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IN THE MATTER OF AN APPLICATION
FOR REGISTRATION OF UNITED KINGDOM
PATENT IN SINGAPORE

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do solemnly and sincerely declare that I am conversant
with the English and German languages and that the
following is true translation prepared by me of
European Patent Specification No. 0,048,876, published
on 11th April 1984.

And I make this Declaration conscientiously believing
the same to be true.

Declared at Wiesbaden, this 18th day of March 1985.

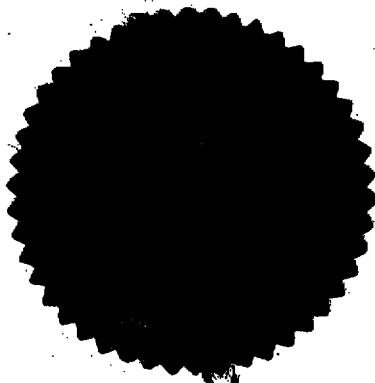
Ursula Beck

Notarial Register No. 33/85

Signed before me this 18th day of March 1985.

Notary Public

de Faria e Castro
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Light-hardenable mixture and light-sensitive copying
material prepared with this mixture

The invention relates to a negative-working light-hardenable mixture which contains, as the light-sensitive compound, a diazonium salt polycondensation product or an organic azido compound and, as the binder, a high-molecular polymer which has sulfonylurethane side groups and which is soluble or swellable in an aqueous alkaline solution, and is preferably used for the preparation of printing plates.

Mixtures of the generic type indicated have been described in DE-A 2,053,363. As the binder, they contain a reaction product of at least one alkylsulfonyl isocyanate, alkoxysulfonyl isocyanate, arylsulfonyl isocyanate or aryloxysulfonyl isocyanate and a polymer which contains hydroxyl groups. However, layers which contain diazonium salt polycondensation products and polymers of this type as binders can be developed only if organic solvents are added to the alkaline developers, having a pH range of 7.5 - 9.5, described in the above publication. The organic solvents which are suitable for these purposes and in most cases are low-boiling can be injurious to the health of the user, in addition to causing an odor nuisance, unless there is adequate exhaustion of the vapors. Disposal of the spent developers is not possible without observing special precautions.

Polymers similar to the abovementioned binders, having sulfonylurethane side groups, have been described in DE-A 2,053,364. These polymers contain terminal unsaturated radicals in the sulfonylurethane side groups and are used as light-crosslinkable

materials, if appropriate in combination with low-molecular polymerisable compounds. These polymers have not been used as polymeric binders for layers based on other light-sensitive systems, such as diazo compounds or azido compounds, evidently due to the fear that uncontrollable reactions in light and particularly reactions in the dark would result from the combination of two constituents which are light-curable by different mechanisms. Thus, it is stated, for example, in DE-A 2,053,364, page 7, lines 6 - 9, that the compounds described therein show substantially less tendency to undesired crosslinking than compounds having acrylic acid side groups or methacrylic acid side groups. Since, however, this tendency is always present, in contrast to saturated binders, and can be reinforced in some cases in the presence of thermally unstable compounds, such as diazo compounds or azido compounds, combinations of this type have hitherto been avoided.

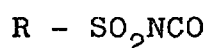
It was the object of the invention to propose light-sensitive mixtures of the indicated generic type, which can be developed, by the use of a solvent-free, non-polluting developer, more readily and more reliably than known mixtures, but which in other respects have the desirable properties of the known copying materials.

The invention relates to a light-hardenable mixture which contains, as the light-sensitive compound, a diazonium salt polycondensation product or an azido compound, and, as the binder, a high-molecular polymer which has sulfonylurethane side groups and which is soluble or at least

swellable in an aqueous-alkaline solution, and wherein the polymer contains alkenylsulfonylurethane or cycloalkenylsulfonylurethane side groups.

According to the invention, a light-sensitive copying material for the preparation of printing plates is also proposed, which copying material is composed of a support and a light-hardenable layer which contains, as the light-sensitive compound, a diazonium salt polycondensation product or an organic azido compound and, as the binder, a high-molecular polymer which has sulfonylurethane side groups and which is soluble or at least swellable in an aqueous-alkaline solution, and wherein the polymer contains alkenylsulfonylurethane or cycloalkenylsulfonylurethane side groups.

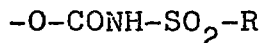
The unsaturated sulfonylurethanes contained in the mixture according to the invention are reaction products of polymeric substances, which contain units with free hydroxyl groups, and of sulfonyl isocyanates of the general formula.



in which R is an aliphatic or cycloaliphatic radical having at least one double bond.

