

[54] **PROCESS FOR THE PRODUCTION OF A LIGHT-SENSITIVE COPYING MATERIAL HAVING A COPPER-CONTAINING SUPPORT, AND COPYING MATERIAL SO PRODUCED**

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[57] **ABSTRACT**

This invention relates to a process for improving the adhesiveness of a negative-working copying layer to a copper-containing support. The invention also relates to a presensitized negative-working copying material comprising a copper-containing support having a layer thereon of enhanced adhesiveness. In the process, the copper-containing support is coated with a layer containing tetramethylthiuram disulfide and/or one or more organic compounds having at least one mercapto group. A light-sensitive compound may be included in the same layer with the sulfur-containing compound.

14 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF A LIGHT-SENSITIVE COPYING MATERIAL HAVING A COPPER-CONTAINING SUPPORT, AND COPYING MATERIAL SO PRODUCED

The present invention relates to a process for the production of a copying material, in which a negative-working light-sensitive copying layer is on a copper-containing support. The process results in an improvement of the adhesion of the copying layer to the support.

In the reproduction field, light-sensitive materials are known in which a support carries a light-sensitive copying layer the solubility of which changes in a solvent, serving as the developer and being selected for this purpose, upon exposure to light. If the change is such that the unexposed copying layer is soluble in the selected solvent or partially soluble so that it can be wiped off of the support with a pad soaked with the solvent or can be removed completely from the support by simple rinsing with the solvent or immersion into the solvent, whereas the exposed copying layer, after the same development treatment, remains entirely or at least to such an extent on the support that the latter is not bared, the light-sensitive material is negative-working; in the reverse case it is positive-working. It would be more correct to speak of a negative- or positive-working. It would be more correct to speak of a negative- or positive-working process since there are some light-sensitive copying materials which are negative- as well as positive-working. The present invention relates to a process for the production of a negative-working material in a wider sense, i.e., the invention also includes the production of those materials which are negative- as well as positive-working.

In the reproduction field, processes are further known for improving the adhesion between the support and the light-sensitive copying layer thereon and numerous such processes can be employed advantageously in the case of metallic supports, particularly in the case of aluminum supports. Further known is a negative-working copying material in which the light-sensitive copying layer is on a copper-containing support. A process for improving the adhesion between a negative-working light-sensitive copying layer and a support which is copper-containing has not been known hitherto. The process known as effective in the case of supports of aluminum yield no improvement or only an unsatisfactory improvement of the adhesiveness in the case of copper-containing supports.

The present invention provides a process for the production of a copying material having a negative-working copying layer of a non-volatile or difficultly volatile light-sensitive composition and a copper-containing support, which process improves the adhesion between the support and the copying layer. A copper-containing support is a support in which the surface layer covered with the copying layer contains at least about 30 percent by weight of copper. Difficultly volatile compositions are compositions which remain undecomposed on the support after 5 minutes of heating at 100° C. so that the copying material is still light-sensitive.

The invention is based on the known process for the production of a copying material with a negative-working copying layer of a non-volatile or difficultly volatile composition on a copper-containing support, in

which the copying layer is produced by applying a solution of the composition to the support and drying the applied solution. In the present invention, prior to or simultaneously with the application of the solution containing the light-sensitive composition, a sulfur-containing organic compound either having at least one mercapto group or being tetramethylthiuram disulfide is applied in the form of a solution to the support and the applied solution is dried.

The treatment of the surface of the support thus can be performed treatment in a manner such that application and drying of the solution containing the sulfur-containing compound is performed prior to the application of the light-sensitive copying layer to the thus pretreated surface or in a manner such that the light-sensitive compound and the sulfur-containing compound are applied in the form of a single solution to the support and the solution is dried. If treatment of the support with the sulfur-containing compound is performed prior to the application of the copying layer, the latter is performed only somewhat later since the copper-containing surface treated with the sulfur-containing compound undergoes a change upon contact with air in which the favorable effect achieved by the treatment is gradually diminished. It is preferred that not more than 2 hours elapse between the treatment with the sulfur-containing compound and the application of the copying layer.

