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The invention relates to a process for preparing relief images, in which a light-sensitive material composed of a support and a light-sensitive layer which contains as essential constituents

- a) a compound which has at least one C-O-C bond which is cleavable by acid,
 - b) a compound which forms a strong acid on irradiation and
 - c) a binder which is insoluble in water and soluble in aqueous-alkaline solutions
- is imagewise irradiated and the non-image areas are washed out with a developer liquid.

Processes of the generic type mentioned and the light-sensitive materials used in these processes are known. These materials produce positive copies of the exposure original, i.e. the layer becomes soluble in a developer at the exposed areas. Such positive-working materials are described in U.S. Patents 3,779,778, 4,101,323, 4,189,323, 4,247,611, 4,250,247, 4,248,957 and 4,311,782.

On exposure of these materials compound b forms, by photolysis, acid, which cleaves the C-O-C groups of compound a, so that as a result the exposed areas of the light-sensitive layers become soluble in a developer.

It is also known to process in a negative manner, by a certain sequence of treatment steps, positive-working reproduction materials based on 1,2-naphthoquinonediazides.

U. S. Patent 3,264,104 describes such a reverse process, in which the light-sensitive layer, which preferably contains thermoplastic polymers, is imagewise exposed, treated with an alkaline solution or with hot water without washing out the exposed areas, is re-exposed without original and then developed as customary. In the developing procedure, the originally imagewise exposed areas are left intact, while the remaining areas are washed out.

A similar process is described in U. S. Patent 3,406,065. Also in this process a layer of the same type is imagewise exposed, treated with aqueous alkali without washing out, then treated with an alkali-resistant lacquer and developed by washing out those areas not imagewise exposed. The developing can be effected either with organic solvents or - when the layer was exposed without original after the first alkali treatment and before the lacquering - with aqueous-alkaline solutions.

These processes have the disadvantage that they require a relatively large number of treatment steps, that the first alkali treatment must always be carried out with particular care in order to release as little as possible of the exposed layer, which is soluble in aqueous alkali, that they require the addition of polymers which are sparingly soluble in alkali and restrict the utilizability of the material for other purposes, or that they additionally require lacquering of the exposed layer. Any material based on 1,2-naphthoquinonediazides has the disadvantage in principle of a relatively low light

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sensitivity.

European Patent Application 0024916 discloses a similar reverse process, in which a material based on 1,2-quinonediazides is heated after imagewise exposure, then
5 re-exposed without original and developed by means of aqueous alkali to give a negative. The material contains in the light-sensitive layer certain photochromic compounds which react during the heating with the light reaction products of quinonediazide and are said to lead to a
10 hardening of the layer. This material is linked to the presence of photochromic substances the light reaction of which produces a discoloration which is troublesome in some applications. It also has the low light sensitivity characteristic of 1,2-quinonediazides.

15 The object of the invention was to propose a reverse process for preparing negative copies by means of a normally positive-working light-sensitive material, which enables a higher light sensitivity and a simpler execution compared to known reverse processes.

20 The invention relates to a process of the generic type indicated at the outset.

In the process according to the invention, the light-sensitive material is warmed to an elevated temperature after imagewise irradiation, cooled down and then
25 irradiated over its entire area and those areas which have not been irradiated imagewise are developed by washing out.

The light-sensitive mixture used for preparing the light-sensitive material can contain as compounds having acid-cleavable C-O-C bonds inter alia monomeric and

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polymeric acetals, monomeric and polymeric orthocarboxylates, enol-ethers and N-acyliminocarbonates. Mixtures of this type are described in the publications mentioned in the introduction. Polymeric acetals and orthocarboxylates are particularly preferred for this use. The proportion of acid-cleavable compound is in general 9 to 75, preferably 15 - 50, % by weight, relative to the non-volatile constituents of the light-sensitive layer.

A large number of known compounds and mixtures are suitable for use as radiation-sensitive components which on irradiation preferentially form or eliminate strong acids, such as diazonium, phosphonium, sulfonium and iodonium salts, halogen compounds, o-quinonediazide sulfochlorides and organometal/organohalogen combinations.