In general, the radical R contains 2 to 12 carbon atoms and one or two, preferably one, olefinic double bonds. If R is an alkenyl group, the latter preferably has 2 to 4 carbon atoms; preferred cycloalkenyl groups are those having 5 to 8 carbon atoms. Examples are vinyl, propenyl, allyl, but-4-en-1-yl, cyclohex-3-en-1-yl, cyclohex-1-enyl and methyl-cyclohex-3-en-1-yl radicals and the like. Propenyl and cyclohexenyl radicals are particularly preferred.

The polymers present in the mixture according to the invention contain, bonded to the key atoms which carry the hydroxyl groups in the starting polymer, the grouping



in which the hydrogen atom in the position on the nitrogen is activated by the carbonyl group and the sulfonyl group to such an extent that it can be eliminated as a proton by means of aqueous alkali, as a result of which development with aqueous-alkaline developers becomes possible.

It has now been found, surprisingly, that the unsaturated sulfonylurethanes described above, in combination with diazonium salt polycondensation products, give layers which can readily and cleanly be developed with purely aqueous developer solutions, whilst corresponding layers containing saturated sulfonylurethane polymers according to Example 16 of DE-A 2,053,363

require at least a small proportion, and preferably almost 50 %, of an organic solvent in the developer. Furthermore, it was found that, surprisingly, the storage stability of the copying materials containing unsaturated sulfonylurethanes is not noticeably poorer than that of corresponding materials containing saturated sulfonylurethanes.

The polymeric unsaturated sulfonylurethanes used in the mixture according to the invention are known per se from DE-A 2,053,364, as already mentioned.

The following can be used as the starting polymers, containing hydroxyl groups, for the preparation of the

polymeric unsaturated sulfonylurethanes: partially hydro-
lised polyvinyl esters; polyvinyl acetals with unconverted
vinyl alcohol units, epoxide resins with free OH groups, partial
esters and ethers of cellulose, and terpolymers of poly-
vinyl chloride, polyvinyl acetate and polyvinyl alcohol.

Polyvinyl butyrals and polyvinyl formals, which have
free OH groups and are commercially available, are parti-
cularly suitable for the preparation of the binders.

The sulfonyl isocyanates necessary for the pre-
paration of the binders used according to the invention
are described in DE-C 1,297,601.

Suitable diazonium salt polycondensation products
are the condensation products of aromatic diazonium salts
capable of condensation, for example those of diphenyl-
amine-4-diazonium salts, with aldehydes, preferably formal-
dehyde. With particular advantage, co-condensation
products are used which, in addition to the diazonium salt
units, also contain other units which are not light-sensi-
tive and which are derived from compounds capable of con-
densation, in particular aromatic amines, phenols, phenol
ethers, aromatic thioethers, aromatic hydrocarbons, aroma-
tic heterocyclic compounds and organic acid amides.

These condensation products are described in

DE-A 2,024,244. Generally, all those dia-
zonium salt polycondensation products are suitable which are
described in DE-A 2,739,774.

The diazonium salt units are preferably derived
from compounds of the formula $(R^1-R^3)_p R^2-N_2X$ in which

X is the anion of the diazonium compound, p is an integer from 1 to 3, R^1 is an aromatic radical having at least one position capable of condensation with an active carbonyl compound, R^2 is a phenylene group and R^3 is a single bond or one of the groups: $-(CH_2)_q-NR^4-$, $-O-(CH_2)_r-NR^4-$, $-S-(CH_2)_r-NR^4-$, $-S-CH_2CO-NR^4-$, $-O-R^5-O-$, $-O-$, $-S-$ or $-CO-NR^4-$, wherein q is a number from 0 to 5, r is a number from 2 to 5, R^4 is hydrogen, an alkyl group having 1 to 5 C atoms, an aralkyl group having 7 to 12 C atoms or an aryl group having 6 to 12 C atoms, and R^5 is an arylene group having 6 to 12 C atoms.

Further suitable light-sensitive compounds are low-molecular or high-molecular organic azides, and in particular low-molecular aromatic azido compounds which contain at least two azido groups. The following are examples of suitable compounds: 4,4'-diazido-stilbene, 4,4'-diazido-stilbene-2,2'-disulfonic acid, 4,4'-diazido-benzophenone, 4,4'-diazido-diphenylmethane, 4,4'-diazido-dibenzalacetone, 4,4'-diazido-dibenzalacetone-disulfonic acid, 1,3-bis-(4-azido-phenyl)-propan-2-one, 1,2-bis-(4-azido-cinnamoyloxy)-ethane, 4,4'-diazido-benzal-cyclohexanone, 4,4'-diazido-benzal-cyclohexanone-disulfonic acid and 2,6-bis-(4-azido-benzal)-4-methyl-cyclohexanone.

