably polyethylene. The thickness of the cover film may be between 5 μm and 200 μm , and typically is between 20 μm and 50 μm .

Where a polymerisable composition of the present invention is used in a three-layer element it is typically in the form of a substantially dry tack-free layer of thickness between 10 and 100 μm .

Whilst the polymerisable composition is preferably applied to the support film as a solution in a suitable solvent and the solvent evaporated off to leave a substantially tack-free solid layer, we do not exclude the possibility that it may be heated and applied in a softened state to the support film. The cover film is then laminated to the solid layer to provide a three-layer element.

As examples of suitable solvents from which the tack-free solid layer may be cast may be mentioned *inter alia* methyl ethyl ketone, methylene dichloride or preferably 1,1,1-trichloroethane since 1,1,1-trichloroethane tends to improve the clarity of the layer, and solutions of the polymerisable composition therein are more stable than in methyl ethyl ketone.

In use, the cover film is removed from the three-layer element and the exposed surface of the solid layer of polymerisable composition is brought into contact with a suitable base-board and laminated to a surface thereof, for example using resilient heated pressure rolls. To produce a resist image, the polymerisation composition is exposed imagewise, preferably through the support film, to radiation having a wavelength in the range of 250 to 600 nanometres, preferably in the range of 320 nanometres to 500 nanometres; the support film is removed, for example by peeling off; and the resist is developed by washing away the unexposed areas with a suitable washing solvent, to leave a base-board bearing a relief resist image on its surface. The resist image, where it is to be used in a so-called additive process, may be post-cured, for example by heating at a temperature in the range of 120°C to 250°C, or by UV curing using conventional UV-curing equipment.

The aforesaid suitable washing solvent is conveniently 1,1,1-trichloroethane. However, we do not exclude the possibility that the washing solvent may be chosen in the light of the nature of the polymeric binder. For example, where polyvinyl butyral is present the washing solvent is typically methyl ethyl ketone; where a methyl methacrylate homo- or co-polymer is present the solvent is typically 1,1,1-

trichloroethane; and where polyvinyl pyrrolidone is present the solvent is typically cyclohexanone.

It will be appreciated that where the resist is generated on a copperised surface of the base-board the non-protected copper may be removed in a so-called subtractive process. Preferably, however, the resist is used as a permanent or non-strippable resist in a so-called additive process in which a metal, e.g. copper, is deposited on the bare portion of the surface of a suitable substrate, for example a ceramic plate or a conventional base-board used for additive plating, e.g. an epoxy glass composite as used in Kollmorgen PCK Technologies CC-4 additive plating process, between the areas of photoresist, e.g. by electroless plating and then optionally by electrolytic deposition.

It is often preferred that the polymerisable compositions according to the present invention do not contain sulphur or certain sulphur-containing compounds which may have a tendency to affect adversely the plating bath when the resist generated from the polymerisable composition is used in an additive process.

The resists prepared from the polymerisable compositions of the present invention, after post-curing, are often (a) able to withstand sodium hydroxide solution at pH 12 and 80°C for 20 hours; chromic acid at pH 1 and 45°C for 20 minutes; a humidity of 92% at 90°C for 1 month without distortion and a solder float test at 285°C for 30 seconds without blistering or loss of adhesion; and (b) are resistant to attack by methylene chloride for 1 minute at ambient temperature with little or no change in surface hardness or appearance.

Accordingly, a further aspect of the present invention provides a process for forming a non-strippable resist on a surface which process comprises the steps of:

(a) applying to a surface a first surface of a solid layer of a polymerisable composition as hereinbefore defined, the second surface of the said layer having adhering thereto a thin flexible polymeric support film, then in either order;

(b) exposing the layer, imagewise, to actinic radiation to form a polymeric image in the layer; and

(c) stripping the support film from the layer; then

(d) washing away the unexposed areas of the layer to form a resist image of polymeric material; and

(e) post-curing the resist image.

The present invention is further illustrated by reference to the following Examples.

Example 1

This example illustrates the preparation of an aromatic/aldehyde oligomer for use in the present invention.

