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Polymers, the rubber-elastic behavior of which does not depend on a chemical crosslinking of linear, highly polymeric molecules, but is caused by a physical interaction between specific parts of the molecules, are known in the art.

In particular, polyurethanes containing polyether or polyester blocks have gained significance as elastomers of this type. Thus, French Patent 2,324,666 describes polyether-urethanes which contain units formed from polyether-diols, specific low-molecular diols and aromatic diisocyanates. French Patent 2,313,410 describes polyether-esters which contain urethane groups and units formed from polyethylene adipate, 1,4-butane diol and aromatic diisocyanates. Polymers of this type are normally no longer accessible to crosslinking reactions.

From German Offenlegungsschrift 29 37 266 photo-hardenable coating compounds for building materials are known, which contain photopolymerizable (meth)acrylic acid esters, ketone resins and photoinitiators. The photopolymerizable compounds are reaction products of (meth)acrylic acid esters of epoxy compounds and polyisocyanates. The compounds are especially suitable

for the production of weatherproof coatings. Less than one third of the mass of these compounds is comprised of ketone resin and they are normally liquid without the addition of a solvent and are, therefore, unsuitable for use in the production of storable light-sensitive recording materials.

U. S. Patent 3,836,492 discloses polymerizable coating compounds which contain reaction products of (meth)acrylic acid and dicarboxylic acid diglycidyl esters, further reacted with diisocyanates, and optionally photoinitiators. They do not contain any polymeric binders and are, therefore, more or less viscous products.

Polyurethanes of a similar structure are also used for the production of photopolymerizable recording materials, for example, for printing plates and photoresists. These polyurethanes have in most cases the character of viscous to highly viscous liquids, or solids. They are normally used as a mixture with other components.

These mixtures contain, as essential constituents, a compound which can be polymerized by free radicals and has terminal, ethylenically unsaturated groups, a binder and an initiator which can be activated by radiation.

Polymerizable mixtures of this type are disclosed,

for example, in U.S. Patents 2,760,863,
3,060,023 and 3,149,975. The polymerizable, ethyleni-
cally unsaturated compounds described in these texts are
low-molecular and high-molecular compounds having terminal
5 or lateral vinyl or vinylidene groups, in particular
acrylic and methacrylic acid esters of low-molecular or
high-molecular polyhydroxy compounds. In practice,
polymerizable compounds which have hitherto gained accep-
tance are almost exclusively photopolymerizable materials
10 based on such esters. Of these compounds, it is parti-
cularly the low-molecular compounds which have been
employed preferentially in industry.

Such mixtures are used in reproduction technology
for the production of printing plates, photoresists, that
15 is to say etch resists and electro-plating resists,
and relief images which may be colored.

A particular group of mixtures of this type, which
are used for the production of photoresists, is used in
the form of a dry, photopolymerizable layer on a temporary
20 support formed from a transparent flexible plastic film,
the layer being laminated under pressure and heat to a
metal carrier, for example a copper plate, which is to be
modified image-wise, the layer being exposed there
and developed to give a photoresist. Such
25 materials and methods of processing are described, for
example, in German Auslegeschrift 1,522,515 and German
Offenlegungsschrift 2,064,079.

The polymerizable compounds used in such mixtures
are frequently compounds which contain urethane groups

