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Positive-working radiation-sensitive mixture

The invention relates to a positive-working, radiation-sensitive mixture, that is to say a mixture which is rendered soluble by irradiation, and which, as the essential constituents, contains

- 5 a) a compound having at least one C-O-C bond which can be split by acid,
- b) a compound which forms a strong acid when irradiated and
- c) a binder which is insoluble in water and soluble
10 in aqueous-alkaline solutions,
and is suitable for the preparation of printing plates and photoresists. Mixtures of the said composition are described, for example, in US-A Nos.
3,779,778, 4,101,323 and 4,189,323, in DE-A Nos.
15 2,718,254 and 2,928,636 and in EP-A Nos.
0,006,626 and 0,006,627.

Although it is mentioned in these printed publications that other polymeric substances can also be added in addition to the alkali-soluble binders, alkali-
20 soluble binders, in particular phenolic resin novolaks, are described virtually exclusively in the illustrative examples.

Other binders or resins are, however, already known as additives for positive-working radiation-sensitive
25 or light-sensitive mixtures based on o-quinone-diazides.

Thus, DE-C No. 1,622,301 describes the addition of polyvinyl alkyl ethers,

DE-A No. 2,236,941 describes the addition of acrylic resins,

DE-A No. 2,733,267 describes the ad-

dition of terpene resins and DE-A No.
2,617,088 describes the addition of reaction products
of organic isocyanates with novolaks to o-quinone-diazide
layers which additionally can contain alkali-soluble
5 novolaks.

In spite of the manifold proposals, some of which
were made a considerable time ago, for the improvement
and modification of the properties of positive-working
light-sensitive layers based on o-quinone-diazides for
10 the most diverse applications, these layers still do not
yet meet all the requirements.

Specifically in the case of positive photoresist
compositions for micro-electronic applications, where a high
resolution and exact line definition, even after
15 baking steps, are of particular importance, resin
additions of the types mentioned have been unable to gain
acceptance. Even polyvinyl alkyl ethers are still not
used very widely, in spite of numerous efforts in micro-
electronics to introduce resists containing these
20 additives into the mass production of
chips. A main obstacle appears to be the fact that
disadvantages, for example a loss of sharpness after
baking, can arise in diazo layers after the ad-
dition of these resins during certain working steps under
25 production conditions.

It was the object of the invention to modify the
mechanical and chemical properties of positive-working
radiation-sensitive layers, based on the compounds which
can be split by acid, and the photolytic acid donors, as

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mentioned at the outset, in such a way that they can be adapted to the most diverse applications.

The invention is based on a positive-working radiation-sensitive mixture which is composed of

- 5 a) a compound having at least one C-O-C bond which can be split by acid,
- b) a compound which forms a strong acid when irradiated,
- c) a binder which is insoluble in water and soluble in aqueous-alkaline solutions and
- 10 d) at least one resin, the solubility properties of which differ from those of the binder (c).

The radiation-sensitive mixture according to the invention is characterized in that the resin having different solubility properties is

- 15 d1) a polyurethane resin obtained from an organic isocyanate and a polymer which contains hydroxyl groups,
- d2) a polyvinyl alkyl ether,
- d3) an alkyl acrylate polymer or
- d4) a hydrogenated or partially hydrogenated derivative of colophony.
- 20

It has been found that, in the indicated types of positive-working layers, the additional resins frequently have effects which are very different from those in layers based on quinone-diazides. In part, this results from the very different mechanical properties of the base constituents of the two types of layer. Whilst quinone-diazides in combination with phenolic resin novolaks usually even increase the brittleness of the layer, ortho-carboxylic acid derivatives, acetals,

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acyliminocarbonates and enol ethers normally have the opposite effect. These substances frequently are oily or low-melting components and, therefore, themselves already contribute to the softness, flexibility and a
5 reduction in brittleness.

Whilst o-quinone-diazide/novolak layers in most cases have a turbid appearance because of the crystalline to amorphous properties of the diazo compounds and the interaction of the latter with this resin, the new layers
10 are completely clear. In the case of pure quinone-diazide/novolak layers, problems can arise regarding the adhesion to silicon wafers, in particular if the surfaces are doped. This can require special pretreatment steps, as can be seen, for example, from US-A Nos.
15 3,549,368 and 3,586,554 and DE-A No.
2,617,914.

It was thus surprising that the resin additives, already known for quinone-diazide layers, produce completely different effects when combined with compounds
20 which can be split by acid. It was not foreseeable that an addition of, for example, a polyvinyl ethyl ether can here improve the latitude in development, that is to say the difference between development time and resistance to the developer, and, in contrast to the effect on
25 diazo layers, even enhances the properties of the layer on baking, that is to say it reduces the tendency to flow and it increases the edge acuity.

Whilst exposed and developed layers which are composed only of novolak, ortho-ester compound and acid-

forming starter, can, in spite of good adhesion to silicon wafers, have holes in unexposed areas - it has not yet been possible unambiguously to elucidate the cause of this - this defect disappears when the resins mentioned
5 are added. Since it was not possible to eliminate the holes, which are formed only during development, by the addition of a wetting agent to the layer, it is assumed that an interaction (hydrogen bridges) which favors the formation of a film takes place between the
10 polyvinyl ethyl ether and the novolak resin.

This is supported by the probability that an interaction between a compound which can be split by acid and a novolak resin would be weaker than the known, relatively extensive formation of adducts or similar
15 aggregates between o-naphthoquinone-diazide and a novolak. As far as they can be compared, corresponding non-diazo layers are more advantageous than diazo layers not only with respect to the resistance to developer, but also with respect to the quantity of added resin, which can
20 be incorporated in order to improve other properties of the layer, without a substantial deterioration in the copying properties.

The quantitative proportion of added resin, relative to the non-volatile constituents of the mixture,
25 is between 1 and 50 % by weight, depending on the type of the resin and the other constituents of the layer.