Paraformaldehyde (25 kilograms) was added to sulphuric acid (specific gravity 1.550; 234.9 kilograms) with stirring in an atmosphere of 5% oxygen in nitrogen at room temperature and the mixture was heated to 65°C. Methacrylic acid (stabilised with 100 ppm hydroquinone and 100 ppm Topanol "O"; 117 litres) was added to the mixture, followed, over a 30 minute period, by the addition of a solution of diphenyl ether (28 litres) in methacrylic acid (25 litres) while the reaction temperature was maintained at 64–67°C. The reaction mixture was stirred at 64–67°C for 3 hours and then allowed to stand for 15 minutes.

Phase separation occurred and the upper organic layer was recovered, sodium nitrite (100 ppm based on methacrylic acid) was added, and it was washed with water (150 litres $\times$ 2) at 60°C. On standing it separated into a lower oligomeric phase and an upper methacrylic acid phase.

The oligomeric phase was cooled to about 30°C, was washed with 50% v/v aqueous methanol, and was dissolved in methylene chloride (80 litres). The solution was analysed for residual acid content and a 10% excess of 10% aqueous ammonia was slowly added to the solution. An emulsion formed which was broken by the addition of methanol (50 litres) and by standing overnight.

The lower layer from the broken emulsion was passed through a 5A molecular sieve column. The methylene chloride was evaporated off to leave an aromatic/aldehyde oligomer (46 kilograms), M_n —972; M_w —2144; acid value, 13 mgs KOH/gram; saponification value 219 mgs KOH/gram; hydroxyl value, 31 mgs KOH/gram; functionality, 3.57; ratio of *para-para* linkages to *ortho-para* linkages of 4.3:1.

Examples 2—13

General Procedure

These examples illustrate the preparation of solid tack-free layers comprising polymerisable compositions according to the present invention.

A solution of aromatic/aldehyde oligomer, polymeric binder, photoinitiator system and, where indicated, a comonomer, a dyestuff, a pigment, a stabiliser, and an antiblocking agent in a suitable solvent was coated onto a Melinex (RTM) polyester support film. In Examples 2—8, the support film was 70 μ m thick; in Examples 9—13, the support film was 23 μ m thick. In Examples 2—9, a 100 μ m wet film thickness coiled wire coating bar was used; in Examples 10—13, a 125 μ m wet film thickness coiled wired coating bar was used. The wet film was dried with a hot air blower and was then allowed to stand at room temperature for 2 hours; a tack-free solid layer of a polymerisable composition of thickness about 35 microns supported on a polyester support film was obtained.

The composition (%w/w) of the tack-free solid layers and the solvents from which they were deposited are shown in Table 1. In addition to the weight percentages shown in Table 1, there were present in Example 9, 0.7% w/w Topanol "O" (RTM) and 0.1% w/w of a silicone acrylate (Ebecryl 350 (RTM)); in

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Examples 10 to 13, 0.2% of the aforementioned silicone acrylate and 10 ppm of a defoaming agent (Silcolapse 430 (RTM)); and in Examples 12 and 13, 10 ppm, benzoquinone.

In Examples 2—8, a polyethylene cover film was laminated to the bare surface of the tack-free solid layer using a hot-roll laminator at 60°C to form a three-layer element. In Example 9, a polyethylene cover film was laminated to the bare surface of the tack-free layer using a pilot coater nip roller at room temperature.

TABLE 1

Ex. No	Aromatic/aldehyde oligomers	Polymeric binder	Co-monomer	Photo-initiator system	Duestuff (Waxoline Green)	Pigment (Monastral Green)	Solvent
2	A:66.6	X:28.5	-	L:4.8	0.1	-	P
3	A:66.6	X:28.5	-	M:1.0 N:3.8	0.1	-	P
4	A:65.4	X:28.0	-	L:4.7 O:1.8	0.1	-	P
5	A:60.8	X:26.1	Z:8.7	L:4.3	0.1	-	P
6	C:47.6	X:28.6	Z:19.0	L:4.8	-	-	P
7	C:57.1	Y:28.6	Z:9.5	L:4.7	0.1	-	P
8	A:57.0	X:28.5	F:9.5	M:1.0 N:3.8	0.2	-	P
9	D:72.2	X:13.5 W: 4.5	-	L:6.4 J:1.8 K:0.5	-	0.3	P
10	E:72.3	X:18.1	-	I:4.5 L:4.5	-	0.04	Q
11	E:72.3	X:18.1	-	I:4.5 L:4.5	-	0.04	R
12	E:72:3	X:18.1	-	I:4.5 L:4.5	-	0.04	P
13	E:72.3	X:18.1	-	I:2.7 L:6.3	-	0.04	P