Examples of sulfur-containing organic compounds which can be successfully used in the process are:

2-mercapto-benzothiazole
2-mercapto-6-methyl-benzothiazole
2-mercapto-4-methyl-benzothiazole
2-mercapto-6-nitro-benzothiazole
2-mercapto-6-ethoxy-benzothiazole
2-mercapto-thiazole
2-mercapto-benzimidazole
2-mercapto-1-methyl-benzimidazole
2-mercapto-benzoxazole
tetramethylthiuram disulfide
thiourea
N,N'-diphenylthiourea
N-(4-mercaptomethylphenyl)-N'-phenyl-urea
N,N'-di-p-tolyl-thiourea
N,N'-di-m-tolyl-thiourea
N,N'-di-o-tolyl-thiourea
2-mercapto-benzoic acid or thiosalicylic acid
phenyl-mercapto-tetrazole
ethyl-mercapto-tetrazole
2-mercapto-1-methyl-imidazole
N-2-naphthylmercapto-acetamide
diphenyl-thiocarbazon
2,5-dimercapto-1,3,4-thiadiazole
5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione
5-mercapto-1-phenyl-1,2,3,4-tetrazole

It is also possible to use mixtures of the sulfur-containing compounds.

With one exception, the sulfur-containing organic compounds to be used in the process have at least one mercapto group, i.e., the group —SH is directly linked to a carbon atom. Some are present in tautomeric forms of which at least one has the —SH group, e.g., thiourea and diphenyl thiourea. The mentioned exception relates to tetramethylthiuram disulfide which is also suitable although it contains no mercapto group according to its conventional formula. Tetramethylthiuram disulfide is perhaps present in a tautomeric form

containing a mercapto group and merely seems to be an exception. The mercapto group present in the sulfur-containing compounds to be used has a free hydrogen atom. It is replaced by no organic group, but the compounds may be used in the form of their water-soluble salts, e.g., their alkali metal salts, particularly their sodium salts. This kind of use is recommended if one must or wishes to work with purely aqueous solutions. In cases where purely aqueous as well as other solutions can be used, organic solvents or organic solvents mixed with water are preferred. The solutions of the sulfur-containing organic compounds are advantageously caused to act while heated, the heat employed for drying the applied layer usually being sufficient. Generally, temperatures between 40° and 100° C. are employed.

In the production of the copying material, the supports used are plates or foils of copper or copper-containing alloys, e.g., brass, pinch-beck, bronze, aluminum bronze, nickel silver and Monel metal. The plate or foil may be on a support of another material, e.g., on an aluminum or steel foil or on a plastic film or on a plate of an electrically insulating material. The products obtained according to the process serve for the production of relief, intaglio or planographic printing plates or for the production of printed circuits, for example.

The difficulty volatile light-sensitive composition serving for the formation of the light-sensitive copying layer may be a light-sensitive compound, e.g., a diazonium salt, a diazonium salt in the form of a so-called diazo resin (condensation product with formaldehyde), an aromatic azido compound, a nitron compound or a compound polymerizable upon exposure to light. The light-sensitive composition also may be a bichromate-containing colloid, e.g., gelatin, gum arabic, polyvinyl alcohol, polyacrylic acid, polyvinyl pyrrolidone or methyl cellulose.

Of particular interest are the copying materials the light-sensitive composition of which is photopolymerizable, particularly materials for the production of printed circuits.

The light-sensitive copying layer may contain the additives known to the reproduction field, such as dye-stuffs or resins without the adhesion-improving effect of the process being affected.

Depending on the circumstances, that embodiment of the process is preferred in which the sulfur-containing organic compound is applied to the copper-containing support simultaneously with the composition forming the light-sensitive constituent of the copying layer. Its quantity generally is 1 to 10, preferably 1.5 to 6.0, percent by weight of the composition, i.e., of the non-volatile constituents of the copying layer solution.

If required, the surface to be coated of copper-containing material is cleaned prior to the application of the solution of the light-sensitive composition only when the application together of light-sensitive composition and sulfur-containing compound is not possible or disadvantageous. Such a treatment may be performed in a relatively simple manner by immersion of the support into the solution. Generally, brief immersion for about 30 seconds to 10 minutes in a 0.1 to 5 percent solution of the sulfur-containing organic compound is sufficient. Preferably, 0.5 to 1.5 percent solutions are used. When using an organic solvent, e.g., iso-

propanol, the solution may be drained off after immersion, and drying may be carried out in a warm air stream, e.g., at 50°C. As indicated above, many of the sulfur-containing compounds may be used in the form of their salts, particularly in the form of their alkali metal salts, in an aqueous solution. It is thus possible to use successfully, in an aqueous solution, the sodium salts of 2-mercapto-benzthiazole, diphenylthiocarbazon, 2,5-dimercapto-1,3,4-thiadiazole, 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione, for example. The salts are advantageously used in 0.1 to 5 percent aqueous solutions. The required treatment time may be reduced by employing the solution in the warm state, e.g., at 50°C. With the same duration of action, the salt concentration may be the lower the higher the temperature of the solution.