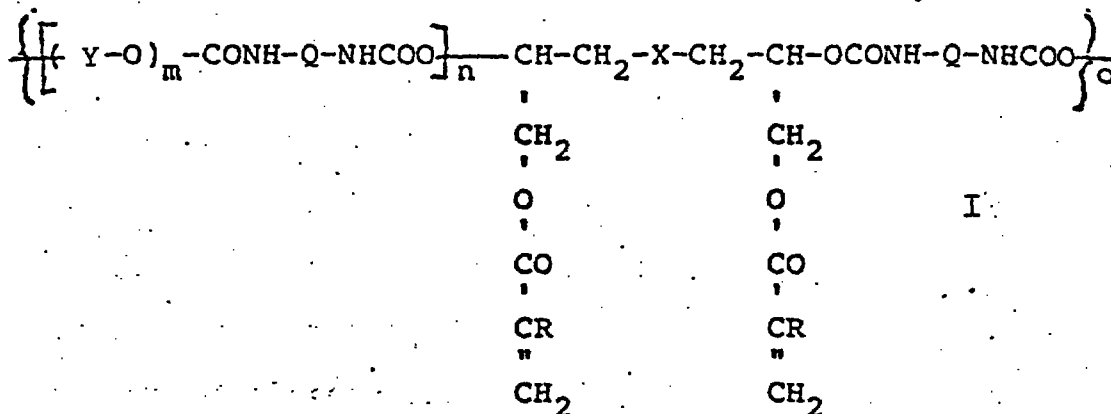


and have terminal acrylic or methacrylic acid ester groups and which can also contain oligo-ether units. Mixtures which contain such oligomeric, polymerizable compounds and which in most cases have a particularly good flexibility are described, for example, in German Offenlegungsschriften 2,822,189, 2,822,190 and 2,822,191, in German Auslegeschrift 2,115,373 and in U.S. Patents 3,850,770 and 3,960,572.

Oligo-urethane compounds of the type described here have also been disclosed for the production of synthetic elastomers having advantageous properties, as is disclosed, for example, in British Patent 1,441,108.

It was the object of the invention to propose radiation-polymerizable mixtures which are distinguished by good flexibility in the non-crosslinked and cross-linked state and which, at the same time, exhibit a very low degree of cold flow in the non-crosslinked state.

According to the invention, a radiation-polymerizable mixture is provided, which contains, as the essential constituents, 40 to 70 % by weight of a binder which is soluble in aqueous-alkaline solutions, a sufficient quantity of a polymerization initiator which can be activated by radiation to initiate the radiation-initiated free-radical polymerization and 30 to 60 % by weight of polymerizable acrylic or methacrylic acid esters and which is characterized in that 10 to 60 % by weight of the quantity of the esters comprise a compound of the general formula I



wherein Q is a divalent, mononuclear or dinuclear aromatic radical which is unsubstituted or is substituted by lower alkyl groups and which can contain, as a linking member, a lower alkylene group, X is one of the groups -O-Ph-Z-Ph-O- and -OOC-(CH₂)_y-COO-, Ph being an optionally substituted phenylene group, Z being an alkylene group having 1 - 4 carbon atoms and y being a number from 2 to 12, R is a hydrogen atom or a methyl group, Y is an alkylene radical having 2 to 6 carbon atoms, m is a number from 4 to 50, n is a number from 1 to 6 and o is a number from 4 to 20, and that the remainder of the polymerizable esters comprise low-molecular acrylic or methacrylic acid esters of dihydric or polyhydric alcohols.

The polyether-ester-urethanes of formula I comprise rubber-elastic linear polymers which are soluble in numerous organic solvents and miscible within wide ratios with many low-molecular, difunctional and polyfunctional acrylic and methacrylic acid esters. They form homogeneous phases with numerous polymeric binders and are



thus particularly suitable for the production of homogeneous, light-sensitive negative-acting layers. It is surprising that these elastic, polymeric urethanes, which on their own cannot be dispersed in aqueous alkalis, produce, in combination with specific acrylates and polymeric binders, layers which can be developed using purely aqueous, solvent-free or predominantly solvent-free developers.

The high elasticity and flexibility of the polymeric urethanes also makes it possible to produce layers which are distinguished, above all in the exposed state too, by good toughness and resistance to abrasion, a property which can be utilized in the case of dry and liquid resists, in dry and liquid solder-stop masks and in printing plates. A further advantage is that the rheological behavior of such layers is particularly adaptable to special technological requirements. For example, in the case of a dry resist which has been processed to give roll material, it is possible virtually to suppress, even under warm storage conditions, the

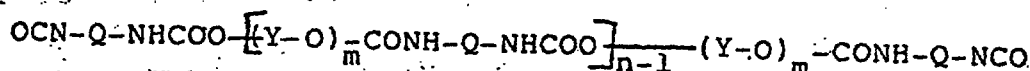


adhesion of the border at the cut edges which causes so many problems.

The preparation of these polyether-ester-urethanes having ethylenically unsaturated side groups is effected in a known manner by reacting oligomeric diisocyanates with specific hydroxyalkyl acrylates or methacrylates.