Symbols used in Table 1

- A: An aromatic/aldehyde oligomer prepared as described in Example 70 of EPA 83307128.5.
- B: An aromatic/aldehyde oligomer prepared as described in Example 84 of EPA 8330728.5.
- C: An aromatic/aldehyde oligomer as described in EPA 83307128.5 of $M_n=920$ and functionality 3.9.
- D: An aromatic/aldehyde oligomer as described in EPA 83307128.5 of $M_n=800$ and functionality 3.0.
- E: An aromatic/aldehyde oligomer as prepared in Example 1.
- F: A vinyl urethane prepared as described in Example 1 of European Patent Publication No. 64809A except that methyl ethyl ketone was used as the reaction solvent.
- I: Diethoxyacetophenone.
- J: Ethyl 4-dimethylaminobenzoate (Quantacure EPD (RTM)).
- K: t-Butylanthraquinone.
- L: 2,2-Dimethoxy-2-phenylacetophenone (Irgacure 651).
- M: Michler's Ketone.

- N: Benzophenone.
O: N,N-dimethyl-2-aminoethyl methacrylate.
P: Methyl ethyl ketone (45% w/w of solution).
Q: 1,1,1-Trichloroethane (Genklene (RTM); 58% w/w of solution).
5 R: Genklene (RTM)/methylene chloride mixture in volume ratio 58.5:41.5 (58% w/w of solution).
W: A methyl methacrylate polymer of $M_n=26,500$ and $M_w=72,200$ (Acryloid (RTM) B44).
X: A copolymer of methylmethacrylate and butyl acrylate, in weight ratio 9:1, $M_n=43200$ and $M_w=65000$.
Y: Polymethylmethacrylate $M_n=12000$.
10 Z: Triethyleneglycol dimethacrylate.

The cover films in Examples 2—9 were removed, easily, from the three-layer element when required.

The tack-free solid layer obtained in Example 10 was clear, in Example 11 it was cloudy and in Examples 12 and 13 it was almost clear.

15 Examples 14—19

These examples illustrate the production of permanent dry film resists by the process of the present invention.

The bare surfaces of portions of the tack-free layers prepared in Examples 2—13 were, after a first storage at room temperature for a defined length of time, contacted with the surface of a conventional board as used in the Kollmorgen PCK Technologies CC-4 "additive" process (which had been scrubbed under water with Scotchbrite (RTM)) and was laminated thereto using a Dynachem (RTM) Model 300 Laminator at 105°C and a through speed of 305 mm (1 foot) per minute in Examples 14—20; at 105°C and 457 mm (1.5 feet) per minute in Example 21; and 100°C and 914 mm (3 feet) per minute in Examples 22—29 to form a laminate which comprised a board, a tack-free layer and a support film.

25 The laminate was allowed to cool for 30 minutes, and was then exposed, through a Stouffer 21-step sensitivity guide disposed on the Melinex (RTM) film, to UV radiation (Parker Graphics Ltd. "Countess" exposure unit provided with two MLU 300 w Philips UV lamps) for a certain period of time.

After the exposure the resists were stored for a certain time, the Melinex (RTM) film was removed and the tack-free layer was washed with 1,1,1-trichloroethane for a certain time; a cured resin which was resistant to washing was obtained at steps up to and including the steps indicated by the step wedge numbers shown in Table 2.

TABLE 2

Ex. No	Solid layer Prepared in Example No	First Storage Time (hours)	Exposure Time (minutes)	Second Storage Time (minutes)	Washing Time (minutes)	Step Wedge No
14	2	0.5	5	30	2	7
15	3	0.5	5	30	2	7
16	4	0.5	5	30	2	7
17	5	0.5	5	30	2	4
18	6	0.5	7	30	2	11
19	7	0.5	8	30	2	10
20	8	0.5	5	30	2	7
21	9	0.5	4	20	1	11
22	10	4	3	5	1	11
23	10	288	3	5	1	11
24	11	4	3	5	1	11
25	11	288	3	5	1	11
26	12	4	3	5	1	8
27	12	288	3	5	1	8
28	13	4	3	5	1	10
29	13	288	3	5	1	a

a : Not determined.