Further examples are the azidostyryl compounds mentioned in GB-A 790,131, the azido-imidazolyl compounds mentioned in

DE-C 950,618 and the diazidostilbene compounds mentioned in US-A 2,848,328.

In general, the mixtures according to the inven-

tion contain 5 to 90, preferably 10 to 70, per cent by weight of diazonium compound or azido compound and 95 to 10, preferably 90 to 30, per cent by weight of the binder described above, relative to the weight of all the non-volatile constituents of the mixture.

To stabilise the light-sensitive mixture, it is advantageous to add to the mixture a compound having an acid character. For this purpose, mineral acids and strong organic acids can be used, amongst which phosphoric acid, sulfuric acid, perchloric acid, boric acid or p-toluenesulfonic acid are preferred. Phosphoric acid is a particularly suitable acid.

Plasticisers, adhesion promoters, dyes, pigments, color-formers and other resins can also be added to the mixtures.

The nature and amount of these additives depend on the envisaged field of application of the mixture according to the invention. In principle, care must be taken here that the added materials do not absorb an excessive proportion of the actinic light necessary for crosslinking and thus reduce the light-sensitivity in practice.

The light-sensitive mixtures can also contain dyes and/or pigments, which can both act as contrast agents and strengthen the layer. Possible dyes are indicated, for example, in US-A 3,218,167 and US-A 3,884,693.

Particularly suitable examples are Victoria Pure Blue FGA, Victoria Pure Blue BO (C.I. 42595), malachite green,

crystal violet, Victoria Blue B (C.I. 44045), Rhodamine 6 GDN (C.I. 45160), Fat Red 5B (C.I. 26125), Neozapon Blue FLE (C.I. Solvent Blue 70), Brilliant Blue salt-acetate, Samaron Navy Blue, Orasol Blue GN, Renol Blue B 2 G (C.I. 74160) and Zapon Fast Fire Red B (C.I. 13900:1).

Metanil Yellow (C.I. 13065), methyl orange (C.I. 13025) or phenylazodiphenylamine can be used for increasing the image contrast after exposure.

Within the scope of the invention, the following distribution by weight of the most important additives in the light-sensitive mixture is preferred, relative to the content of non-volatile constituents, that is to say the constituents of the solid light-sensitive layer obtained after the evaporation of the solvent.

Acid	: 0 to 5 %
Dye or pigment	: 0 to 10 %
Image contrast promoter (dye)	: 0 to 10 %

Commercially, the light-sensitive mixtures according to the invention can be used in the form of a solution or dispersion, for example as a so-called resist, and these are applied to an individual support, such as is customary, for example, for chemical milling, for the production of copied circuits or stencils, labeling, screen-printing forms and the like, and are exposed after drying and imagewise developed by the user himself. In this case, the constituents of the light-sensitive mixture are dissolved in a suitable solvent. Alcohols, ketones, esters and ethers, and the like, are suitable as solvents. Partial ethers of glycols or ketoalco-

hols, for example ethylene glycolmonomethyl ether, have proved to be advantageous solvents for this purpose.

The light-sensitive mixture according to the invention can, however, also be marketed particularly well in the form of a solid light-sensitive layer, present on a support material, for the production of printing forms, relief images, etch resists, stencils, matrices, screen-printing forms, individual copies and the like. A particularly important application is represented by storage-stable pre-sensitised printing plates for planographic printing.

The coating of the support material is effected from appropriate organic solvents or solvent mixtures, and in particular by die-coating, spraying or dipping.

Examples of suitable supports are magnesium, zink, copper, mechanically, chemically and electro-chemically roughened aluminum, anodically oxidised aluminium, steel and also polyester film or cellulose acetate film, nylon fix gauze and the like, it being possible for their surfaces to have been subjected to a pre-treatment, if required. The support material can here have the function of a final support or that of a temporary support material, from which the light-sensitive layer is transferred by means of lamination to the workpiece which is to be processed.

The recording material prepared with the use of the light-sensitive mixtures is employed, on the one hand, for the production of images on suitable supports or receiving sheets and, on the other hand, for the pro-

duction of reliefs which are used as printing forms, screens, resists and the like.

Furthermore, it is also possible to use the light-sensitive mixtures for the preparation of lacquers which can be hardened by UV radiation and which can be employed as surface protection, or for the formulation of printing inks which can be hardened by UV.