Possible diazonium salts are those compounds which are known in diazotype and have utilizable absorption between 300 and 600 nm. Those compounds are preferable which do not contain basic substituents.

The onium salts mentioned are as a rule used in the form of their salts which are soluble in organic solvents, usually as a deposition product with complex acids such as tetrafluoroboric acid or hexafluorophosphoric, hexafluoroantimonic or hexafluoroarsenic acid.

Sulfonyl halides of positive-working o-quinonediazides can also be used.

In principle it is possible to use as halogen-containing radiation-sensitive compounds which form hydrohalogenic acid any organic halogen compound which is also known as a photochemical free-radical starter, for example

those which have more than one halogen atom on a carbon atom or in an aromatic ring. Examples have been described in U.S. Patents 3,515,552, 3,536,489 and 3,779,778, German Auslegeschrift 2,610,842 and German Offenlegungsschriften 2,718,259 and 2,243,621.

The amount of the starter can also vary widely according to the chemical nature of the starter and the composition of the mixture. Favorable results are obtained using about 0.1 to 10% by weight, relative to total solids, with 0.2 to 5% being preferable. It is advisable to use a relatively small amount of acid donor in particular for copying layers which are more than 10 μ m thick.

Preferably the mixtures also contain a polymeric binder which is preferably insoluble in water and soluble in organic solvents. Since aqueous-alkaline solutions can advantageously be used as developer liquids for the exposed copying layers and these aqueous-alkaline solutions are generally preferred over developers based on organic solvents, in particular those binders are preferable which are soluble, or at least swellable, in aqueous alkalis.

The type and amount of water-insoluble-binders can vary according to the intended use; proportions of total solids between 30 and 90, in particular between 55 and 85, % by weight are preferable.

Phenolic resins, above all novolaks, which have proved themselves in the case of many positive copying materials, have been found to be particularly advantageous also in this case. The novolaks can also have been modi-



fied in a known manner by reacting some of their hydroxyl groups with, for example, chloroacetic acid, isocyanates, epoxides or carboxylic anhydrides. Other alkali-soluble resins, such as copolymers of maleic anhydride and styrene,
5 vinyl acetate and crotonic acid, methyl methacrylate and methacrylic acid and the like, are also suitable for use as binders.

Numerous other resins can also be used in addition, and they can be either water-soluble or alkali-insoluble,
10 for example polyvinyl acetates, polyurethanes, polyacrylates, polyvinyl ethers and polyvinylpyrrolidones, which in turn can have been modified by comonomers, and hydrogenated or partially hydrogenated colophony derivatives. The most favorable content of these resins in the mixture
15 depends on the application requirements and on the effect on developing conditions, and it is in general no more than 50% by weight. Contents of about 2 to 35% by weight, relative to the quantity of non-volatile constituents of the layer, are preferable. The light-sensitive layer can
20 also contain, in small amounts for special requirements such as flexibility, adhesion, gloss and the like, substances such as polyglycols, cellulose ethers, for example ethylcellulose, wetting agents and finely divided pigments.

25 Finally, soluble or also finely divided dispersible dyestuffs can be added to the light-sensitive mixture as well as, according to the intended purpose, UV absorbers. Triphenylmethane dyestuffs, in particular in the form of their carbinol bases, have been found to be particularly

suitable for use as dyestuffs.

Preferable supports for layers which are more than 10 μm thick are plastic films which then serve as temporary supports for transfer layers. Polyester films
5 are preferred for this purpose and for color proofing films. Metals are usually used as supports for layers which are less than about 10 μm thick. Mechanically or electrochemically roughened and optionally anodized aluminum which can also have been chemically pretreated, for example with poly-
10 vinylphosphonic acid, silicates or phosphates, and multi-metal plates containing Cu/Cr or brass/Cr as the uppermost layer can be used for offset printing plates. To obtain letterpress plates, the layers according to the invention can be applied to zinc or magnesium plates and to their
15 commercially available microcrystalline alloys for powderless etching, and to etchable plastics such as polyoxymethylene. To obtain gravure forms or screens, the layers according to the invention, by virtue of their firm adhesion and etch resistance, are suitable on copper or nickel
20 surfaces. The mixtures according to the invention can also be used as photoresists.