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Examples 14 to 29 were repeated except that a Stouffer step wedge was not used, that after removal of the Melinex (RTM) film the washing step was omitted and the cured layer was post-cured by exposure for 4 hours (Examples 14—21) or 1 hour (Examples 22—29) to a Philips HPR 125w mercury discharge reprographic lamp at a distance of 40 centimetres.

The post-cured layer was unaffected by 3 drops of methylene chloride disposed on its surface for 1 minute.

The board and post-cured layer were dipped in Multicore Rosin Foam Flux PC26. After the flux-treatment a first portion was placed, resist surface down, for 30 seconds on a 60:40 tin-lead solder bath at 285°C; a second portion was placed, resist surface down, on the solder bath for 6 seconds, removed for 21 seconds and contacted for a further 6 seconds. Both portions were cleaned with 1,1,1-trichloroethane and the result was found to be neither dulled nor blistered. A 2 mm cross-hatch pattern was produced on both portions, pieces of 3M Scotch (RTM) 610 tape were pressed firmly against the surface of both resists and removed with a sharp tug. Less than 5% of the resist was removed from the board.

Examples 14—21 were repeated except that the laminate was exposed, for 4 minutes, through a standard photo-tool, having 170 µm lines and spaces, disposed on the Melinex (RTM) film. Twenty minutes after the end of exposure, the Melinex (RTM) film was removed and the solid layer was washed with 1,1,1-trichloroethane for 1 minute; a resist pattern consisting of approximately 170 micron lines and spaces was thereby produced.

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Claims

1. A polymerisable composition comprising

(a) at least one polymerisable olefinically unsaturated oligomer which

(i) comprises the repeating units $-\text{Ar}^1-\text{CHR}^1-$ wherein Ar^1 is an aromatic group, or a suitable

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15	3	0.5	5	30	2	7
16	4	0.5	5	30	2	7
17	5	0.5	5	30	2	4
18	6	0.5	7	30	2	11
19	7	0.5	8	30	2	10
20	8	0.5	5	30	2	7
21	9	0.5	4	20	1	11
22	10	4	3	5	1	11
23	10	288	3	5	1	11
24	11	4	3	5	1	11
25	11	288	3	5	1	11
26	12	4	3	5	1	8
27	12	288	3	5	1	8
28	13	4	3	5	1	10
29	13	288	3	5	1	a

a : Not determined.

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Examples 14 to 29 were repeated except that a Stouffer step wedge was not used, that after removal of the Melinex (RTM) film the washing step was omitted and the cured layer was post-cured by exposure for 4 hours (Examples 14—21) or 1 hour (Examples 22—29) to a Philips HPR 125w mercury discharge

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reprographic lamp at a distance of 40 centimetres. The post-cured layer was unaffected by 3 drops of methylene chloride disposed on its surface for 1 minute.

The board and post-cured layer were dipped in Multicore Rosin Foam Flux PC26. After the flux-treatment a first portion was placed, resist surface down, for 30 seconds on a 60:40 tin-lead solder bath at 285°C; a second portion was placed, resist surface down, on the solder bath for 6 seconds, removed for 21 seconds and contacted for a further 6 seconds. Both portions were cleaned with 1,1,1-trichloroethane and the result was found to be neither dulled nor blistered. A 2 mm cross-hatch pattern was produced on both portions, pieces of 3M Scotch (RTM) 610 tape were pressed firmly against the surface of both resists and removed with a sharp tug. Less than 5% of the resist was removed from the board.

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Examples 14—21 were repeated except that the laminate was exposed, for 4 minutes, through a standard photo-tool, having 170 µm lines and spaces, disposed on the Melinex (RTM) film. Twenty minutes after the end of exposure, the Melinex (RTM) film was removed and the solid layer was washed with 1,1,1-trichloroethane for 1 minute; a resist pattern consisting of approximately 170 micron lines and spaces was thereby produced.