Particularly preferably, the mixture is used for the preparation of planographic printing forms, the preferred support material being aluminum.

Aluminum which is pretreated for this purpose in a customary manner, for example by mechanical, chemical or electrochemical roughening and, if appropriate, subsequent anodic oxidation is particularly preferred. A further treatment of this support material, for example with polyvinylphosphonic acid, alkali metal silicate, phosphate, hexafluorozirconate, chromate, borate, polyacrylamide and cellulose derivatives, is advantageous.

The copying materials obtained from the mixtures are processed in the known manner by imagewise exposure and washing-out of the unexposed layer areas with a suitable developer.

The copying material is exposed in the known manner under an original, using sources of copying light, which emit the greatest possible spectral proportion in the near ultra-violet range. Exposure can also be effected by laser radiation. Lasers of appropriate power, which are suitable for irradiation, are relatively shortwave lasers, for example Ar lasers, krypton ion

lasers and helium/cadmium lasers, which emit approximately between 300 and 600 nm, and in the case of some layers also CO₂ lasers which emit at 10.6 μm, or yttrium-aluminum-garnet lasers which emit at 1.06 μm.

The developer solutions used are aqueous-alkaline solutions having a pH value in the range from 8 to 14, preferably 10 to 13, which contain buffer salts, for example water-soluble alkali metal phosphates, alkali metal silicates, alkali metal borates, alkali metal carbonates, alkali metal acetates or alkali metal benzoates. Further constituents used are surfactants, preferably anionic surfactants, and, if appropriate, water-soluble polymers. Although the copying materials according to the invention are preferably processed with purely aqueous developers, it can be advantageous in certain cases, for example when combined with light-sensitive compounds of low solubility in water or when alkali-insoluble resins are added to the light-sensitive mixture, to add small proportions, that is to say less than 10 % by weight, preferably less than 5 % by weight, of organic solvents which are miscible with the solution. The development can be carried out in the known manner by dipping, spraying, brushing or dabbing.

The light-sensitive mixtures according to the invention have the following advantages:

They have a high light-sensitivity in practice, scope for sharp differentiation between image areas and non-image areas, high resolving power, easy and complete development without stains, high printing runs, good compatibility of the constituents of the layer in the

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solvents suitable for coating, for example ethylene glycol monomethylether, ethylene glycol monoethyl ether, diacetone-alcohol and mixtures of the above solvents with butyl acetate, ethylene glycol methyl ether-acetate and methyl isobutyl ketone, and scope for ready development in solvent-free aqueous developer solutions.

The examples which follow are intended to illustrate the invention. Parts by weight and parts by volume have the same relationship as the g and cm³, and percentage data and quantitative ratios are to be understood as units by weight, unless stated otherwise.

Example 1

11.3 parts by weight of a polyvinyl butyral having a molecular weight of about 70,000 - 80,000, and containing 71 % by weight of vinyl butyral units, 2 % by weight of vinyl acetate units and 27 % by weight of vinyl alcohol units, were dissolved in 170 parts by weight of anhydrous tetrahydrofuran. A mixture of 5.11 parts by weight of propenylsulfonyl isocyanate and 30 parts by weight of tetrahydrofuran was added dropwise at room temperature in the course of 15 minutes to the clear solution. In doing this, the internal temperature rose from about 25°C to about 31°C. The solution was stirred for a further 4 hours at room temperature and then added dropwise to 5,000 parts by volume of water. The white, fibrous product obtained was filtered off with suction and dried.

The yield amounted to 16.4 parts by weight of a polymer which had a softening point of about 161°C and an acid number of 81.0.

A coating solution was prepared from 97.0 parts by weight of the binder described above, 48.3 parts by weight of a diazonium salt polycondensation product prepared from 1 mole of 3-methoxy-diphenylamine-4-diazonium sulfate and 1 mole of 4,4'-bis-methoxymethyl-diphenyl ether in 85 % strength phosphoric acid and isolated as the mesitylenesulfonate, 4.8 parts by weight of phosphoric acid (85 %), 3.5 parts by weight of Viktoria Pure Blue FGA (C.I. Basic Blue 81) and 1.6 parts by weight of phenylazodiphenylamine in 3,500 parts by weight of ethylene glycol monomethyl ether and 1,036 parts by weight of tetrahydrofuran.

The solution was applied to an aluminum foil which had been roughened by brushing with an aqueous suspension of an abrasive and then pretreated with a 0.1 % strength aqueous solution of polyvinylphosphonic acid, and was dried.