The coating can be effected directly or by dry layer transfer from the temporary support onto conductor board materials, which consist of insulating boards bearing a layer of copper on one or both sides, onto glass or
25 ceramic materials which may have been pretreated in an adhesion-promoting manner and onto silicon, silicon oxide and silicon nitride discs.

Customary equipment and conditions can be adopted.

for the drying after the coating, temperatures of about 100°C and briefly up to 120°C being withstood without loss of radiation sensitivity.

The imagewise exposure can be carried out with customary copying equipment, such as fluorescent tubes, pulsed xenon lamps, metal halide doped high-pressure mercury vapor lamps and carbon arc lamps. Exposure can also be effected using the coherent light of a laser. For the purposes of the present invention short-wave lasers of suitable power, for example argon lasers, crypton ion lasers, dye lasers and helium cadmium lasers which emit between 300 and 600 nm are suitable. The laser beam is controlled by means of a predetermined programmed line and/or screen movement.

Irradiation with electron beams is a further imaging possibility. In this case, acid donors which show little or no sensitivity toward daylight can also be used.

After the imagewise irradiation or exposure, the material is warmed without further intermediate treatment. The warming can be effected by irradiation, convection, by contact with heated surfaces, for example rolls, or by dipping into a warmed bath of an inert liquid, for example water. The temperature can be between 80 and 150, preferably 100 to 130, °C. Such temperatures are withstood by the mixtures without the properties of the unexposed areas changing significantly. The heating time can vary very widely depending on the kind of heat treatment. If heat is transferred via a medium, the time is generally between

5 and 30, preferably between 5 and 20, minutes. If continuous infra-red equipment is used, dwell times of 1 to 2 minutes can already be adequate for thin layers.

After the heating and cooling down the light-sensitive layer is subjected to a total exposure in order to convert completely light-sensitive areas of the layer still present into their light decomposition products. The afterexposure can advantageously be carried out under the same light source as was used for the imagewise exposure.

The afterexposure is followed by a developing with customary developers, during which those areas of the layer are washed out which were not hit by the light in the original imagewise exposure. Suitable developers are preferably aqueous solutions of alkaline substances, for example alkali metal phosphates, silicates, carbonates or hydroxides, and which can also contain wetting agents or minor amounts of organic solvents. In certain cases, organic solvents or mixtures thereof with water are also suitable for use as developers. The developing can be carried out immediately after the heating and cooling down or also after an interval of, for example, several hours without the hardened areas of the layer being attacked. From this fact it can be inferred that hardening of the exposed areas by warming is irreversible.

The process according to the invention has the advantage that it neither requires additional treatment steps with liquids nor a special composition of the light-sensitive material. It is thus possible to prepare posi-

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tive or negative copies, as desired, using customary positive materials based on acid-cleavable compounds. The single additional treatment step, namely the heating, can usually be carried out in a convenient way using existing drying equipment. The afterexposure without original is most simply carried out by again using the copying light source.

The process enables the known high image resolution of positive materials also to be used for preparing negative copies. A further advantage over the known reverse methods by means of positive materials based on o-quinonediazides is the high light sensitivity of the materials used in the process according to the invention. It is thus possible to obtain even negative copies having a high resolution and a thick layer.

Since the light reaction in the light-sensitive mixtures used in the process according to the invention is based on a mechanism which is completely different from that of o-quinonediazide layers it was not to be expected that the acid-cleavable mixtures could be processed in a similar way to give a negative image. In particular, it was not to be expected that these mixtures could produce an equally good result, using simpler process steps.

The process according to the invention can be used for preparing printing forms for letterpress, gravure and planographic printing and photoresist stencils for the subtractive and additive manufacture of conductor boards, for electroplating nickel rotary cylinders or for preparing

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masks in microelectronics using the lift-off technique. If the resist stencil is intended to remain on a circuit, the resist stencil is distinguished from an identical stencil prepared by the positive method by better dielectric values. Even as a planographic form the negative-processed, exposed and heated layers produce longer print runs than the same layers after processing by positive copy.