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Claims

1. A polymerisable composition comprising

(a) at least one polymerisable olefinically unsaturated oligomer which

(i) comprises the repeating units $-(Ar^1-CHR^1)-$ wherein Ar^1 is an aromatic group, or a suitable

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substituted derivative thereof, each of which aromatic groups may be the same or different; and R¹, each of which groups in the oligomer backbone may be the same or different, is hydrogen or a hydrocarbyl group; and

- (ii) has pendant and/or terminal acyloxymethyl groups in which the acyl group is derived from an olefinically unsaturated carboxylic acid;
- (b) one or more polymeric binders which has a molecular weight of between 10,000 and 1,000,000; and
- (c) a photoinitiator system for initiating polymerisation of the at least one oligomer.
- 2. A polymerisable composition as claimed in claim 1 wherein the aromatic groups Ar¹ in the at least one polymerisable olefinically unsaturated oligomer have the structure $\text{---}\text{O---Y}^1\text{---O---}$ wherein O is a phenylene group and Y¹ is (i) a direct link between two phenylene groups, or
- (ii) a divalent residue which contains one or more in-chain atom each of which may be carbon or a hetero atoms and may have one or more atoms appendant thereto.
- 3. A polymerisable composition as claimed in claim 2 wherein Y¹ is oxygen.
- 4. A polymerisable composition as claimed in claim 1 wherein the at least one polymerisable olefinically unsaturated oligomer is derived from formaldehyde.
- 5. A polymerisable composition as claimed in claim 1 wherein the oligomer has on average between 2 and 6 pendant and/or terminal acyloxymethyl groups per oligomer molecule.
- 6. A polymerisable composition as claimed in claim 1 wherein the oligomer has a number average molecular weight of between 900 and 1100 and a weight average molecular weight of between 1900 and 2500.
- 7. A polymerisable composition as claimed in claim 1 wherein the polymeric binder is a homo- or co-polymer of methyl methacrylate.
- 8. A polymerisable composition as claimed in claim 1 wherein the photo-initiator system is based on dimethoxyphenyl-acetophenone and/or diethoxy-acetophenone.
- 9. A polymerisable composition as claimed in claim 1 which comprises (a) 55—85% w/w of one or more oligomers, (b) 10—30% w/w of one or more methyl methacrylate homo- or co-polymers, (c) a photoinitiator system and optionally (d) various additives as hereinbefore defined, the combined weight percentages of components (a)—(d) totalling 100%.
- 10. A three-layer element comprising a polymerisable composition as claimed in claim 1 sandwiched between a support film and a cover film.
- 11. A process for the preparation of a three-layer element as claimed in claim 10 which process comprises applying the polymerisable composition according to claim 1 to the support film to form a substantially tack-free solid layer on one surface thereof and then laminating the cover film to the substantially tack-free solid layer.
- 12. A process for the preparation of a non-strippable resist on a surface which process comprises the steps of
 - (a) applying to the surface a first surface of a solid layer of a polymerisable composition as claimed in claim 1, the second surface of the said layer having adhering thereto a thin flexible polymeric support film, then in either order;
 - (b) exposing the layer, imagewise, to actinic radiation to form a polymeric image in the layer; and
 - (c) stripping the support, film from the layer; then
 - (d) washing away the unexposed areas of the layer to form a resist image of polymeric material; and
 - (e) post-curing the resist image.
- 13. An aromatic/aldehyde oligomer as defined in claim 6, further characterised in that the oligomer has on average between 3 and 4 pendant and/or terminal aryloxymethyl groups per oligomer molecule.

Patentansprüche

- 1. Polymerisierbare Zusammensetzung, dadurch gekennzeichnet, daß sie
 - (a) mindestens ein polymerisierbares olefinisch ungesättigtes Oligomer, das
 - (i) die Struktureinheit $\text{---Ar}^1\text{---CHR}^1\text{---}$ enthält, worin Ar¹ eine aromatische Gruppe oder ein geeignet substituiertes Derivat derselben ist, wobei jede der aromatischen Gruppen gleich oder verschieden sein kann; und R¹, wobei jede dieser Gruppen in der oligomeren Hauptkette gleich oder verschieden sein kann, ein Wasserstoffatom oder einen einwertige Kohlenwasserstoffgruppe ist; und
 - (ii) seitenständige und/oder endständige Acyloxymethylgruppen hat, in denen die Acylgruppe von einer olefinisch ungesättigten Carbonsäure abgeleitet ist;
 - (b) ein oder mehr als ein polymeres Bindemittel besitzt, das ein Molekulargewicht zwischen 10.000 und 1.000.000 hat; und
 - (c) ein Fotoinitiatorsystem für die Initiierung der Polymerisation des mindestens einen Oligomers umfaßt.
- 2. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die aromatischen Gruppen Ar¹ in dem mindestens einen polymerisierbaren olefinisch ungesättigten Oligomer die Struktur $\text{---O---Y}^1\text{---O---}$ besitzen, worin O eine Phenylengruppe und Y¹ (i) eine direkte Bindung zwischen zwei Phenylengruppen oder (ii) ein zweiwertiger Rest ist, der ein oder mehr als ein innenkettiges Atom