The starting components are as follows:

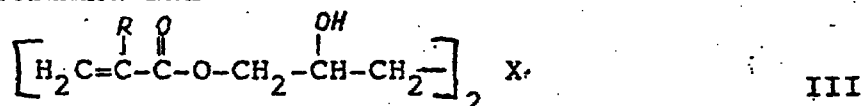
A. Fluid to viscous, oligomeric, linear ether-urethanes containing isocyanate end groups of the general formula II



II

wherein the symbols Q, m, n and Y have the meaning indicated above. These oligomeric, commercially available ether-urethanes are prepared in accordance with known processes by reacting polyether diols with tolylene diisocyanates in a molar excess. This gives a mixture of homologous oligomers containing isocyanate end groups. Resins of a viscous consistency are obtained if the molar excess in this reaction is selected so that the average value of n is within the range from 1 to 4.

B. Bis-acrylic acid ester-diols of the general formula III



III

wherein X and R have the meaning indicated above.

The elastic polyurethanes are obtained by polyaddition of the components A and B.

The properties of the polymers can be varied and, above all their rubber-elasticity can be considerably improved by intermolecular polymerization of the acrylate groups.

5 The polyaddition reactions are carried out by known processes. The reactions can be carried out in non-polar and polar solvents, for example in toluene, acetone, ethyl methyl ketone or tetrahydrofuran. The reaction can be accelerated by heating the reaction media, 10 and it is also advisable to use a catalyst, for example tin-II laurate, or a metal chelate, such as iron trisacetyl-acetate. After the polyaddition reaction has been carried out, the polymers can be isolated by removing the solvent, for example by distillation or freeze-drying, 15 if appropriate they can, however, also be precipitated and filtered off by stirring the reaction mixtures into other liquid media, for example methanol. The polyaddition reactions can also be carried out in the absence of a solvent, by intimately mixing the components, if 20 appropriate with the addition of catalysts, in suitable mixers, for example cam kneaders, and, if appropriate, warming in the course of this process.

Linear, non-crosslinked polyurethanes which still contain the acrylate groups mentioned above, are obtained 25 in all cases. These polymers possess rubber-elastic properties and they are thermoplastic.

Depending on the application, the molecular weights of the polyurethanes can vary within wide ranges. In general, advantageous products are obtained if the reduced specific viscosities (RSV), measured on 1% strength solutions in dimethylformamide at 25 °C, are about 0.15 to 1.4 dl/g. Products having RSV values within the range from 0.2 to 0.9 dl/g are preferred.

Preferred average values of m are 8-20, of n 2-4, of o 5-12 and of y 2-6.

10 Q is a mononuclear or dinuclear arylene group which generally has 6 to 20 carbon atoms. The aromatic nuclei can be substituted by lower alkyl groups having 1 to about 4 carbon atoms. If two aromatic nuclei are present, these can be condensed with one another or linked
15 by means of a single valency or via an alkylene group having 1 to 4 carbon atoms. The following are examples of suitable arylene groups: phenylene, tolylene, xylylene, naphthylene, diphenylene and methyl-substituted and ethyl-substituted diphenylene groups, and diphenylmethane and
20 2,2-diphenylpropane groups having free valencies in the 2-, 3- or 4-position of both nuclei, preferably in the 4,4'-position.

Y is a linear or branched alkylene group. Preferred representatives are ethylene, 1,2-propylene and 1,4-butylene groups.

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Z is an alkylene group in which the free valencies are preferably at one C atom. Preferred groups are methylene groups, 1,1-ethylene groups and 2,2-propylene groups.

5 The phenylene groups attached to Z can be substituted, for example, by alkyl groups having 1 - 4 C atoms, alkoxy groups having 1-4 C atoms or halogen atoms. Owing to their ready accessibility, compounds having unsubstituted phenylene groups are preferred.

10 R is preferably a methyl group.

 As already mentioned, the unsaturated polyurethanes are used as photoreactive compounds in photopolymerizable mixtures or mixtures which can be polymerized by radiation. In this case, they are employed with an initiator which
15 can be activated by radiation, particularly by light, a polymeric binder, generally a saturated binder and, in order to improve the light-sensitivity and, in some cases, the developability of the layer with aqueous solutions, combined with other low-molecular acrylic
20 or methacrylic acid esters.