The Examples which follow describe preferable embodiments of the process according to the invention. Unless otherwise stated, percentages and quantitative ratios are understood as meaning units by weight.

Example 1

A coating solution of

- 15 7 parts by weight of a cresol/formaldehyde novolak having a softening range of 105-120°C as determined by the DIN 53,181 capillary method,
- 2 parts by weight of 2-naphth-2-yloxy-5,5-dimethyl-oxazol-4-one,
- 20 0.1 part by weight of 2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloromethyl-s-triazine,
- 0.1 part by weight of 4-diethylaminoazobenzene in
- 90.8 parts by weight of a solvent mixture of ethylene glycol monoethyl ether and butyl acetate (4:1)
- 25 was applied to aluminum mechanically roughened on one side by wire brushes and dried. The thickness of the layer obtained corresponded to a weight of 2 g/m².

After the drying, the layer was exposed under a positive original, developed with a 3.5% strength solution

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of trisodium phosphate which had been adjusted to a pH of 12.6 by adding sodium hydroxide, rinsed down with water and finally made ready for printing by wiping with 1% strength phosphoric acid.

5 Another sample of the same material was processed as a negative printing plate by exposing under a negative original, then heating for 10 minutes at 100°C and after-exposing without an original for the same time or longer. On developing in the same developer for the same time the
10 reverse image of the original was produced, and was then also treated with printing ink for printing. The reverse plates thus treated produced on average, compared to the positive plate, an offset printing machine print run which was about 20% higher.

15 Similar results were obtained if the same amount of 2-(4-benzyloxyphenoxy)-8-methyl-1,3-benzoxazin-4-one was used as cleavable compound in place of the oxazolone mentioned.

Example 2

20 To prepare a positive dry resist for etching and electroplating conditions, the following solution was prepared:

61.2 parts by weight of methyl ethyl ketone,
20 parts by weight of the novolak indicated in Example 1,
25 10 parts by weight of the reaction product of 187 parts by weight of phenol/formaldehyde novolak (melting range 110-120°C, in accordance with DIN 53,181) and 6.56 parts by weight of the addition product of 3 moles of toluene diisocyanate and 1 mole of tri-

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methylolpropane,

4.5 parts by weight of the bis-(5-ethyl-5-methoxymethyl-1,3-dioxolan-2-yl) ether of 2-ethyl-2-methoxymethyl-1,3-propanediol,

5 4.0 parts by weight of 1,3-bis-(3,4-dihydronaphth-2-yl-oxy)-propane

0.2 part by weight of 2-[4-(2-ethoxyethoxy)-naphth-1-yl]-4,6-bis-trichloromethyl-s-triazine and

0.05 part by weight of crystal violet base.

10 A biaxially stretched and heatset 25 μ m thick polyethylene terephthalate film was coated with this solution, dried and laminated with a 12 μ m thick polypropylene top film in such a way that an evenly thick resist layer was formed between the two films.

15 In a commercially available laminator, two of these resist films, after the top films had been peeled off, were laminated under pressure and heat onto both sides of two bright-rolled brass plates for manufacturing contact springs for switches. After cooling down, peeling
20 off of the support films and brief further drying in a drying cabinet at 80°C, one coated metal sheet was exposed positively and the other negatively on both sides using an exactly in-register pair of originals in the shape of a bag. The negatively exposed plate was heated for about
25 10 minutes at 130°C in a continuous oven having IR radiators, after exposed on both sides without original after cooling down and after an interval jointly developed with the positive-exposed plate in spray developing equipment which was filled with a developer solution of

2.67 parts by weight of sodium metasilicate x 9 water,
1.71 parts by weight of trisodium phosphate x 12 water and
0.17 part by weight of monosodium phosphate in
95.45 parts by weight of completely demineralized water.

- 5 The two plates of identical appearance were rinsed down to remove alkaline developer residues and then etched on both sides using commercially available ferric chloride solution until they had been etched through to show vertical edges.