In the case of a polyvinyl alkyl ether, the proportion of added resin can be 2 to 40 %, preferably 5 - 25 %. In the case of polyvinyl alkyl ethers

having longer-chain alkoxy radicals in the side positions, for example polyvinyl isobutyl ether, the most advantageous quantity added is lower than in the case of polyvinyl ethyl ether. If polyvinyl methyl ether is added to the new layers, it is a surprising observation that not only the adhesion and softness, but above all the elastic/film-forming properties are outstanding. Thus, when polyvinyl methyl ether is added to positive dry resist layers based on compounds which can be split by acid, even large holes drilled in through-hole plated circuits are covered by the resist layer (tenting). Depending on the substance which can be split by acid and on the layer thickness, up to 40 % of polyvinyl methyl ether can be present in the layer, with good results. The maximum quantity is reached when the resistance to developer is markedly reduced, or other influence factors, for example atmospheric humidity, adversely affect the result of copying.

Good technological results are also obtained with the addition of polyacrylate resins, in particular polyethyl acrylates, which, like polyvinyl ethyl ethers, render the layer elastic and stronger, without adversely affecting the copying properties. Polyacrylate resins are preferably to be understood as the lower polyacrylic and polymethacrylic acid alkyl esters, but copolymers of these are also suitable. The acrylate resins even improve the resistance to developer, since their high-molecular constituents reduce the rate of dissolution of unexposed parts of the layer. In general, their quantity can be 1-20,

preferably 5-15 % by weight. In the case of greater quantitative proportions, there is a risk of exposed parts of the layer being detached in the form of blobs, and this can lead to undesired depositions at other
5 points. In the manufacture of dry resist layers, this must be compensated by other means and, in the new positive systems which can be varied very widely, this is indeed possible by an appropriate selection of the compound which can be split by acid.

10 In addition, to a surprisingly greater extent than in the case of diazo layers, and to a greater extent than with the polyvinyl alkyl ethers which are in themselves tacky, the adhesion to metal surfaces can be improved, when polyacrylate resins are used, and/or the behavior
15 of the positive layers when separated from polyester films and polyolefine films can be controlled. It is thus possible to optimize the adhesion to such an extent that mixtures of this type can be cast as solutions onto polyester films, dried and then cleanly transferred (laminated) to copper. Even with optimized diazo layers,
20 this method succeeds only when specially pretreated polyester films are used, as is described, for example, in DE-A No. 2,403,054.

The best results are obtained with polyethyl
25 acrylate, of which 2-12 % are added when it has a low viscosity, and 1-6% are added when it has a high viscosity. Generally, relatively low-molecular polymers are preferred.

Polybutyl acrylate, polybutyl methacrylate and

copolymers thereof can also be used, albeit with a less pronounced effect. Mixtures of polyvinyl alkyl ethers and polyalkyl acrylates permit a further fine adjustment of the desired properties, without an adverse synergistic effect occurring.

Finally, during experiments to improve the new light-sensitive layers for different applications, it has additionally been found that advantageous effects can also be obtained by an addition of terpene resins, that is to say derivatives of colophony. The quantitative proportions are here about 3-50, preferably 7-45 % by weight. Resins of this type have been used for a long time in lacquer technology, since they are based on inexpensive natural raw materials and are available in manifold variations for numerous applications.

The use of resins of this type in positive diazo layers has been described in the past (DE-ANo. 2,733,267). Amongst the large number of resins, known as additives for layers of this type, the resins of this group, in combination with the compounds which can be split by acid, are very advantageously distinguished with respect to the quality of the coating, the resistance to developer and the adhesion, evidently because they are also readily compatible with the other constituents of the layer, in particular the compounds which can be split by acid. Even resins which in themselves have a solid to crumbly consistency, can have an advantageous influence on the properties of the layer.

A review of the available colophony resins is

given by Karsten: Lackrohstoff-Tabellen [Tables of Lacquer Raw Materials], published by Vincentz, Hanover. Those resins are preferred which have already proved suitable for the preparation of printing inks and hot-5 melt adhesives. They can be combined with the other resins mentioned.

Hydrogenated and partially hydrogenated colophony derivatives, in particular terpene resin esters, such as the methyl esters, glycerol esters, triethylene 10 glycol esters or alkyd esters of terpene resins, are preferred, since they are more resistant to oxidation. The most advantageous combinations are determined in detail by experiments, depending on the intended use. Thus, terpene resins are less suitable for micro-electronic 15 resists and electroplating resists, even though they can also be used for these purposes. They are particularly suitable as additives in layers for products, such as dry resists and color proofing / films, where baking processes of the layer hardly occur, or not at all, but 20 instead the flexibility and adhesion of the layer are important.

Finally, polyurethane resins are also suitable as additive resins; these are obtained by reacting organic monoisocyanates or polyisocyanates with polymeric hydroxy 25 compounds. Examples of polymeric hydroxy compounds which can be used are polyethers or polyesters, and preferably phenolic resins, in particular novolaks. In general, the polyurethanes can be added in quantities of 3-30, preferably 5-20 %. In this case, it is

possible and advantageous to use the same novolak, which is also contained in an unmodified form in the layer, for the reaction with the isocyanate. Thus, the resin mixture used in this case can be a reaction product of novolak and isocyanate, which still contains a relatively large excess of unconverted novolak.

The light-sensitive mixtures according to the invention also contain a significant proportion of an alkali-soluble resin, preferably a novolak. The quantity is between 20 and 90, preferably 45-80% by weight of the quantity of the non-volatile constituents. The total quantity of alkali-soluble resin and additive resin is between 25 and 91, preferably between 50 and 85, % by weight. The quantity of the compound which can be split by acid is 9-75 and preferably 15-50 %, and the quantity of the photolytic acid donor is 0.1-10 and preferably 0.2-5 %. These constituents are described in detail in the printed publications quoted above, to which reference is made here. The ortho-carboxylic acid derivatives which are described in US-A No. 4,101,323 and DE-A No. 2,928,636, and the polyacetals which are described in DE-A No. 2,718,254, are used with particular advantage.