enthält, wobei jedes von diesen Atomen ein Kohlenstoff- oder ein Heteroatom sein kann und ein oder mehr als ein daran hängendes Atom besitzen kann.

3. Polymerisierbare Zusammensetzung nach Anspruch 2, dadurch gekennzeichnet, daß Y^1 Sauerstoff ist.

5 4. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das mindestens eine polymerisierbare, olefinisch ungesättigte Oligomer von Formaldehyd abgeleitet ist.

5. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Oligomer durchschnittlich zwischen 2 und 6 seitenständige und/oder endständige Acyloxymethylgruppen pro Oligomermolekül besitzt.

10 6. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Oligomer ein Durchschnittsmolekulargewicht (Zahlenmittel) zwischen 900 und 1100 und ein Durchschnittsmolekulargewicht (Massemittel) zwischen 1900 und 2500 besitzt.

7. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das polymere Bindemittel ein Homo- oder Copolymer von Methylmethacrylat ist.

15 8. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Fotoinitiatorsystem auf Dimethoxyphenylacetophenon und/oder Diethoxyacetophenon basiert.

9. Polymerisierbare Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie (a) 55—85 Masse-% eines oder mehrerer Oligomere, (b) 10—30 Masse-% eines oder mehrerer Methylmethacrylat-Homo- oder -Copolymere,

20 (c) ein Fotoinitiatorsystem und (d) wahlweise verschiedene Additive, wie vorstehend definiert, enthält, wobei sich die Prozentsätze der Komponenten (a)—(d) zu insgesamt 100% addieren.

10. Dreischichtiges Bauteil, dadurch gekennzeichnet, daß es eine polymerisierbare Zusammensetzung nach Anspruch 1 enthält, die schichtweise zwischen einer Trägerfolie und einer Deckfolie angeordnet ist.

25 11. Verfahren für die Herstellung eines dreischichtigen Bauteils nach Anspruch 10, dadurch gekennzeichnet, daß es das Aufbringen der polymerisierbaren Zusammensetzung nach Anspruch 1 auf die Trägerfolie zur Bildung einer im wesentlichen nicht klebenden festen Schicht auf einer Oberfläche derselben und die nachfolgende Laminierung der Deckfolie auf die im wesentlichen nicht klebende feste Schicht umfaßt.

12. Verfahren zur Herstellung eines nicht abziehbaren Photolacks auf einer Oberfläche, dadurch gekennzeichnet, daß das Verfahren die folgenden Schritte umfaßt:

(a) Aufbringen einer ersten Oberfläche einer festen Schicht einer polymerisierbaren Zusammensetzung nach Anspruch 1 auf die Oberfläche, wobei die zweite Oberfläche der genannten Schicht eine an ihr haftende, dünne, flexible, polymere Trägerfolie besitzt, dann in irgendeiner Reihenfolge:

35 (b) bildweises Belichten der Schicht mit einer aktinischen Strahlung, um eine polymeres Bild in der Schicht zu erzeugen; und

(c) Abziehen der Trägerfolie von der Schicht; dann

(d) Wegwaschen der unbelichteten Flächen der Schicht, um eine Photolackbild des polymeren Materials zu erzeugen; und

40 (e) Nachhärten des Photolackbildes.

13. Aromatisch/aldehydisches Oligomer, wie in Anspruch 6 definiert, ferner dadurch gekennzeichnet, daß das Oligomer durchschnittlich 3 bis 4 seitenständige und/oder endständige Acyloxymethylgruppen pro Oligomermolekül besitzt.