The copying layer was exposed under a negative original for 35 seconds with a metal halide lamp of 5 kW power.

The exposed layer was treated with a developer solution of the following composition

5 parts by weight of sodium lauryl-sulfate,
1.5 parts by weight of sodium metasilicate x 5 H₂O,
1 part by weight of trisodium phosphate x 12 H₂O and
92.5 parts by weight of water
by means of a dabber, the unexposed layer areas

being removed, and then rinsed with water and dried.

On the copy, step 5 of a silver film continuous tone step wedge having a density range from 0.05 to 3.05, the density increment being 0.15, was still fully blackened.

On a sheet-fed offset machine, the printing plate obtained gave a run of 30,000 sheets.

Example 2

22.6 parts by weight of the polyvinyl butyral described in Example 1 and 20.45 parts by weight of propenylsulfonyl isocyanate were reacted as described in Example 1. After precipitation in water, a white, fibrous material having an acid number of 144.1 was obtained.

A coating solution was prepared from
30.3 parts by weight of the reaction product described above,
15.1 parts by weight of the diazonium salt polycondensation product described in Example 1,
1.0 part by weight of phosphoric acid (85 %),
1.1 parts by weight of Victoria Pure Blue FGA (C.I. Basic Blue 81) and
1.1 parts by weight of phenylazodiphenylamine in
1,600 parts by weight of ethylene glycol monomethyl ether.

The solution was applied to an electrochemically roughened and anodically oxidised aluminum foil which had been post-treated with polyvinylphosphonic acid. The layer weight after drying was 0.8 g/m^2 .

Processing was carried out as described in Example 1. After imagewise exposure, the offset plate was in

this case dipped for one minute into the developer and then sprayed with water from a rose. The layer was developed perfectly, that is to say that sharply differentiated images of even very small dot and line elements were obtained, there were no stains or layer residues on non-image areas and high resolution was achieved.

Example 3

A coating solution was prepared from

34.1 parts by weight of the polymeric reaction product described in Example 2,

11.4 parts by weight of the diazonium salt polycondensation product described in Example 1,

0.5 part by weight of phosphoric acid (85 %),

1.1 parts by weight of Metanil Yellow (C.I. 13065) and

1.5 parts by weight of Victoria Blue B (C.I. 44045) in 1,6000 parts by weight of ethylene glycol monomethyl ether.

The solution was applied to the support indicated in Example 2.

The dry layer weight was 0.8 g/m^2 . Processing was carried out as described in Example 1. The printing form thus obtained gave long runs on a sheet-fed offset machine.

Example 4

22.6 parts by weight of the polyvinyl butyral indicated in Example 1 and 4.09 parts by weight of propenylsulfonyl isocyanate were reacted as described in Example 1.

A coating solution was prepared from:

48.4 parts by weight of a 6.26 % strength solution of
the above-described polymer in tetrahydrofuran,
1.51 parts by weight of the diazo polycondensation pro-
duct described in Example 1,
0.15 part by weight of phosphoric acid (85 %) and
0.11 part by weight of Victoria Pure Blue FGA (C.I.
Basic Blue 81) in
140 parts by weight of ethylene glycol monomethyl
ether.

The solution was applied to the support descri-
bed in Example 2 in such a way that, after drying, a
layer weight of 0.85 g/m^2 was obtained.

The exposed layer was treated, in a manner simi-
lar to that described in Example 1, with a developer so-
lution of the following composition:

5 parts by weight of sodium lauryl-sulfate,
3 parts by weight of sodium metasilicate x 5 H₂O and
92 parts by weight of water.

The printing form obtained gave more than 70,000 prints
on sheet-fed offset machines.

Example 5

22.6 parts by weight of the polyvinyl butyral
indicated in Example 1 and 26.02 parts by weight of
cyclohex-3-en-1-yl-sulfonyl isocyanate were reacted as
described in Example 1.

A coating solution was prepared from

30.3 parts by weight of the above reaction product
having an acid number of 142.6,

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15.1 parts by weight of the diazonium salt polycondensation product described in Example 1,
1.2 parts by weight of phosphoric acid (85 %),
1.1 parts by weight of phenylazodiphenylamine and
1.5 parts by weight of Victoria Pure Blue FGA (C.I. Basic Blue 81) in
1,600 parts by weight of ethylene glycol monomethyl ether.

The solution was applied to the support described in Example 2, to give a dry layer weight of 0.8 g/m². After imagewise exposure under a source of UV light, a treatment with the developer mentioned in Example 4 was carried out.