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In general, the polymerizable mixture contains 20 to 100, preferably 30 to 60, % by weight of polymerizable or crosslinkable compounds and 0 to 80, preferably 40 to 70, % by weight of binders. In turn, 5 5 to 100, preferably 10 to 60, % by weight of the polymerizable compounds can consist of urethanes according to formula I.

Suitable low-molecular acrylic or methacrylic acid esters are the esters of these acids with dihydric or polyhydric alcohols, for example ethylene glycol, 10 diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of 200 to 1,000, 1,4-butane diol, neopentylglycol, trimethylolethane, trimethylolpropane, 1,3-butane diol and bisphenol A/ 15 bis-hydroxyethyl ether. The low-molecular bis-acrylates and bis-methacrylates which contain urethane groups and which are obtained by reacting 2 moles of a hydroxyalkyl acrylate or methacrylate with 1 mole of an aliphatic or cycloaliphatic diisocyanate, for example 20 2,2,4-trimethylhexamethylene diisocyanate, are also suitable.

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The mixtures according to the present invention also contain binders which are soluble or at least swellable in aqueous alkaline solutions, since layers containing such binders can be developed with the preferred aqueous alkaline developers.

5 Binders of this type can contain the following groups, for example: $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{NH}_2$ and $-\text{SO}_2-\text{NH}-\text{CO}-$. The following may be mentioned as examples of these: maleate resins, polymers formed from N-(p-tolyl-sulfonyl)-carbamic acid β -methacryloyloxyethyl esters
10 and copolymers of these and similar monomers with other monomers, styrene/maleic anhydride copolymers and methyl methacrylate/methacrylic acid copolymers.

Copolymers which are particularly advantageous are those formed from methacrylic acid, alkyl methacrylates
15 and methyl methacrylate and/or styrene, acrylonitrile and others, such as are described in German Offenlegungsschriften 2,064,080 and 2,363,806. Styrene/maleic anhydride or styrene/maleic acid ester copolymers can also be employed successfully.

20 A large number of substances can be used as photo-initiators in the mixture according to the invention. Examples are benzoin, alkylbenzoin, benzoin ethers, multi-nuclear quinones, for example 2-ethylanthraquinone,

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or acridine derivatives, for example 9-phenyl acridine, 9-p-methoxyphenyl acridine, 9-acetylamino acridine or benz(a) acridine; phenazine derivatives, for example 9,10-dimethylbenz(a) phenazine, 9-methylbenz(a) phenazine 5 or 10-methoxybenz(a) phenazine, quinoxaline derivatives, for example 6,4',4"-trimethoxy-2,3-diphenyl quinoxaline or 4',4"-dimethoxy-2,3-diphenyl-5-aza quinoxaline, or quinazoline derivatives.

Besides monomers, binders and photoinitiators, 10 the mixtures according to the invention can also contain a number of further customary additives, for example inhibitors for preventing thermal polymerization of the monomers, hydrogen donors, sensitometric regulators, dyestuffs, colored pigments, non-colored pigments, 15 color precursors, indicators and plasticizers.

These constituents should appropriately be chosen in such a way that, as far as possible, they do not have too strong an absorption in the actinic range of wave-lengths which is important for the initiation process.

20 Actinic radiation should be understood as meaning any radiation which has an energy corresponding at least to that of short-wave, visible light. Long-wave UV radiation is particularly suitable, but electron radiation, X-ray radiation and laser radiation are also suitable.

25 The photopolymerizable mixture according to the invention can be put on the market dissolved, in a known manner, in solvents or solvent mixtures and can be employed in a variety of ways by the consumer, for example for the production of electro-plating resists, etch resists, special



stencils for screen printing and solder-stop masks.

The mixtures according to the invention can also be used for the production of dry resist films. These are composed of a finished photo-resist layer which is present
5 on a temporary support, for example a transparent plastic film, and which is laminated by the consumer to the support which is to be etched or electro-plated image-wise, and is exposed and developed there, the temporary support being removed before development.