45 Revendications

1. Composition polymérisable, comprenant

(a) au moins un oligomère polymérisable à non-saturation oléfinique qui

50 (i) comporte les motifs répétés $-(Ar^1-CH(R^1)-)$ dans lesquels Ar^1 est un groupe aromatique ou un dérivé substitué convenable de ce groupe, lesdits groupes aromatiques pouvant être identiques ou différents; et les groupes R^1 , qui peuvent être identiques ou différents dans le squelette de l'oligomère, représentent l'hydrogène ou un groupe hydrocarbyle; et

(ii) porte des groupes acyloxyméthyle latéraux et/ou terminaux dont le groupe acyle est dérivé d'un acide carboxylique à non-saturation oléfinique;

55 (b) un ou plusieurs liants polymériques de poids moléculaire compris entre 10 000 et 1 000 000; et

(c) un système photo-initiateur destiné à déclencher la polymérisation de l'oligomère dont il existe au moins un représentant.

2. Composition polymérisable suivant la revendication 1, dans laquelle les groupes aromatiques Ar^1 de l'oligomère polymérisable à non-saturation oléfinique dont il existe au moins un représentant, ont la formule $-\phi-Y^1-\phi-$ dans laquelle ϕ est un groupe phénylène et Y^1 représente (i) une liaison simple entre deux groupes phénylène, ou (ii) un résidu divalent qui contient un ou plusieurs atomes en chaîne, chacun pouvant être un atome de carbone ou un hétéro-atome et pouvant porter un ou plusieurs atomes attachés.

3. Composition polymérisable suivant la revendication 2, dans laquelle Y^1 est l'oxygène.

65 4. Composition polymérisable suivant la revendication 1, dans laquelle l'oligomère polymérisable à



non-saturation oléfinique dont il existe au moins un représentant est dérivé du formaldéhyde.

5. Composition polymérisable suivant la revendication 1, dans laquelle l'oligomère porte en moyenne 2 à 6 groupes acyloxyméthyle latéraux et/ou terminaux par molécule d'oligomère.

6. Composition polymérisable suivant la revendication 1, dans laquelle l'oligomère a une moyenne en nombre du poids moléculaire comprise entre 900 et 1100 et une moyenne en poids du poids moléculaire comprise entre 1900 et 2500.

7. Composition polymérisable suivant la revendication 1, dans laquelle le liant polymérique est un homopolymère ou un copolymère de méthacrylate de méthyle.

8. Composition polymérisable suivant la revendication 1, dans laquelle le système photo-initiateur est à base de diméthoxyphényl-acétophénone et/ou de diéthoxyacétophénone.

9. Composition polymérisable suivant la revendication 1, qui comprend (a) 55 à 85% en poids d'un ou plusieurs oligomères, (b) 10 à 30% en poids d'un ou plusieurs homopolymères ou copolymères de méthacrylate de méthyle, (c) un système photo-initiateur et, à titre facultatif, (d) divers additifs tels que définis ci-dessus, les pourcentages en poids cumulés des composants (a) à (d) totalisant 100%.

10. Élément à trois couches, comprenant une composition photopolymérisable suivant la revendication 1 intercalée entre un film de support et un film de protection.

11. Procédé de préparation d'un élément à trois couches suivant la revendication 10, qui consiste à appliquer la composition polymérisable suivant la revendication 1 au film de support pour former une couche solide pratiquement non collante à sa surface puis à stratifier le film protecteur sur la couche solide pratiquement non collante.

12. Procédé de préparation d'une réserve non détachable sur une surface, procédé qui comprend les étapes consistant

(a) à appliquer à la surface une première surface d'une couche solide d'une composition polymérisable suivant la revendication 1, à la seconde surface de laquelle adhère un mince film de support polymérique flexible, puis dans un ordre quelconque;

(b) à exposer la couche, d'après une image, à une radiation actinique pour former une image polymérique dans la couche; et

(c) à détacher le film de support de la couche; puis

(d) à enlever par lavage les zones non exposées de la couche pour former une image de réserve de matière polymérique; et

(e) à effectuer une post-maturation de l'image de réserve.

13. Oligomère aromatique/aldéhydique suivant la revendication 6, caractérisé en outre en ce qu'il porte en moyenne, par molécule, entre 3 et 4 groupes aryloxyméthyle latéraux et/ou terminaux.

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