The printing form obtained gave more than 80,000 good prints on a Heidelberg-GTO sheet-fed offset printing press.

Example 6

22.6 parts by weight of the polyvinyl butyral described in Example 1 and 27.97 parts by weight of methylcyclohex-3-en-1-yl-sulfonyl isocyanate (mixture of the isomeric 3- and 4-methyl compounds) were reacted as indicated in Example 1. After precipitation in water, a white flocky material was obtained which had an acid number of 131.6 and was readily soluble in 3 % strength aqueous ammonia solution.

A coating solution was prepared from
30.3 parts by weight of the polymer described above,
15.1 parts by weight of the diazo polycondensation product described in Example 1,

1.2 parts by weight of phosphoric acid (85 %),
1.1 parts by weight of phenylazodiphenylamine and
1.5 parts by weight of Victoria Pure Blue FGA (C.I.
Basic Blue 81) in
1,600 parts by weight of ethylene glycol monomethyl
ether

and spin-coated onto the support described in Example
2 in such a way that the layer weight was 0.8 g/m^2 .
Processing was carried out as indicated in Example 1,
but using the developer from Example 4. The printing
form thus obtained gave more than 60,000 good prints on
a sheet-fed offset machine.

Example 7

11.3 parts by weight of the polyvinyl butyral in-
dicated in Example 1 and 13.88 parts by weight of vinyl-
sulfonyl isocyanate were reacted as described in Example
1. After precipitation in water, 19.3 g (77 % of the-
ory) of a white, fibrous material having an acid number
of 183.9 were obtained.

A coating solution was prepared from
30.3 parts by weight of the reaction product described
above,
15.1 parts by weight of the diazo polycondensation pro-
duct indicated in Example 1,
1.0 part by weight of phosphoric acid (85 %),
1.1 parts by weight of phenylazodiphenylamine and
1.5 parts by weight of Victoria Pure Blue FGA (C.I.
Basic Blue 81) in
1,650 parts by weight of ethylene glycol monomethyl

ether.

The solution was applied to the aluminum foil described in Example 2, to give a dry layer weight of 0.7 g/m^2 .

The copying layer was exposed under a negative original for 70 seconds with a metal halide lamp and treated, as described in Example 1, with the developer from Example 4.

The printing form thus obtained gave more than 40,000 good prints on a sheet-fed offset machine.

Example 8

A coating solution was prepared from
26.75 parts by weight of an 8 % strength solution of
the reaction product described in Example 1,
in tetrahydrofuran,
2.14 parts by weight of 2,6-bis-(4-azido-benzal)-4-
methyl-cyclohexanone and
0.23 part by weight of Rhodamine 6 GDN extra (C.I.
45160) in
100 parts by weight of ethylene glycol monomethyl
ether and
50 parts by weight of tetrahydrofuran.

The solution was applied to the support indicated in Example 2. The dry layer weight was 0.73 g/m^2 . Processing was carried out as described in Example 1. With the printing form thus obtained, long runs were achieved on a sheet-fed offset machine.

Example 9

A coating solution was prepared from

26.75 parts by weight of an 8.0 % strength solution of the reaction product described in Example 1, in tetrahydrofuran,

2.14 parts by weight of 2,6-bis-(4-azido-benzal)-4-methyl-cyclohexanone and

0.23 part by weight of Victoria Pure Blue FGA (C.I. Basic Blue 81) in

100 parts by weight of ethylene glycol monomethyl ether and

50 parts by weight of tetrahydrofuran.

The solution was applied to the support indicated in Example 2 in such a way that, after drying, a layer weight of 0.7 g/m^2 was obtained.

After exposure under a negative original, the plate was developed with a developer solution of the following composition

5 parts by weight of the triethanolammonium salt of lauryl-sulfate,

1 part by weight of sodium metasilicate x 5 H_2O ,

1.5 parts by weight of trisodium phosphate x 12 H_2O and

92.5 parts by weight of water

and was made ready for printing by inking with greasy ink.

Many thousands of good prints were obtained with the plate thus obtained on a Heidelberg-GTO sheet-fed offset machine.

Example 10

A coating solution was prepared from

26.75 parts by weight of an 8.0 % strength solution of the reaction product described in Example 1, in

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tetrahydrofuran,

2.14 parts by weight of 2,6-bis-(4-azido-benzal)-4-methyl-cyclohexanone,

0.23 part by weight of Rhodamine 6 GDN extra and

0.21 part by weight of 2-benzoylmethylene-1-methyl-8-naphthothiazine in

100 parts by weight of ethylene glycol monomethyl ether and

50 parts by weight of tetrahydrofuran.