The light-sensitive mixtures can additionally also contain soluble or finely divided dispersible dyes and also, depending on the intended application, UV absorbers. Triphenylmethane dyes, in particular in the form of their carbinol bases, have proved to be

particularly suitable dyes. The most advantageous quantitative proportions of the components can readily be determined, in an individual case, by preliminary experiments.

- 5 Suitable solvents for the mixture of substances according to the invention are ketones, such as methyl ethyl ketone, chlorinated hydrocarbons, such as trichloroethylene and 1,1,1-trichloroethane, alcohols, such as n-propanol, ethers, such as tetrahydrofuran, alcohol
10 ethers, such as ethylene glycol monoethyl ether, and esters, such as butyl acetate. Mixtures can also be used which, for special purposes, can also additionally contain solvents, such as acetonitrile, dioxane or dimethylformamide. In principle, any solvents can be used
15 which do not irreversibly react with the components of the layer.

The selection of the solvents must, however, be matched to the intended coating process, the layer thickness and the drying apparatus. Thin layers of up to about
20 5 μm for test quantities are preferably applied on a whirler, by pouring them on. Using solutions having a solids content of up to about 40%, layer thicknesses of more than 60 μm can be obtained in this way by a single application or by using a wire bar. For coating
25 on both sides, dip-coating is preferred, and rapid drying-on can be achieved by the use of low-boiling solvents. Web coating is carried out by application by means of rollers, slot dies or by spraying; individual plates can be coated with the aid of a curtain-coater.

Preferred supports for layers of more than 10 μm thickness are plastic films which then serve as temporary supports for the transfer layers. For this purpose and for colour proofing films, polyester films, for example those composed of polyethylene terephthalate, are particularly preferred. Polyolefine films, such as polypropylene, however, are likewise suitable. The layer supports used for layer thicknesses of less than about 10 μm are in most cases metals. The following can be used for offset printing plates: mechanically or electrochemically roughened and, if appropriate, anodized aluminum which additionally can also have been chemically pretreated, for example with polyvinylphosphonic acid, and also multi-metal plates with Cu/Cr or brass/Cr as the top layer. For letter press printing plates, the layers according to the invention can be applied to zinc plates or magnesium plates for powderless etching processes, and they can also be applied to plastics, such as polyoxymethylene, which can be etched. Due to their good adhesion and etch resistance on copper or nickel surfaces, the layers according to the invention are suitable for gravure printing forms or screen printing forms. The mixtures according to the invention can likewise be employed as photoresists in chemical milling, and a large number of special substrates for this purpose is commercially available.

Moreover, wood, textiles and the surfaces of many materials can be coated, which advantageously are provided with an image by projection and are resistant to

the action of alkaline developers.

Finally coating can be effected directly or by dry layer transfer from a temporary support film to printing circuit board materials which are composed of 5 insulating plates having a copper coating on one side or on both sides, to glass or ceramic materials which, if appropriate, have been subjected to an adhesion-promoting pretreatment, for example thin metal layers on Al_2O_3 /ceramic plates for strip conductors in micro- 10 wave technology.

The thinnest coatings, down to less than 1 μm , are applied for microelectronics to silicon wafers, the surfaces of which can carry oxide layers or nitride layers and can be p-doped or n-doped. Especially 15 in this field of application, the mixtures according to the invention display their special properties, such as adhesion, resistance to flow on baking, and hence resolution, dimensional stability and resistance to plasma etching.

20 For drying after coating, the customary equipment and conditions can be adopted ; temperatures of about 100°C , and up to 120°C for short periods, are tolerated without a loss in radiation sensitivity.

For exposure, the customary copying equipment, 25 such as tubular lamps, pulsed xenon lamps, metal halide-doped high-pressure mercury vapor lamps and carbon arc lamps can be used. Furthermore, exposure in conventional projection and enlarging apparatus under the light of metal filament lamps, and contact exposure with ordinary

incandescent bulbs are possible. The exposure can also be carried out with the coherent light of a laser. Short-wave lasers of appropriate power, for example argon lasers, krypton ion lasers, dyestuff lasers and
5 helium/cadmium lasers, which emit between 300 and 600 nm, are suitable for the purposes of the present invention. The laser beam is controlled by means of a preset programmed line-scanning and/or screen-scanning motion.

Exposure with electron beams is a further possibility for producing an image. Electron beams can
10 thoroughly decompose and crosslink the mixture according to the invention, in the same way as many other organic materials, so that a negative image is formed when the unirradiated portions are removed by solvents or by
15 exposure without an original, and development. If the intensity of the electron beam is relatively low and/or the scanning speed is relatively high, however, the electron beam effects a differentiation in the direction of higher solubility, that is to say the irradiated
20 portions of the layer can be removed by the developer.

The layer which has been imagewise exposed or irradiated can be removed by means of the same developers which are used for the known layers based on compounds which can be split by acid, or the copying conditions for
25 the new layers can advantageously be matched to the known auxiliaries, such as developers and programmed spray-development devices. The aqueous developer solutions can, for example, contain alkali metal phosphates, silicates or hydroxides and also wetting agents as well as relatively

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small proportions of organic solvents. In certain cases, solvent/water mixtures can also be used as the developer. The selection of the most advantageous developer can be fixed by experiments with the particular
5 layer used. If necessary, the development can be mechanically assisted.

In the following text, examples of the light-sensitive mixtures according to the invention are given. Unless otherwise stated, the percentage ratios and
10 quantitative ratios are to be understood as weight units. The relationship of parts by weight (p.b.w.) and parts by volume (p.b.v.) is the same as that of g/cm³.

Example 1

To prepare microelectronic circuit elements of
15 high packing density, a commercially available silicon disk, which had been polished in the conventional manner and provided with a 0.2 μ m thick SiO₂ layer by oxidation, was coated with the following positive photoresist composition.