10 The mixture according to the invention is particularly suitable for this form of application. However, it can also be produced on a factory scale in the form of a presensitized copying material on a suitable support, for example on aluminum or zinc, for the photomechanical
15 production of offset or letterpress formes, for example flexographic printing formes. It is also suitable for the production of relief images, screen printing stencils, color-proofing films and the like. Its advantages become effective in all cases where good and perma-
20 nent flexibility and elasticity of the exposed layer together with low cold flow of the unexposed layer are required as well as high resistance of the exposed layer to corrosive chemicals.

Production of the light-sensitive materials
25 using the mixture according to the invention is effected in a known manner. Thus the mixture can be taken up in a solvent and the solution or dispersion can be applied in the form of a film to the intended support by casting, spraying, dipping or roller application and the

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like, and can then be dried. Thick layers (for example layers of 250 μ m and more) can also be produced by extrusion or compression in the form of a self-supporting film which is then laminated to the support.

5 Suitable supports for the mixtures which have been processed to give copying layers are metals, for example aluminum, zinc, copper, steel, chromium, brass and other metal alloys; screen printing stencil supports, for example those made of nickel or Perlon gauze; and
10 plastic films, it being possible to give a special surface treatment to the plastic films, for example polyester films.

The copying layers are exposed and developed in a known manner. Suitable developers are aqueous solutions, preferably aqueous alkaline solutions, for example
15 solutions of alkaline metal phosphates, carbonates or silicates, to which, if desired, small quantities, for example up to 10% by weight of water-miscible organic solvents or wetting agents can be added. Layers in
20 which the proportion of polymerizable compounds consists mainly of the polyurethanes corresponding to formula I require a relatively high proportion of organic solvent for development. Development can be effected by hand or in commercially available spray or brush developing
25 machines.



As mentioned above, the mixtures according to the invention can be employed for a very wide variety of fields of application. They are used with particular advantage for the production of photoresist layers or
5 etch resists on metallic supports. They are suitable above all for application to copper supports. The excellent adhesion and flexibility of the exposed parts of the layer proves successful in these preferred application forms, not only during development, but also during
10 subsequent etching of the support, in which the layers exhibit good flexibility and resistance to etching.

The mixtures can be employed and handled particularly well in the form of so-called dry resist materials, such as have been mentioned above, since they can also be
15 transferred in a dry state onto metal supports to form well-adhering layers. In this case, polyester films are particularly suitable as temporary supporting films.

The examples which follow illustrate individual embodiments of the mixture according to the invention.
20 Unless otherwise specified, percentages and quantity ratios are to be understood as meaning weight units. Parts by weight and parts by volume are in the same ratio as g to ml.

Example 1

25 A solution was prepared from the following:
6.5 parts by wt. of a terpolymer formed from n-hexyl methacrylate, methacrylic acid and styrene (60:30:10) having an average molecular weight of approx. 35,000 and an acid number of 195,

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3.2 parts by wt. of polyethylene glycol 400 dimethacrylate,
0.8 part by wt. of the elastomer described below,
0.1 part by wt. of 9-phenyl acridine,
0.035 part by wt. of an azo dyestuff obtained by coupling a 2,4-dinitro-6-chlorobenzenediazonium salt with 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxy-ethylaniline,

2.5 parts by wt. of methyl ethyl ketone and
3 parts by wt. of ethanol.

10 The elastomer used was prepared as follows:

A. 426 parts by wt. of glycidyl methacrylate and 216 parts by wt. of adipic acid were mixed by stirring in a 1 liter four-necked flask, equipped with a stirrer, a thermometer, a reflux condenser and a drying tube, and, after adding 19.7 parts by wt. of p-methoxyphenol and 6.4 parts by wt. of benzyl triethylammonium chloride, the mixture was heated cautiously to an internal temperature of 80°C. A clear solution was obtained after approx. 2 hours, and this was kept at 80°C for a further 14 hours. After this time, the content of free glycidyl methacrylate was less than 0.5%.