- 10 The switch components thus obtained were completely identical in respect of width and edge quality of the spring strips, confirming the copying quality and etch resistance of the reverse layer by comparison to the directly positive-processed positive layer.

15 Example 3

To prepare microelectronic switching elements of high packing density, commercial, customarily manufactured polished silicon discs oxidized at the surface to give a 0.2 μm thick SiO_2 layer were coated with the following positive photoresist solution.

- 20 19 parts by weight of the novolak indicated in Example 1,
9.5 parts by weight of triethylene glycol-bis-diphenoxymethyl ether,
0.2 part by weight of 2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloromethyl-s-triazine and
25 1.3 parts by weight of low-viscosity polyethyl acrylate (Plexisol B 574)

were dissolved in 70 parts by weight of a solvent mixture of ethylene glycol ethyl ether acetate, butyl acetate and



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xylylene (8:1:1), and the solution was filtered through a 0.5 μm filter. Spin-coating with this solution at 9,000 rpm produced approximately 1.2 μm thick resist layers which were then dried for 10 minutes at 90°C in a circulating air cabinet. After cooling down and conditioning to the room conditions defined, exposure took place in a wafer contact exposure device for 1 second using a 200 watt Hg high pressure lamp under a commercially available chromium mask with highly resolved test areas. Developing took place at 25°C for 1 minute in an agitated solution of the developer which was mentioned in Example 2 but which had been diluted 1:1 with completely demineralized water. A positive image of the original was obtained.

A further sample of the light-sensitive material was heated for 30 minutes at 120°C after the imagewise exposure under the corresponding reversed chromium mask, afterexposed without original and then developed in the same way as above. A similar resist mask was obtained which is equally suitable for microlithographic processes such as SiO_2 etching or doping uses. The further heating before developing increased the etch resistance without the developed resist profiles being changed by the heat treatment (no postbake flow). It is also possible by means of this reverse process to utilize the advantages of the higher resolution and sharper resist edges of the positive resist material compared to the customary negative microresists to be processed with organic solvents.

Example 4

An aluminum plate of electrolytically roughened

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and anodized aluminum was provided with a 2.2 μm thick layer of

2 parts by weight of the novolak of Example 1,

0.4 part by weight of a polymeric orthocarboxylate of

5 trimethyl orthoformate and 1,2,6-hexanetriol,

0.13 part by weight of the s-triazine indicated in Example

2 and

0.007 part by weight of crystal violet base.

This layer was imagewise irradiated in a laser exposure
10 device (Laserite^(R) 150 R from Eocom Corp., U.S.A.) with an
argon ion laser at 6 mJ/cm^2 . The sensitivity of layer
variants was determined by varying the writing speed. The
exposed parts of the layer were removed within 2 minutes
using a developer composed of

15 5.5 parts by weight of sodium metasilicate x 9 water,

3.4 parts by weight of trisodium phosphate x 12 water,

0.4 part by weight of monosodium phosphate (anhydrous)

and

90.7 parts by weight of completely demineralized water..

20 By coloring the unirradiated areas with fatty ink,
the laser trace can be shown up even more clearly.

Reverse processing was carried out with an identical plate by heating the plate to at least 90°C in a customary continuous infra-red heating device after the
25 laser irradiation, then after-exposing under a copying
lamp over the entire area and, finally, developing in the
same way as the positive plate.

Example 5

This Example demonstrates how nickel rotary



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stencils for textile printing can be prepared with the following photoresist solution by electroplating. A solution was prepared of

- 40 parts by weight of methyl ethyl ketone,
- 5 15 parts by weight of ethylene glycol ethyl ether acetate,
- 5 parts by weight of diethylene glycol monoethyl ether,
- 28 parts by weight of the novolak of Example 1,
- 3.5 parts by weight of polyvinyl ethyl ether (Lutonal A 25),
- 10 8.3 parts by weight of the polyacetal of 2-ethylbutyraldehyde and triethylene glycol,
- 0.2 part by weight of 2-(6-methoxynaphth-2-yl)-4,6-bis-trichloromethyl-s-triazine and
- 0.01 part by weight of crystal violet base.
- 15 A 75 μ m thick layer of good surface quality was applied by two-fold spray coating with intermediate drying to a bright-rolled, slightly elastically expandible nickel cylinder which had been provided with a conductive release layer. The cylinder, rotating during this process, was then sufficiently dried
- 20 for about 30 minutes under infra-red radiators.