18 parts by weight of a cresol/formaldehyde
20 novolak having a softening range of 105-120°C according to DIN 53,181,

9.5 parts by weight of a triethylene glycol-bis-diphenoxymethyl ether,

1.2 parts by weight of 2-(4-ethoxynaphth-1-yl)-
25 4,6-bis-trichloromethyl-s-triazine and

1.3 parts by weight of a polyethyl acrylate of low viscosity (Plexisol[®] B 574) were dissolved in 70 parts by weight of a solvent mixture composed of ethylene glycol ethyl ether-acetate,

butyl acetate and xylene in a ratio of 8:1:1 and the solution was filtered through a 0.5 μ m filter.

On whirler-coating of the support, at 9,000 r.p.m., a resist layer of about 1.2 μ m thickness was obtained, which was dried for a further 10 minutes at 90°C in a circulating air oven. After cooling and conditioning to defined room conditions of 23°C and 40-50% relative humidity, the resist layer was exposed for about 1 second in a wafer contact-exposure apparatus under a commercially available chromium mask having highly resolved test areas, using a 200 watt Hg high-pressure lamp.

Development was carried out at 25°C in an agitated developer composed of

- 15 2.67 % of sodium metasilicate x 9 H₂O,
 1.71 % of trisodium phosphate x 12 H₂O and
 0.17 % of monosodium phosphate, dissolved in
 95.45 % of fully desalinated water.

The disk was then rinsed with fully desalinated water and blown dry with nitrogen.

By virtue of the film-forming properties of the additive resin, the adhesion and etch resistance on etching with NH₄F-buffered hydrofluoric acid were markedly improved. It was possible further to enhance this behavior by increasing the proportion of additive resin up to about twice the quantity stated. If, in doing this, a tendency to fog appeared, depending on the layer thickness, drying and exposure, it was possible to eliminate this tendency by increasing the concentration

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of the developer, without impairing the effect achieved by the increased quantity of resin.

Similar results were obtained when, instead of the aromatic-aliphatic ortho-ester used, the same quantity
5 of an aliphatic ortho-ester, namely the bis-(2,5-diethyl-5-butyl-1,3-dioxan-2-yl) ether of triethylene glycol, was used.

Example 2

A positive dry resist layer of 50 μ m thickness
10 was applied to a 25 μ m thick polyester film, which had been pretreated with trichloroacetic acid/polyvinyl alcohol, and was laminated with a polyethylene cover film. The dry resist layer was prepared by coating with the following solution:

- 15 34.5 parts by weight of ethylene glycol monomethyl ether,
 21.0 parts by weight of methyl ethyl ketone,
 27.5 parts by weight of the novolak as in Example 1,
 5.4 parts by weight of polyglycol 2000
20 9.7 parts by weight of the polyacetal obtained from 2-ethyl-butyraldehyde and triethylene glycol,
 0.3 part by weight of 2-[4-(2-ethoxy-ethoxy)-naphth-1-yl]-4,6-bis-trichloromethyl-s-triazine,
 1.9 parts by weight of a commercially available
25 coating aid based on silicone and
 0.02 part by weight of crystal violet base.

After peeling off the cover film, a copper-clad insulation board was coated with this dry resist layer by lamination, under the action of

pressure and heat, in a commercially available laminator for the production of printed circuit boards. After the support film had been peeled off from the coated printed circuit board material, which had cooled down in 5 the meantime, the latter was exposed for 50 seconds under a corresponding original, using a 5 kW metal halide lamp arranged at a distance of 140 cm. It is also possible to expose through the support film. Preferably, however, the dry resist layer is exposed in direct contact with the 10 original and after further drying, for example for 10 minutes at 80°C. Subsequently, the layer was developed in a spray apparatus with the following developer solution:

- 0.6 % of NaOH,
- 0.5 % of sodium metasilicate x 5 H₂O,
- 15 1.0 % of n-butanol and
- 97.9 % of fully desalinated water.

By a stepwise replacement of the polyglycol by polyethyl acrylate, the softness of the layer can be adjusted to a lower value, as desired, and the resistance 20 to developer as well as the quality as an electroplating resist can be improved. If drying during the coating step is not very vigorous, polyester without the pre-treatment mentioned can be used as the support film.

Example 3

25 Using ethylene glycol monomethyl ether as the solvent, a 25 µm thick positive dry resist layer which was composed of

- 65.0 % of the novolak as in Example 1,
- 19.5 % of a poly-ortho-ester, prepared by a

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polycondensation reaction of trimethyl orthoformate with 2-ethyl-2-hydroxymethyl-4-oxa-octane-1,8-diol, mean molecular weight 1470,

0.7 % of the triazine derivative indicated in

5 Example 1,

0.06 % of crystal violet base,

5.9 % of a vinyl acetate/crotonic acid copolymer (95:5) and

5.9 % of a polyester obtained from adipic acid
10 and propane-1,2-diol

was applied to the support film mentioned in Example 2.

For the preparation of through-hole plated printed circuit boards, this dry resist was laminated onto a commercially available base material which was copper-
15 clad on both sides and which, depending on the circuit, had been provided with bores of up to 2 mm diameter. Subsequently, the support-film was peeled off, and the layer was dried further for a short period and exposed and developed as in Example 1. In this case, the
20 plate, coated on both sides, was also exposed on both sides, and it was developed by spraying simultaneously from both sides in an appropriate spray-development machine.

Without addition of the copolymer and the plastic-
25 izer, the resist was too weak with respect to its film properties. The stability of the resist skin over the drilled holes with these additives on spray-development was already good in the case of holes of 0.5 mm diameter. When this resin and the plasticizer were replaced, in stages or completely,

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by polyvinyl methyl ether (Lutonal[®] M 40) the plasticizing resin, positive dry resists were obtained which were outstandingly suitable for covering drilled holes of up to 2 mm diameter.

- 5 When the proportion of polyvinyl methyl ether was increased to 20% and the novolak content of the layer was reduced at the same time to 60%, spray-development even of 15 μ m thick positive dry resists was reliably possible over drilled holes of 1 mm diameter, without
10 tearing of the resist film.