B. 143 parts by wt. of an oligomeric diisocyanate of the formula II indicated above, Q being the tolylene radical and Y being the 1,4-butylene radical and which had a mean molecular weight of about 2,000 and an isocyanate group content of 4.1 % by wt. (Adiprene L 100), dissolved in 300 parts by vol. of methyl ethyl ketone, were placed in a 1 liter four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, a condenser and a drying tube, and 0.87 part by wt. of benzoquinone and 0.85

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part by vol. of a solution prepared by dissolving 6.3 parts by wt. of iron-III acetylacetonate and 0.45 part by weight of triethylamine in methyl ethyl ketone and making up to 100 parts by vol. with methyl ethyl ketone, 5 were added. A solution of 31.33 parts by wt. of the reaction product obtained in accordance with A in 300 parts by vol. of methyl ethyl ketone was filled into the dropping funnel and was added dropwise, in the course of 40 minutes, to the solution in the flask, which had been 10 heated to 70°C and was stirred. After stirring for a further two hours at 30°C, 10 parts by vol. of ethanol were added to the clear reaction mixture. Distilling off the solvent from the viscous solution gave a non-adhesive, rubberlike mass, which was soluble, giving a 15 clear solution, in a large number of organic solvents, such as tetrahydrofuran, acetone or toluene. The reduced specific viscosity of the product was 0.72 dl/g (measured on a 1% strength solution in dimethylformamide at 25°C).

20 This coating solution was applied by spin-coating onto a biaxially stretched and thermofixed polyethylene terephthalate film 25 μm thick in such a way that a layer weight of 45 g/m^2 was obtained after drying at 100°C.

The resulting dry resist film was laminated at 25 120°C, using a commercially available laminating device, to a phenoplast laminated sheet backed with a copper foil 35 μm thick, and was exposed for 4 seconds using a commercially available exposure apparatus (output 5 kW). The image used was a line original which had

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line widths and intervals down to 60 μm .

After exposure, the polyester film was stripped off and the layer was developed in a 0.8% strength sodium carbonate solution for 60 seconds in a spray processor.

The sheet was rinsed with tap water for 30 seconds, subjected to incipient etching for 30 seconds in a 15% strength solution of ammonium peroxydisulfate and was then electro-plated successively in the following electrolyte baths:

1. 40 minutes in a type "Glanz kupfer-Bad" copper electrolyte bath made by Schlötter, Geislingen/Steige: current density 2.5 A/dm²
metal build-up approx. 20 μm
2. 10 minutes in a type "Norma" nickel bath made by Schlötter, Geislingen/Steige: current density 5 A/dm²
metal build-up 10 μm
3. 10 minutes in a type "Autronex CC" gold bath made by Blasberg, Solingen: current density 1.0 A/dm²
metal build-up 2.0 μm .

The electrolytic pattern produced on the sheet exhibited no sub-layer phenomena or damage at any point. This sheet could be stripped in a 5% strength KOH solution at approx. 40 - 50°C. The copper exposed in this way can be removed by etching in customary etching agents.

This example was carried out as follows on an industrial scale:

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A polyester film web 110 cm wide was continuously coated with a solution of the composition indicated above, using a slot die. After passing through a drying zone, the resist layer had a thickness of 38 μm , and it was covered with a polypropylene film. The dry resist film thus produced was stored on a large roll. The large roll was then cut up by means of a slitting machine into manageable resist rolls having a width of 45 cm and a web length of 50 m. An optimum winding tension was set in order to ensure that the roll was built up uniformly, layer for layer, over the supporting core and did not slip sideways, that is to say did not telescope. Rolls produced in this way were stored in a drying cabinet at 40°C.

Even after storage times of more than 12 weeks, the cut edges of the rolls were unaffected and were completely free from emergence of resist which would lead to sticking. This dry resist could be processed in the same manner as above.

The dry resist described above was very elastic and flexible, even when overexposed 10 times, that is to say after 40 seconds exposure in the exposure apparatus described. An exposed resist strip can, for example, be bent through 180° several times at room temperature without the bent area tearing. The resist can be extended by a factor of 3 to 4 by stretching. This behavior is important, for example when manually retouching finished printed circuit boards. Flexible resists are also required for the manufacture of through-hole



plated circuits ("Tenting process").