Exposure took place for a sufficiently long time under a positive of the motive to be printed and the tonal gradations of which had been converted by means of a screen of 32 lines/cm into image areas of differing hiding power. The exposure time had to be 6 times as long for a positive layer which was half as thick and based on o-naphthoquinonediazide. A solution of

- 0.5% of NaOH,
- 0.8% of sodium metasilicate x 9 water,



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1.0% of ethylene glycol mono-n-butyl ether in
97.7% of completely demineralized water
was used for developing. For this purpose, the rotating
exposed cylinder was dipped into a trough which had a
5 corresponding size and was half-filled with the developer.
The developer resistance of the layer was very good, and
made possible steep sides of the resist edges. When the
cylinder had rotated in the developer for 6 minutes, the
developer trough was removed and the cylinder was rinsed
10 with water and dried in air.

Nickel up to a thickness of 0.1 mm was electro-
coated at the bared areas of the cylinder core. After the
cylinder core had been shrunk and the resist stencil had been
stripped with acetone and the nickel stencil had been removed from the
15 core, a resilient rotary stencil printing form was
obtained. The ink was transferred imagewise through the
holes of the rotary stencil onto the textile materials to be printed. The
range of tone which is possible is increased compared to
stencils based on diazo layers and negative resists, since
20 the relatively thick layer is safer in preventing the
narrowing of relatively small image points, i. e. relatively
small holes, in electroplating.

The same resist layer can analogously be used as
a reverse layer when a negative film is used as an
25 original. Since there are no negative resists on the
market which can be processed to give a correspondingly thick
layer and the re-copying of silver films with a large
area is expensive, the negative processing of this highly
sensitive positive resist recommends itself. For this

purpose, the all-round exposure under the negative film was followed by an additional heating stage for a further 30 minutes under the existing infra-red radiators and the cylinder was afterexposed without original under the light source. The final result was a nickel printing cylinder which was identical to that obtained in the positive procedure.

Similar results were obtained when the polyacetal of n-heptanal and tetraethylene glycol was used as the cleavable compound.

Example 6

This Example demonstrates how the direct positive and reverse negative processes are combined for the manufacture of microconductor boards. For this purpose, a positive dry resist film was prepared similarly to Example 2, with a resist layer of 12 μ m thickness and the following composition:

- 64 parts by weight of the novolak of Example 1,
- 11 parts by weight of polyvinyl methyl ether (Lutonal M 40),
- 15 parts by weight of the polyacetal of 2-ethylbutyraldehyde and hexane-1,6-diol,
- 9.5 parts by weight of the polyortho-ester of trimethoxymethane and 5-oxa-7,7-dihydroxymethylnonan-1-ol,
- 25 0.4 part by weight of 2-acenaphth-5-yl-4,6-bis-trichloromethyl-s-triazine and
- 0.1 part by weight of crystal violet base.

In a commercially available laminator, this resist film was applied under pressure and heat to through-hole

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copper-clad boards of insulating material, and allowed to cool down, and the support film was peeled off. Whether the resist film covers the holes during this step (tenting) or tears, is immaterial in this favorable process, since the eyelets are bared anyhow in this first process step. A negative original where only the hole regions were transparent was used for this purpose. A double was used of the negative conducting path original where the conducting paths had been retouched away, i.e. covered over.

After exposure of the eyelets, these regions were developed, i.e. washed out, using the same developer as in Example 4. Before the reinforcement by electroplating and tinning or Pb/Sn deposition in the zone on the eyelets, the negative conducting path original was used for exposure, but was not followed by developing.