Similar results were obtained when using the polymeric ortho-ester obtained from trimethyl orthoformate and 2-ethyl-2-hydroxymethyl-5-methyl-4-oxa-heptane-1,7-diol.

15 Example 4

A positive photoresist composition of
76 parts by weight of the solvent mixture as in
Example 1,

- 13.6 parts by weight of the novolak as in Example 1,
20 6.6 parts by weight of 1,3-bis-[2-(5-ethyl-5-butyl-1,3-dioxacyclohexoxy)]-2-ethyl-2-butyl-propane,
1.1 parts by weight of the triazine indicated in
Example 2 and

- 2.7 parts by weight of polyvinyl ethyl ether
25 (Lutonal[®] A 25)
was used, as in Example 1, for applying fine circuit patterns to a silicon wafer.

After whirler-coating with this solution at 6,000 rpm and further drying in a circulating air oven,

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a positively pre-sensitized wafer was obtained which was stable on storage and the light sensitivity of which was several times greater than that of commercially available positive photoresist layers of the same 5- thickness, based on o-naphthoquinone-diazide. In a comparison with the AZ 1350 J^(R) photoresist, which is widely used in microelectronics and is based on o-quinone-diazides, 3 seconds were required for the non-diazo layer and 20 seconds were required for the diazo 10 layer when copying was carried out as in Example 1, but with the interposition of a filter which lengthens the exposure times. Both these exposure times are optimized for good resolution down to about field 3/2 of the ITEK test original, when developed for 1 minute 15 in the developer solution indicated in Example 1.

The plasma-etching behavior of both layers was also investigated, in each case for 30 minutes at 120°C, without and with baking of the exposed and developed wafer. When the plasma-etching was taken up to the maximum temper- 20 ature of 230°C, 80 nm of SiO₂ being etched away in 10 minutes, the baked test patterns were almost identical. Under these conditions, the unbaked patterns displayed a significant attack on the coating and a corresponding broadening of the etched lines.

25 When the polyvinyl ethyl ether was omitted from the above coating solution and a layer of the same thickness was prepared on the wafer at a lower whirling speed, the copying properties obtained were poorer, since the layer was less homogeneous and some of the

edges had a torn appearance. On baking, the layer profile of this comparison layer deteriorated further due to deformation, and the worst result was obtained on plasma-etching. Altogether, the layer described in this example was the best in respect of suitability for plasma-etching, resolution and light-sensitivity.

Example 5

For the manufacture of positive photoresist compositions for the preparation of autotype copper gravure printing cylinders, the following were dissolved, with stirring, in a mixture of 1,1,1-trichloroethane, n-butyl acetate and ethylene glycol monoethyl ether-acetate (5:3:2) to give solutions of 100 parts by weight in total in each case:

- 10 parts by weight of the novolak as in Example 1,
3 parts by weight of 1,8-bis-(3,4-dihydro-naphth-2-yloxy)-3,6-dioxa-octane,
0.25 part by weight of 2-(acenaphth-5-yl)-4,6-bis-trichloromethyl-s-triazine,
0.1 part by weight of crystal violet base
and either
- 1) 2 parts by weight of a colophony resin esterified with pentaerythritol (Resin B-106 ^(R)) or
 - 2) 5 parts by weight of the glycerol ester of partially hydrogenated rosin (Staybelite ^(R) Ester 5) or
 - 3) 4 parts by weight of the glycerol ester of partially hydrogenated colophony (Staybelite ^(R) Ester 610)
- (all these products were obtained from Hercules Inc.).

One quarter of a freshly copper-plated rotary

copper cylinder was in each case coated, using a spray gun, to a thickness of about 3 μ m with the three photoresist compositions provided with the additive resin 1, 2 or 3, and with a comparison solution without an additive resin, and the layers were dried by means of warm air or infrared lamps. Subsequently, the layers were exposed under a screened negative of the motif to be printed, and the copper surface was bared imagewise by pouring 0.8 % strength sodium hydroxide solution onto the slowly rotating cylinder; in the case of these layers, this process was completed within 2 - 4 minutes. Subsequently, the cylinder was rinsed with water and dried by further rotation in warm air.

Before the conventional intaglio etching with ferric chloride solution, retouching was carried out on the four layer portions which were to be compared, by mechanically putting in markings and additional lines, using a burin for correction. This was achieved most simply and cleanly, that is to say with the smoothest edges without fine spalling of the edge resists, in the case of the third layer variant, followed by layers 1 and 2. The comparison layer was relatively the most brittle and, after etching, displayed the most extensive undercutting of the lands.

25 Example 6

This example demonstrates the improvement in the oleophilic character and in the resistance to developer of an offset printing form.

A coating solution composed of

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7 parts by weight of a modified phenol/formaldehyde novolak (prepared from 140 parts by weight of a novolak and 6.5 parts by weight of the addition product obtained from 3 moles of a tolylene diisocyanate and 5 1 mole of trimethylolpropane),

2 parts by weight of 2-(naphth-2-yloxy)-5,5-dimethyl-1,3-oxazolin-4-one,

0.4 part by weight of 2-(4-methoxy-anthrac-1-yl)-4,6-bis-trichloromethyl-s-triazine and

10 0.1 part by weight of 4-diethylamino-azobenzene in

90.8 parts by weight of a solvent mixture composed of tetrahydrofuran, ethylene glycol monomethyl ether and butyl acetate (5:4:1)

15 was applied to aluminum which had been wire-brushed on one side.

The thickness of the layer obtained corresponded to a layer weight of 2 g/m^2 .

After drying, the coated aluminum was exposed 20 under a positive original, developed with a 3.5 % strength aqueous solution of trisodium phosphate, the pH of the solution having been adjusted to 12.6 by the addition of sodium hydroxide, and was then rinsed with water and finally made ready for printing by wiping 25 with 1 % strength phosphoric acid. Even if the plate was left lying in the developer solution for 12 times the period sufficient for development, there was virtually no damage to the image areas. Subsequently, such a plate was used for printing, and it took up the printing

ink very rapidly, in fact more rapidly than a corresponding printing plate prepared with only unmodified phenol/formaldehyde novolak. The quality of the surface of the printing plate after baking of the printing form at 230°C was likewise better. Similar results were obtained when, instead of the modified resin indicated, 6 parts by weight of the condensation product obtained from 5 parts by weight of octadecyl isocyanate and 100 parts by weight of the same novolak were used.