The process according to the invention entails considerable advantages. It is known that, during development of negative-working copying layers, e.g., during removal of the areas not struck by light upon image-wise exposure, the developer used therefor must not act randomly, e.g., for a randomly long time, since the exposed areas also are attacked by the developer when it acts intensively. By means of the present process, a copying means is obtained which, due to the improved adhesion between the copying layer and the copper-containing support, has an improved developer resistance. The improved adhesion of the copying layer to the support furthermore is of great advantage for copying materials which are etched after development, e.g., in order to produce an etched printing plate or a printed circuit. In these cases, the resistivity of the copying layer to etching liquids also is excellent. It is also very remarkable that the storability of the light-sensitive material, provided its copying layer is formed from a composition storable for a long time (for months) without a loss of light-sensitivity, is substantially improved by the use of the sulfur-containing compound.

The process will be further illustrated by reference to the following examples. In these examples, all quantities in percent are by weight.

The examples often indicate accelerated tests of the storability. In these tests, the copying material to be tested is left in several pieces for different times (e.g., from 30 minutes to 6 hours) at 100° C. in a drying cabinet. Certain qualities, e.g., the developer resistance, are then tested. According to experience, such storages represent a guide showing which one of two materials compared has the better storage capacity and whether a minimum storage life of 2 to 3 months can be expected.

In the test of the so-called developer resistance, after proper image-wise exposure to light, the materials are covered with a layer of the conventionally used developer and left under the developer layer for the time indicated, then rinsed with water or wiped with a wet pad. When the exposed areas are then maintained to such a sufficient degree that a flawless print can be made therefrom in a printing machine, the material is regarded as completely developer-resistant.

EXAMPLE 1

The copper surface of a bimetal plate of aluminum and copper is cleaned by being briefly treated with 3 percent sulfuric acid, rinsed with distilled water and then with acetone, and dried. The copper surface is

then whirl-coated with the following light-sensitive solution:

3.0 g of the diazo compound 1-[(4'-methylbenzene-1'sulfonyl)-imino]-2-(2'',5''-dimethyl-phenylamino-sulfonyl)-benzoquinone-(1,4)-diazide-(4) (the preparation thereof is described in Example 1 of U.S. Pat. No. 3,175,906.

2.0 g of a styrene copolymer containing carboxyl groups (Lytron 820, registered trade mark of Monsanto Chemical Co.)

0.5 g of polyvinyl acetate (viscosity in 20 percent ethyl acetate solution about 40 cp at 20° C.)

0.1 g of crystal violet

0.2 g of 2-mercapto-benzothiazole

80 ml of ethylene glycol monomethyl ether, and 20 ml of dimethyl formamide.

The solution applied is dried with a warm air stream at 60° C.

When using the thus obtained light-sensitive bimetal plate, the copying layer thereof is exposed for 2½ minutes under a negative original to a xenon lamp of 5,000 watts and then developed with a developer consisting of a 1.5 percent aqueous sodium metasilicate solution ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) to which 0.6 percent of polyethylene glycol (molecular weight about 6,000) and 0.045 percent of the calcium complex of alizarine yellow have been added. A positive image appears on the copper surface. The light-hardened areas of the copying layer (stencil) have an excellent adhesion to the copper and are not attacked by the developer. When the light-sensitive bimetal plates obtained are subjected to the accelerated storability test described above, it can be seen that, after a storage of 2 hours, the developer resistance is still 1 to 2 minutes and, only after a storage of 4 hours, is there no longer any developer resistance.

The exposed and developed bimetal plate is then etched by means of an etching solution containing 44.0 percent of iron-III-nitrate and 0.5 percent of iron-III-chloride dissolved in water. By the etching process, the copper is removed in the bared (unexposed) areas and the aluminum is bared. When the procedure is the same as above without the addition of 2-mercapto-benzothiazole, a material is obtained the copying layer of which has such a poor adhesion to the copper that defects easily occur during development; etching is impossible. After an accelerated storage of 2 hours, there is no longer any developer resistance.