The solution was spin-coated onto the support described in Example 2. The dry layer weight was 0.75 g/m².

The copying layer was exposed under a negative original for 35 seconds with a metal halide lamp of 5 kW power: this gave a clearly visible dark red, positive image.

The exposed layer was treated, with the aid of a dabber, with a developer solution of the following composition

5 parts by weight of sodium lauryl-sulfate,

1 part by weight of sodium metasilicate x 5 H₂O and

94 parts by weight of water,

the non-image areas being removed, and was then rinsed with water and wiped with a blade. On the copy, step 5 of the silver film continuous tone wedge described in Example 1 was still fully blackened.

The printing plate obtained gave a run of 170,000 sheets on a sheet-fed offset machine.

Example 11

A coating solution was prepared from
26.75 parts by weight of an 8 % strength solution of
the reaction product described in Example 1, in
tetrahydrofuran,
2.1 parts by weight of 4,4'-diazido-stilbene-3,3'-
disulfonic acid,
0.23 part by weight of Rhodamine 6 GDN extra and
50 parts by weight of ethylene glycol monomethyl
ether.

The solution was applied to the support indicated in Example 2. The dry layer weight was 0.75 g/m^2 .
Processing was carried out as described in Example 1.

The developer used had the following composition

5 parts by weight of sodium lauryl-sulfate,
0.5 part by weight of sodium metasilicate $\times 5 \text{ H}_2\text{O}$ and
94.5 parts by weight of water.

This printing form gave long runs on sheet-fed
offset machines.

Example 12

A coating solution was prepared from
54.35 parts by weight of an 8.34 % strength solution of the
reaction product described in Example 1, in tetra-
hydrofuran,
0.91 part by weight of the diazonium salt polyconden-
sation product described in Example 1,
0.18 part by weight of phosphoric acid (85 %),
0.06 part by weight of phenylazodiphenylamine and

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0.13 part by weight of Victoria Pure Blue FGA in
150 parts by weight of ethylene glycol monomethyl
ether.

The solution was applied to electrochemically roughened and
anodically oxidised aluminum in such a way that, after
drying, a layer weight of 1.1 g/m^2 was obtained.

Processing was carried out in a manner similar
to that described in Example 1. The printing form
obtained gave runs of more than 150,000 prints on
sheet-fed offset machines.

Example 13

22.6 parts by weight of a terpolymer composed of
91 % of vinyl chloride, 3% of vinyl acetate, 6 % of
vinyl alcohol and having a mean molecular weight of 15,500
and a softening point of 77°C , were reacted, as described
in Example 1, with 4.52 parts by weight of propenyl-
sulfonyl isocyanate. The product obtained had an acid
number of 42.3.

A coating solution was prepared from
56.55 parts by weight of a 6.35 % strength solution of
the above-described reaction product in tetra-
hydrofuran,

1.79 parts by weight of the diazonium salt polyconden-
sation product described in Example 1,
0.18 part by weight of phosphoric acid (85 %),
0.06 part by weight of phenylazodiphenylamine and
0.13 part by weight of Victoria Pure Blue FGA in
140 parts by weight of ethylene glycol monomethyl ether.

The solution was applied to an electrochemically

roughened and anodically oxidised aluminum foil which had been post-treated with polyvinylphosphonic acid. After drying, the layer weight of the light-sensitive layer was 1.0 g/m^2 .

Processing was carried in a manner similar to that described in Example 1.

This printing form gave good runs on sheet-fed offset machines.

Example 14

A coating solution was prepared from
3.03 parts by weight of the reaction product described in Example 1,
1.51 parts by weight of a diazonium salt polycondensation product prepared from paraformaldehyde and diphenylamine-4-diazonium chloride in 85 % strength phosphoric acid,
0.05 part by weight of phosphoric acid (85 %),
0.15 part by weight of crystal violet and
0.11 part by weight of phenylazodiphenylamine in
170 parts by weight of ethylene glycol monomethyl ether.

The solution was applied to an electrochemically roughened and anodically oxidised aluminum foil in such a way that, after drying, a layer weight of 0.3 g/m^2 was obtained.

Processing was carried out in a manner similar to that described in Example 1.

The printing form obtained gave many thousands of good prints in sheet-fed offset machines.