10 Example 7

This example describes the galvanoplastic preparation of a rotary nickel stencil for textile printing and wallpaper printing.

15 An approximately 25 μ m thick layer of the following composition:

35 % of novolak

25 % of the condensation product obtained from 187 parts by weight of phenol/formaldehyde novolak and 6.5 parts by weight of the isocyanate addition product indicated in Example 6,

15 % of polyvinyl methyl ether (Lutonal [®] M 40),

24 % of N-diphenoxymethyl- ϵ -amino-caprolactam,

1 % of the triazine indicated in Example 5 and

0.1% of crystal violet base

25 was applied by 3-fold spray-coating with intermediate drying to a bright nickel cylinder which was slightly contractible and had been provided with a conductive release layer.

The coated cylinder was adequately exposed under

a positive of the motif which was to be printed and the tone gradations of which had been converted, in the conventional manner by means of a screen of 32 lines per centimeter, into image portions of different dot coverage.

5 5 times this exposure time was required for a positive layer having half the thickness and based on naphthaquinone-diazides. Development was carried out with a solution of

10 0.5 % of sodium hydroxide,
0.8 % of sodium metasilicate x 9 H₂O and
1.0 % of ethylene glycol mono-n-butyl ether in
97.7 % of fully desalinated water.

This was effected by immersing the rotating exposed cylinder in a trough of appropriate size, which
15 was half-filled with developer. The resistance of the layer to developer was very good, giving steep flanks of the resist edges. After about 6 minutes' rotation of the cylinder in the developer, the developer trough was pulled away, and the cylinder was
20 rinsed with water and dried in air.

Since, compared with diazo layers, the resist used was not only relatively thick, but also had good adhesion and was elastic and not brittle, it was comparatively easy, safely and therefore substantially more rapidly, to
25 retouch, mechanically by means of a burin or a fine drill, the register seam which is formed on exposure of the round cylinder by the abutting or overlapping of the film.

An elastic rotary printing form was obtained by galvanic deposition of nickel up to about 0.1 mm thickness,

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contraction of the cylinder core, stripping of the resist with acetone or 5 - 10 % strength sodium hydroxide solution and pulling the deposited nickel foil from the core. It was possible to transfer ink imagewise to the materials to be
5 printed through the holes having a slight conical taper. Since thicker layers were thus possible, smaller holes, that is to say lighter image dots, could be better protected from filling up, and the range of tones could thus be widened.

10 A similar result with respect to adhesion and mechanical properties of thick layers was obtained when, instead of the polyvinyl methyl ether, approximately the same percentage of hydrogenated methyl ester of colophony was used. The development then took about
15 $1/3$ as long again, and this was compensated for by the use of a developer of somewhat higher concentration. In place of the amide-acetal which can be split by acid, 1,2,6-tris-(3,4-dihydro-naphth-1-yloxy)-hexane can also be used.

Example 8

20 An aluminum plate of electrolytically roughened and anodized aluminum, which had been pretreated with polyvinylphosphonic acid, was provided with a 2.2 μ m thick layer of

2 parts by weight of the novolak as in Example 1,

25

0.4 part by weight of the polymeric ortho-ester obtained from trimethyl orthoformate and 2-methyl-2-hydroxy-methyl-4-oxa-octanediol, molecular weight 2,580,

0.13 part by weight of 2-[4-(2-ethoxy-ethoxy)-

naphth-1-yl]-4,6-bis-trichloromethyl-s-triazine,

0.007 part by weight of crystal violet base and

0.2 part by weight of polybutyl acrylate
(Plexisol[®] D 592).

5 This layer was irradiated imagewise with an argon ion laser at 10 mJ/cm^2 in a laser irradiation apparatus (Laserite^(R) 150 R from Messrs. Eocom Corp.). The exposed layer portions were removed in the course of 2 minutes, using a developer containing

10 5.5 parts by weight of sodium metasilicate x 9 H_2O ,

3.4 parts by weight of trisodium phosphate x 12 H_2O ,

0.4 part by weight of monosodium phosphate
15 (anhydrous), and

90.7 parts by weight of fully desalinated water.

It was possible to make the image stand out even more clearly by inking the unirradiated areas with greasy ink.

20 When the printing plate was directly compared with an otherwise identical printing plate which did not contain any polybutyl acrylate, the following differences were found. Although the additive resin somewhat slows down the speed of development, it improves the
25 quality of the coating and the ink receptivity. The main advantage was an increase of more than 50% in the obtainable print run, whereby a highly sensitive printing plate, which can be provided with an image by means of a laser, becomes available for a range of runs of more

than 100,000. Similar results were obtained when the polycondensation product prepared from trimethyl orthoformate and 1,2,6-hexanetriol was used as the compound which can be split by acid. Without a
5 substantial change in the advantages achieved, it was possible to replace up to 50% of the additive resin by a copolymer based on butyl methacrylate and methyl methacrylate (Plexisol ^(R) PM 709) or by a polyisobutyl vinyl ether (Lutonal ^(R) I 60) of low viscosity.

10 Example 9

To produce a positive dry resist for etch-resists and galvano-resists, the following solution was prepared:

57 parts by weight of methyl ethyl ketone,
15 20 parts by weight of the novolak as in Example 1,

10 parts by weight of the modified novolak indicated in Example 7,

4.5 parts by weight of the bis-(5-ethyl-5-methoxymethyl-1,3-dioxan-2-yl) ether of 2-ethyl-2-methoxymethyl-1,3-propanediol,
20

4.0 parts by weight of 1,3-propanediol bis-(3,4-dihydro-naphth-2-yl) ether,

0.2 part by weight of the triazine indicated
25 in Example 2,

0.05 part by weight of crystal violet base and

4.2 parts by weight of a polyurethane obtained from a diisocyanate and an aromatic polyester (Estane ^(R) 5715 from Goodrich Co.).