EXAMPLE 2

With the use of a bimetal plate of steel and copper, a light-sensitive material is produced as in Example 1 but with the difference that the coating solution contains another light-sensitive diazo compound, viz. the mixed condensate described in the following and, additionally, 0.5 g of an epoxide resin (melting range 64° to 75° C., epoxide equivalent weight 450 to 525).

For the preparation of the mixed condensate, 32.3 g of 3-methoxy-diphenylamine-4-diazonium sulfate are dissolved in 170 g of 85 percent phosphoric acid, 25.8 g of 4,4'-bis-methoxy-methyldiphenylether are added dropwise and condensation is performed for 5 hours at 40° C. After dilution with 250 ml of water, the chloride of the condensation product is precipitated by the addition of 220 ml of 19 percent hydrochloric acid. The chloride of the condensate is again dissolved in water and the mesitylene sulfonate of the diazo mixed con-

densate is precipitated by means of the sodium salt of mesitylene sulfonic acid.

After an accelerated storage of 4 hours, the light-sensitive material thus obtained has a developer resistance of 5 minutes; after a storage of 6 hours the developer resistance is about 3 minutes.

In use, the copying layer of the light-sensitive bimetal plate obtained is exposed for 2½ minutes under a negative original. It is then developed with a developer containing 50 parts by volume of ethylene glycol monoethyl ether and 50 parts by volume of 10 percent phosphoric acid, the unexposed areas of the bimetal plate being removed thereby. After about 45 seconds, the copying layer is fully developed; its developer resistance is about 7 minutes. By etching with an aqueous solution of

35.0 percent of iron-III-chloride

3.2 percent of hydrochloric acid (HCl)

2.5 percent of nitric acid (HNO_3), and

0.25 percent of ammonium nitrate,

the bared copper is then removed so that the steel areas of the bimetal plate are bared. No undercutting occurs. After wiping over with 1 percent phosphoric acid, the plate may be used for printing, the prints being made from a stencil consisting of the layer cross-linked by light and the copper beneath. The layer cross-linked by light also may be removed with a suitable solvent; the stencil consists then only of copper.

Without the content of 2-mercapto-benzthiazole, a bimetal plate is obtained which has a developer resistance of 1 to 2 minutes, i.e., a poor developer resistance, which does not withstand etching.

It is remarkable that the effect of the sulfur-containing compound improving adhesion of the layer to the copper surface is still present when a certain time elapses between the cleaning of the copper surface and coating thereof. A material is thus obtained having a developer resistance of 6 minutes when the copper surface is left for 15 minutes in the open between drying of the acetone and the application of the coating solution.

EXAMPLE 3

The copper surface of a bimetal plate of aluminum and copper which has been cleaned as in Example 1 is coated with a solution of

3.0 g of the diazo condensate employed in Example 2

2.0 g of polystyrene resin (Lytron 820)

0.5 g of polyvinyl acetate (as in Example 1)

0.1 g of crystal violet

0.32 g of N,N'-diphenylthiourea

80 ml of ethylene glycol monomethyl ether, and

20 ml of dimethyl formamide

and dried.

In use, the copying layer of the material thus obtained is exposed to light under a negative. Development is performed with the developer described in Example 2; a good developer resistance (up to 7 minutes) can be observed. Etching is performed with an aqueous solution of 44 percent of iron-III-nitrate and 0.5 percent of iron-III-chloride, a good etching resulting therefrom.

Without the content of N,N'-diphenylthiourea, a material is obtained the stencil of which is damaged considerably during etching.

EXAMPLE 4

After cleaning with dilute sulfuric acid, the copper surface of a bimetal plate of aluminum and copper is coated with the solution described in Example 2 but containing, instead of 0.25 g of 2-mercaptobenzothiazole, 0.2 g of 2-mercapto-benzimidazole, and dried.

The material obtained is exposed to light and developed as described in Example 2. The developer resistance is 5 minutes; the stencil is resistant to etching.

A material prepared without the content of 2-mercapto-benzothiazole has a developer resistance of only 2 minutes and is not resistant to etching.

EXAMPLE 5

The procedure is the same as in Example 2 but with the use of a bimetal plate of aluminum and copper and a coating solution in which the 0.25 g of 2-mercaptobenzothiazole is replaced by 0.2 g of 2-mercaptobenzoxazole. The printing plate material obtained is resistant to the developer for 5 minutes and resistant to etching.

Without the content of 2-mercapto-benzoxazole, a material is obtained the developer resistance of which is only 2 minutes and which is not resistant to etching.