The layers described make it possible to resolve, with sharp outlines, lines of a width of 80 μm ; the resist flanks stand upright on the base copper. This behavior was demonstrated by exposure using an appropriate resolving test original and subsequently developing with 0.8% strength sodium carbonate solution. The developer resistance was then at least five times the development time.

10 Example 2

The solution described in Example 1 was spin-coated onto a phenoplast laminated sheet having a backing of copper foil 35 μm thick in such a way that a dry weight of 37 - 38 g/m^2 was obtained. The sheet was then dried for 3 minutes at 100°C in a circulating air drying cabinet. The sheet thus produced was treated further in complete analogy with Example 1, but using a line original having line widths and intervals down to 5 μm . When exposed in this way directly through the line original, which acted as an exposure mask, without a PET intermediate film, electroplated tracks were resolved, with sharp outlines, down to a width of 25 μm .

Example 3

The procedure followed was as in Example 1, using 0.7 part by wt. of the product described in the following text instead of the elastomer used in Example 1:

177 parts by wt. of the diisocyanate indicated in Example 1 under B in 250 parts by vol. of methyl ethyl ketone were initially placed in a 1 liter three-necked

flask, equipped with a thermometer, a dropping funnel, a condenser, a drying tube and a magnetic stirrer, and 1 part by wt. of 1,4-benzoquinone, 0.05 part by wt. of iron-III acetylacetonate and 2 parts by vol. of a 1% strength
5 solution of triethylamine in methyl ethyl ketone were added.

After this solution had been heated to 60°C, a solution of 45.3 parts by wt. of 2,2-bis-[4-(2-hydroxy-3-methacryloyloxy-propoxy)-phenyl]-propane, a commercial product (C theoretical: 67.97%; C found: 67.9%; H theoretical: 7.03; H found: 7.1%; OH number theoretical: 219; OH
10 number found: 216; Br number theoretical: 62.5; Br number found: 65) in 150 parts by vol. of methyl ethyl ketone was added dropwise to the solution in the course of 30 minutes and the reaction product was kept at 65 - 70°C
15 for 2 hours; 5 parts by vol. of alcohol were then added. Distilling off the solvent gave a dry, elastic rubber, which would dissolve again in methyl ethyl ketone and other organic solvents, such as toluene and tetrahydrofuran. The product had a reduced specific viscosity
20 of 0.68 dl/g (measured on a 1% strength solution of dimethylformamide at 25°C).

A dry resist film was prepared in complete analogy with Example 1 and was laminated, exposed and developed. Neither in these stages nor in the sub-
25 sequent electroplating operations, were there substantial differences from the results of Example 1.

The adhesion to copper of the freshly laminated, but not yet exposed resist was particularly noteworthy. This adhesion was tested in analogy with a "cross-hatch

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cut test for paints and similar coatings" as specified in DIN 53,151. Six longitudinal and six transverse cuts were made with a razor blade in a resist sample, so that 25 quadrilaterals were formed on an area of about 1 cm².

- 5 A piece of pressure-sensitive adhesive strip 12 mm wide was pressed onto this area diagonally over the slit pattern. The film was then pulled off at an angle of 90°. Only 30 seconds after lamination, the material investigated exhibited no crevices at all.

10 Examples 4 to 7

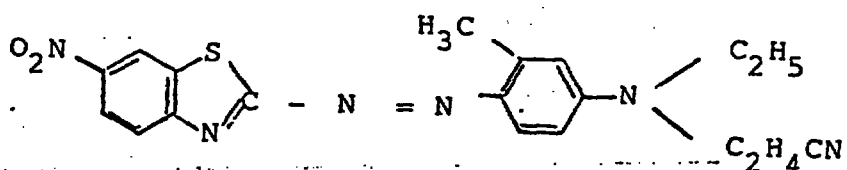
- The table which follows summarizes four examples which do not differ from Examples 1 and 2 in technical execution, but contain differences in the formulation. Property variants in the resists caused thereby are
15 recorded in the table by means of keywords. The quantities are quoted in parts by weight.