A biaxially stretched and heat set, 25 μ m thick polyethylene terephthalate film was coated with this solution, dried and laminated with a 12 μ m thick polypropylene cover film, in such a way that a uniformly 5 thick resist layer was formed between the two films.

For the manufacture of contact springs for switches, bright brass plates were coated on both sides with this resist, from which the cover films had been peeled off in a commercially available laminator, under the 10 action of pressure and heat. After cooling, peeling off the support films and brief further drying in a drying cabinet (80°C), the coated workpiece was sufficiently exposed on both sides under a pair of congruent originals in the form of a pouch. Spray-development 15 was then carried out on both sides with the developer mentioned in Example 2 and, after residues of the alkaline developer had been rinsed off, the wet plates were etched on both sides with a commercially available ferric chloride solution until they were etched through so as to give 20 smooth flanks.

Before breaking apart, the chemically milled components thus prepared in a grouping were, for baring and gold-plating of the contact ends, exposed under the corresponding original, developed and finally electro- 25 goldplated thinly in the bared areas. Subsequently, these switch components were bent into the correct shape and installed. Because of the good adhesion and flexibility of this layer, in particular due to the two added, readily compatible polyurethane resins, the

resist was able to remain as an insulating layer and protective layer on these contact springs, even after and, in some cases, during the action of heat. Without these additives, the resist cracked off in small pieces after a certain period of resilient stress. Furthermore, the separability from the polyester support film after lamination was improved to such an extent that it was possible to omit the hydrophilic pretreatment of the polyester film.

10 Example 10

A 0.7 μ m thick layer of the following composition:

52 parts by weight of the novolak as in Example 1,
21 parts by weight of the condensation product
15 obtained from 144 parts by weight of phenol/formaldehyde novolak and 4.6 parts by weight of tris-(4-isocyanatophenyl) thionophosphate and

27 parts by weight of the polymeric ortho-ester obtained from trimethyl orthoformate and 2-chloromethyl-
20 2-hydroxymethyl-4-oxa-1,8-octanediol
was whirler-coated onto an oxidized silicon wafer.

Imaging can be effected by electron beams, without a starter having to be added, since the polyortho-ester, which can be split by acid, itself contains detachable
25 chlorine in a chloromethyl group. This resin combination at the same time provides high resolution and thermal stability (dimensional stability).

Imaging was carried out by irradiation with 11 keV electrons at an energy of about 3×10^{-2} J/cm².

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After 60 seconds' development with the developer solution of Example 1, it was possible to remove the irradiated layer portions. Both in plasma-etching and in etching with hydrofluoric acid, this layer showed less lateral attack on the layer than a corresponding resist which did not contain any modified novolak but did contain 73 parts of novolak. For high-temperature plasma-etching, both layers were simultaneously baked for 30 minutes at 120°C, during which the flanks of the highly-resolving electron beam resist described above were flattened to a markedly smaller extent.

If the irradiation was carried out at an energy of at least 0.5 joule/cm², the organic resist materials were thoroughly decomposed and crosslinked. A negative image was formed, when the unirradiated portions were removed by means of solvents or by exposure without an original and development with the developer of Example 1.

Example 11

Highly light-sensitive positive color proofing films were prepared, for example for checking the mounting in multi-colour offset printing. The copying layers had the following composition:

47 parts by weight of the novolak as in Example 1,

38 parts by weight of a colophony derivative of the alkyd resin type (Neolyn[®] 20 from Hercules Inc.),

13 parts by weight of 2,2-bis-(4-diphenoxymethoxy-phenyl)-propane,

0.5 part by weight of 2,5-diethoxy-4-(p-tolylthio)-benzene-diazonium hexafluorophosphate and

1.5 parts by weight of Zaponechtblau HFL (C.I. 2,880) or

5 1.2 parts by weight of Zaponechtrot BB (C.I. 2,864) or

2.0 parts by weight of Fettgelb 5 G (C.I. Supplement 572).

The layer thicknesses of between 1 and 3 μ m and
10 the quantities of dye were mutually matched in such a way that the red, the blue and the yellow color proofing film had the same light-sensitivity, that is to say, when both the exposure time and the development time with an aqueous-alkaline developer are the same,
15 they will give the same length of wedge steps of a continuous tone test wedge copied simultaneously. These color proofing films are markedly more resistant to scratching and adhesive tape than comparative color proofing films prepared without the addition of a modified terpene resin.

20 Example 12

A 25 μ m thick polyester film was coated with a 70 μ m thick positive dry resist layer of the following composition:

61 parts by weight of a novolak (1:1 mixture
25 of the novolak of Example 1 and a phenol/formaldehyde novolak having a softening range of 110-120°C),

10 parts by weight of polybutyl acrylate as in Example 8,

6 parts by weight of a polyurethane obtained

from a diisocyanate and an aromatic polyester (Estane[®] 5702 from Goodrich),

22.7 parts by weight of the polyacetal obtained from benzaldehyde and 1,5-pentanediol,

5 0.3 part by weight of 2-(5-methyl-6-methoxy-naphth-2-yl)-4,6-bis-trichloromethyl-s-triazine and

0.05 part by weight of crystal violet base, and was laminated with a polyethylene cover film.

Using this resist, printed circuit board material
10 of a copper-clad insulating material was coated in the conventional manner in a laminator and was copied under a corresponding original. Compared with a 12 μ m thick positive diazo dry resist which is available on the market and which, for copying, required about
15 130 seconds and 1.5 minutes of spray-development with the developer mentioned in Example 2, this 70 μ m thick resist required only about 60 seconds' exposure with a development time of about 3 minutes. When the Cu surface, lamination conditions, drying, exposure and
20 development, within 5 - 10 minutes after exposure, are mutually matched in an optimum manner, 70 μ m deep reliefs of excellent edge acuity and form are obtained, lines of a line width and spacing of up to about 70 μ m being well reproduced. After the usual electroplating steps,
25 the resist was used as a solder mask and, for this purpose, it was rendered more heat-resistant and more adhesive by the additive resins.