Example 15

A coating solution was prepared from:

16.0 parts by weight of an 8.0 % strength solution of the reaction product described in Example 1, in tetrahydrofuran,

0.725 part by weight of the diazonium salt polycondensation product described in Example 1,

0.072 part by weight of phosphoric acid (85 %),

0.01 part by weight of phenylazodiphenylamine,

0.5 part by weight of Renol Blue B2G-H (Pigment Blue 15:3, C.I. 74160), in

86.6 parts by weight of ethylene glycol monomethyl ether.

The solution was applied to an electrochemically roughened and anodically oxidized aluminum foil which had been post-treated with polyvinylphosphonic acid. After drying, the layer weight of the light-sensitive layer was 1.0 g/m².

Processing was carried out in a manner similar to that described in Example 1.

This printing form gave good runs on sheet-fed offset machines.

Example 16

Analogously to the reaction described in Example 1,

45.2 parts by weight of a polyvinyl butyral having a molecular weight of more than 80,000 and containing 77 - 80 % by weight of vinyl butyral units, 2 % by weight of vinyl acetate units and 18 -21 % by weight of vinyl alcohol units, were dissolved in

580 parts by weight of anhydrous tetrahydrofuran, and a solution of
31.7 parts by weight of propenylsulfonyl isocyanate in
60 parts by weight of tetrahydrofuran was added there-
to at room temperature and the mixture was al-
lowed to react for a further 4 hours at room tem-
perature.

A coating solution was prepared from
906.7 parts by weight of a 12 % strength solution of
the above-described binder in tetrahydrofuran,
10.88 parts by weight of the diazonium salt
polycondensation product described in
Example 1,
1.08 parts by weight of phosphoric acid (85 %),
0.8 parts by weight of Victoria Pure Blue FGA and
0.36 parts by weight of phenylazodiphenylamine in
5,800 parts by weight of ethylene glycol monomethyl
ether,
2,500 parts by weight of tetrahydrofuran and
770 parts by weight of butyl acetate.

The solution was applied to an electrochemically
roughened and anodically oxidised aluminum foil which had been
post-treated with polyvinylphosphonic acid. After
drying, the layer weight was 0.5 g/m^2 .

The plate was exposed to the laser light of an argon
ion laser in such a way that the layer was subjected to
an energy of 5 mJ/cm^2 .

The exposed layer was developed with an emulsion
lacquer which is marketed by Messrs. Western Litho under

the name "Jet Black Medium".

On a sheet-fed offset machine, the printing plate obtained gave a run of more than 40,000 sheets.



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What is claimed is:

1. A light-hardenable mixture which contains, as the light-sensitive compound, a diazonium salt polycondensation product or an organic azido compound and, as the binder, a high-molecular polymer which has sulfonylurethane side groups and which is soluble or at least swellable in an aqueous-alkaline solution, wherein the polymer contains alkenylsulfonylurethane or cycloalkenylsulfonylurethane side groups.
2. A light-hardenable mixture as claimed in Claim 1, wherein the polymer is the reaction product of a polymer which contains units with free hydroxyl groups and of an alkenylsulfonyl isocyanate or cycloalkenylsulfonyl isocyanate.
3. A light-hardenable mixture as claimed in Claim 2, wherein the polymer which contains units with free hydroxyl groups is a partially hydrolyzed polyvinyl ester, a polyvinyl acetal with unconverted vinyl alcohol units, an epoxide resin, a partial ester or ether of cellulose, or a terpolymer comprising units of vinyl chloride, vinyl acetate and vinyl alcohol.
4. A light-hardenable mixture as claimed in Claim 3, wherein the polymer is a polyvinyl butyral or polyvinyl formal with unconverted vinyl alcohol units.
5. A light-hardenable mixture as claimed in Claim 1, wherein the diazonium salt polycondensation product comprises recurring $A-N_2X$ and B units which are linked by intermediate members, preferably methylene groups, which



are derived from carbonyl compounds capable of condensation, preferably formaldehyde, A being the radical of an aromatic diazinium compound which is capable of condensation with formaldehyde, and B being the radical of a compound which is free from diazonium groups and capable of condensation with formaldehyde, in particular the radical of an aromatic amine, a phenol, a phenol ether, an aromatic thioether, an aromatic hydrocarbon, an aromatic heterocyclic compound or an organic acid amide.

6. A light-sensitive copying material for the preparation of printing plates, composed of a support and a light-hardenable layer which contains, as the light-sensitive compound, a diazonium salt polycondensation product or an organic azido compound and, as the binder, a high-molecular polymer which has sulfonylurethane side groups and which is soluble or at least swellable in an aqueous-alkaline solution, wherein the polymer contains alkenyl-sulfonylurethane or cycloalkenylsulfonylurethane side groups.