The hole region was reinforced by electroplating. The coated board was then heat-treated for 20 minutes at 110°C, afterexposed over the whole area and only then developed. The bared copper was then etched away in an ammoniacal etching bath, a Cu microconductor circuit being obtained which had the following advantages: resolution to a conducting path width of Less than 50 μm , two copying steps with one single coating, use of virtually only one (negative) original and equipment already present anyhow.

If the second copying step is not carried out as described using the reverse process but in the positive process, heat treatment and afterexposure are admittedly eliminated; but in addition a positive film of the conduct-

ing path original is necessary. An advantage of the two process variants is that the second copy is not impaired by the electroplating process and this prevents the copy of the conducting paths from having to take place unevenly over the hole regions already reinforced by electroplating.

Example 7

A positive photoresist solution of

52 parts by weight of butanone,

10 34 parts by weight of the novolak of Example 1,

9 parts by weight of 1,3-bis-(5-butyl-5-ethyl-1,3-dioxan-2-yloxy)-2-butyl-2-ethylpropane,

4.8 parts by weight of the polyethyl acrylate of Example 3,

0.18 part by weight of 2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloromethyl-s-triazine and

15 0.02 part by weight of crystal violet base

was applied on a conductor board support to give a dry layer weight of 3.9 g/m^2 . After drying for 5 minutes at 100°C , the coated supports were irradiated for 5 seconds

20 with 11 keV at $5 \mu\text{A}$ in an electron beam exposure device, heated for a further 15 minutes at 100°C , afterexposed without original under UV light and developed for 30 seconds as in Example 5. This produced a sharp resist image which it was possible to use for etching the support

25 material at the bared non-irradiated areas.

Similar results were obtained when the polyortho-ester of Example 6 was used as the cleavable compound and a heat treatment was carried out for 30 minutes at 100°C .

The negative processing of the positive layer is

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possible at an incident energy of about 5×10^{-2} joule/cm² to 250×10^{-2} Joule/cm². The practical electron beam sensitivity can be improved still further by optimizing time and temperature of the post-heating stage.

- 5 When the positive method is used, i.e. irradiation with electron beams and subsequent removal of the irradiated areas using the same developer for 30 seconds, requires, on the other hand, minimum energies of 55×10^{-2} or 80×10^{-2} Joule/cm².

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Patent Claims:

1. A process for preparing relief images, in which
a light-sensitive material composed of a support and
5 a light-sensitive layer which contains as essential
constituents
a) a compound which has at least one C-O-C bond which
is cleavable by acid,
b) a compound which forms a strong acid on irradiation
10 and
c) a binder which is insoluble in water and soluble in
aqueous-alkaline solutions
is imagewise irradiated and the non-image areas are
washed out with a developer liquid, wherein the material
15 is warmed to an elevated temperature after imagewise
irradiation, cooled down and then irradiated over its
entire area and those areas of the layer which have not
been irradiated imagewise are developed by washing out.
- 20 2. The process as claimed in claim 1, wherein the
material is warmed to a temperature of 80 to 150° C.
3. The process as claimed in claim 1, wherein the
material is warmed for 1 to 30 minutes.
25
4. The process as claimed in claim 1, wherein an
orthocarboxylic acid derivative, an acetal, an enol-ether
or an N-acyliminocarbonate is used as the acid-cleavable
compound (a).



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5. The process as claimed in claim 1, wherein a novolak is used as binder (c).

5 6. The process as claimed in claim 1, wherein a material is used the light-sensitive layer of which also contains at least one resin having solubility properties which differ from those of binder (c).

10 7. The process as claimed in claim 1, wherein the non-image areas are washed out by means of an aqueous-alkaline developer solution.

15 8. The process as claimed in claim 1, wherein a light-sensitive material as defined in claim 1 is image-wise exposed under an original and developed, the support is modified at the bared areas by etching or metal deposition, and the residual layer, before or after the modification of the support, is exposed under a further original, warmed, cooled down, irradiated
20 over its entire area and developed after the modification.

9. The process as claimed in claim 8, wherein the original used in the first imagewise exposure is the partially covered original for the second exposure.



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