Example 13

For the coating of zinc plates for the manu-

facture of letter press printing blocks,

28.5 parts by weight of the novolak as in

Example 1,

10 parts by weight of Staybelite ^(R) Ester 5 (see
5 Example 5),

7.5 parts by weight of a polyethyl acrylate of
low viscosity,

10.5 parts by weight of the bis-(5-phenoxy-1,3-
dioxan-2-yl) ether of 2-phenoxy-1,3-propanediol,

10 2.2 parts by weight of the triazine indicated
in Example 8 and

0.3 part. by weight of Zaponechtviolett BE
(C.I. 12,196)

were dissolved in

15 41 parts by weight of ethylene glycol monoethyl
ether.

A liquid curtain of this coating solution was
produced by continuously pumping it around through a
coater gap, and degreased zinc plates which had been
20 chemically roughened by superficial washing with 0.5 %
strength nitric acid, were pushed through this liquid curtain
and were thus coated. After drying of the layer
which was adjusted to a weight of 2.9 g/m² by setting
the coater curtain and the speed of transport of the plates,
25 the resulting highly light-sensitive positive zinc etching
plate, precoated for storage stability, was exposed under
a positive original of an autotype with a screen of 44
lines per centimeter and was developed in the manner usual in
process work. For this purpose, using the developer

of Example 7, the exposed layer was incipiently swollen in a dish, a tray or a continuous apparatus, and then removed by mechanical means, in the simplest case by wiping over with a pad.

After removal of the exposed layer portions by
 5 the development, a violet-blue resist image was present on the metallic-white zinc, and this was processed to give a letter press printing plate by etching with nitric acid, with the addition of flank-protecting agents, in a powderless etching machine. The most advantageous
 10 etching depth corresponding to the screen was reached after about 5 minutes. For correction of the tone, in particular in the case of multi-color etching, it is possible to carry out a further etching step. The block is directly suitable for the printing of many
 15 images and for the preparation of mats. Since the resist layer is still light-sensitive, it can be copied and etched once more, in spite of the etching which has already been carried out, for example for inserting negative lettering. Furthermore, it is possible, in
 20 the case of thicknesses of less than 1.75 mm, to bend the zinc etching plate into round shapes. This is possible even if the layer is to be baked, say for 5 - 15 minutes at 100 - 200°C, in order to obtain greater stability on printing. Due to the added resins and
 25 the particular blend thereof, it has improved adhesion, flexibility and etch resistance under these conditions.

Example 14

An 18 μ m thick positive dry resist layer of the following composition:

54 parts by weight of the novolak as in
Example 1,

21 parts by weight of the modified terpene
resin as in Example 11,

5 8.5 parts by weight of polyvinyl ethyl ether,
8 parts by weight of a polymeric ortho-ester,
prepared from trimethyl orthoformate and a mixture of
2-ethyl-5-methyl-2-hydroxymethyl-4-oxa-1,7-heptanediol
and 2-ethyl-2-hydroxymethyl-4-oxa-1,7-octanediol,

10 8 parts by weight of the polyacetal obtained
from diethylene glycol divinyl ether and cyclohexane-1,4-
diol,

0.45 part by weight of the triazine indicated
in Example 12 and

15 0.05 part by weight of crystal violet base
was coated on a 25 μ m thick polyester film and laminated
with a polyolefine film.

This was used for coating, by lamination, ceramic
or glass substrates which are used for microwave circuits,
20 hybrid components or displays, in most cases in a size
of 10 cm x 10 cm, and which were of the following types:
aluminum oxide thinly coated with metal (Al_2O_3/Al ,
 Al_2O_3/Ti or $Al_2O_3/Ti/Ni/Au$) or glass/Cr, glass/Ni, glass/
Sn-In oxide or glass/Sn-In oxide/Cu.

25 On all these supports, this layer combination had
good adhesion on lamination without preheating of the
substrates and it gave clean sharp-edged copies and showed
resistance to various etching and electroplating processes.
Copying and etching of copper, both with iron-III-

chloride and with copper-II chloride etching solution,
can be repeated several times. This layer even
withstands etching of the conductive transparent Sn-In
oxide layer with strong hydrochloric acid at 60°C, after
5 which, surprisingly, second copying is still possible.



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Patent Claims

1. A positive-working radiation-sensitive mixture composed of
 - a) a compound having at least one C-O-C bond which can be split by acid,
 - b) a compound which forms a strong acid when irradiated,
 - c) a binder which is insoluble in water and soluble in aqueous-alkaline solutions and
 - d) at least one resin, the solubility properties of which differ from those of the binder (c), wherein the resin having different solubility properties is
 - d1) a polyurethane resin obtained from an organic isocyanate and a polymer which contains hydroxyl groups,
 - d2) a polyvinyl alkyl ether,
 - d3) an alkyl acrylate polymer or
 - d4) a hydrogenated or partially hydrogenated derivative of colophony.
2. A radiation-sensitive mixture as claimed in claim 1, which contains the component d) in a quantity of 1 to 50 % by weight, relative to the non-volatile constituents of the mixture.
3. A radiation-sensitive mixture as claimed in claim 1, wherein the compound (a) which can be split by acid is an ortho-carboxylic acid derivative, an acetal, an enol ether or a N-acyliminocarbonate.



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4. A radiation-sensitive mixture as claimed in claim 1, wherein the binder (c) is a novolak.

5. A process for the preparation of relief images, which comprises laminating a light-sensitive material, which is composed of a temporary support film and a light-sensitive thermoplastic layer to a support material under the action of pressure and heat, imagewise exposing the light-sensitive layer and, after the temporary support film has been peeled off, washing out the exposed layer areas by means of an aqueous-alkaline developer solution, wherein the light-sensitive thermoplastic layer comprises a light-sensitive mixture as claimed in claim 1.