Example	Binder	Quantity	Acrylate monomer	Quantity	9-Phenyl acridine	Dyestuff of Example 1	Properties and remarks
4	Terpolymer formed from butyl methacrylate/methacrylic acid/styrene (66.7:20:11.3); Acid no. 122-125	6.5	PEG-400 di-methacrylate	3.0	0.1	0.035	slightly tacky layer, particularly good adhesion to metal. Good gold bath stability in gold baths at a low current efficiency
			Elastomer from Example 1	0.6			
5	as Example 1	6.5	Bis-urethane dimethacrylate*)	5.0	0.1	0.035	Particularly suitable for lead-tin electroplating
			Elastomer from Example 1	0.6			
6	Copolymer formed from vinyl acetate/crotonic acid (60:10) Acid no. 70	6.0	Elastomer from Example 1	4.0	0.2	0.025	Developed with trichloroethane
7	Terpolymer formed from butyl methacrylate/methyl methacrylate/methacrylic acid (45:35:20) Acid no. 157	6.5	as Example 4	3.0 0.6	0.1	0.035	Developed with a 3% strength aqueous solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$

*) prepared from 1 mole of trimethylhexamethylene diisocyanate and 2 moles of β -hydroxyethyl methacrylate

Example 8

10 parts by wt. of the elastomer described in Example 1 were dissolved in 35 parts by vol. of methyl ethyl ketone together with 0.18 part by wt. of 9-phenyl
 5 acridine and 0.02 part by wt. of the red azo dyestuff of the following structure



This solution was spin-coated onto a polyester film 23 μm thick in such a way that a film weight of
 10 approx. 50 g/m^2 was obtained after drying at 100°C. This dry resist film was laminated at 120°C, using a commercially available laminating device, to a phenoplast laminated sheet which was backed with a copper foil 35 μm thick. After exposure for 90 seconds through a mask
 15 carrying a conductive pattern, using a 5 kW exposure apparatus, the polyester film was stripped off and the layer was developed with the aid of a cottonwool pad impregnated with 1,1,1-trichloroethane. The metal layer exposed was electroplated and finished in a custom-
 20 ary manner (compare Example 1). After the electroplating, the resist layer which had been crosslinked by light could be removed with aqueous alkali solution and the copper which was uncovered could be removed by etching in customary etching media.

Example 9

A sufficient quantity of the coating solution described in Example 1 was cast (spin-coating process) onto a polyester film resting on a rotating plate in such a way that a resist layer 50-100 μ m thick was obtained after drying at 100°C. The resist was laminated at 120°C, using a commercially available laminator, to a phenolic resin or epoxide printed circuit board equipped with a printed circuit. Exposure was then carried out using a commercially available exposure apparatus containing a 5 kW MH lamp, through a mask which covered the points to be soldered, developing was carried out for 2 minutes in a commercially available spray processor using 0.8% strength sodium carbonate solution, the material was blown dry and exposed for a further 40 seconds in order to achieve subsequent hardening. The printed circuit boards pretreated in this way were soldered in a commercially available immersion soldering bath, filled with a eutectic Sn/Pb mixture (63 Sn/37 Pb). Before being soldered, the prepared board was wetted with a solution of colophony in isopropanol. The immersion time in the soldering bath, heated to 250°C, was 10 seconds. The resist-free areas to be soldered exhibited a satisfactory build-up of solder.

The hardened resist layer withstood the heat to which it was exposed in the soldering operation without being affected.

Example 10

A dry resist film was prepared as in Example 8,

(19)

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but 8 parts by wt. of elastomer and 2 parts by wt. of polyethylene glycol 400 diacrylate were used instead of 10 parts by wt. of the elastomer. Processing was carried out as described in Example 8, with the exception that the exposure time was 8 seconds. Similarly good results were obtained.

Patent Claim

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wherein

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(5)

X is one of the groups -O-Ph-Z-Ph-O- and
-OOC-(CH₂)_y-COO-,

Ph being an optionally substituted phenylene
group,

5 Z being an alkylene group having 1 - 4 carbon atoms and
y being a number from 2 to 12,

R is a hydrogen atom or a methyl group,

Y is an alkylene radical having 2 - 6 carbon atoms,

m is a number from 4 to 50,

10 n is a number from 1 to 6 and

o is a number from 4 to 20,

the remainder of the polymerizable esters being low
molecular weight acrylic or methacrylic acid esters

15 of di- or polyhydric alcohols.