EXAMPLE 6

The procedure is the same as in Example 2 with the use of a bimetal plate of aluminum and copper but the 0.25 g of the 2-mercaptobenzothiazole is replaced by 0.1 g of thiourea.

The light-sensitive bimetal plate thus obtained is resistant to the developer used for up to 4½ minutes; a printing plate produced without the content of thiourea has a resistance of only 2 minutes.

EXAMPLE 7

After conventional cleaning with 3% H₂SO₄, and rinsing with water and acetone, a bimetal plate of aluminum and copper is dried and then immediately whirl-coated with the following solution:

- 1.0 g of gelatin
- 3.0 g of the water-soluble diazo mixed condensate employed in Example 2, but separated as the chloride
- 0.01 g of wetting agent (alkyl phenol with 8 to 12 alkyl-C atoms and oxethylated with 10 to 12 moles of ethylene oxide)
- 0.1 g of crystal violet
- 0.2 g of 2-mercapto-benzothiazole, dissolved in 3 ml of isopropanol, and
- 100 ml of water.

After drying of the plate under the warm air stream of an electric hair dryer and drying for 5 minutes at 100° C., exposure is carried out for 2½ minutes under a negative original with the use of a xenon lamp. Subsequent development with water lasts for only 1 minute, the unexposed areas of the copying layer of the bimetal plate being removed and the copper being bared thereby. Etching with an aqueous solution of 44 percent of iron-III-nitrate and 0.5 percent of iron-III-chloride lasts for about 1 minute.

With a bimetal plate produced in the same manner but without the content of 2-mercapto-benzothiazole, the copying layer does not adhere to the copper surface and separates during development with water, even when very thoroughly wiped with a cotton pad.

The improved storability of the bimetal plate produced with 2-mercapto-benzothiazole is shown upon accelerated storage. After 30 minutes and subsequent image-wise exposure, the plate still can be developed with water.

EXAMPLE 8

The procedure is the same as in Example 7 but gum arabic is used instead of gelatin. The results are the same as those indicated in Example 7.

EXAMPLE 9

The procedure is the same as in Example 3 but, instead of 0.32 g of N,N'-diphenylthiourea, 0.1 g of tetramethylthiuram disulfide is used. A developer resistance of 6½ minutes is found. Upon etching with an aqueous solution containing 29 percent of iron-III-nitrate and 0.2 percent of iron-III-chloride, only very slight undercuttings occur whereas considerable undercuttings occur in the case of a plate produced without the addition of tetramethylthiuram disulfide.

EXAMPLE 10

After cleaning with dilute H₂SO₄, a bimetal plate of aluminum and copper is coated with the following aqueous solution:

- 10.0 g of polyvinyl alcohol containing acetyl groups (saponified to about 88 percent; viscosity 3 to 5 cp in a 4 percent aqueous solution at 20° C.)
- 3.0 g of water-soluble diazo mixed condensate as in Example 7
- 0.5 g of wetting agent as in Example 7
- 0.5 g of crystal violet
- 0.25 g of 2-mercapto-benzothiazole, dissolved in 3 ml of isopropanol, and
- 100 ml of water.

After drying the coating, the light-sensitive bimetal plate obtained is exposed for 3 minutes under a negative to a xenon lamp of 5,000 watts. Development is performed with water, the unexposed areas of the copying layer being dissolved away. After brief drying in the open, the bimetal plate is hardened for 1 to 2 minutes by means of a 3 percent tannin solution. The plate is then etched with the etching solution described in Example 3.

A material produced in the same manner but without the use of the 2-mercapto-benzothiazole does not withstand the developing process without being damaged. In the subsequent etching process, parts of the stencil separate from the copper.

EXAMPLE 11

The procedure is the same as in Example 10 but a polyvinyl alcohol containing acetyl groups and of a higher molecular weight is used (viscosity 17 to 23 cp). Also in this case, the effect of the content of 2-mercapto-benzothiazole is good developer and etching resistance, whereas without such a content a material with an insufficient developer and etching resistance is obtained.

EXAMPLE 12

The procedure is the same as in Example 10 but, instead of the 10 g of the polyvinyl alcohol containing acetyl groups, 7.5 g of a polyvinyl alcohol containing no acetyl groups and having a somewhat higher molecular weight (viscosity 8 to 11 cp) are used. Also in this

case, the material produced without the content of mercaptobenzothiazole is useless because it has no developer and etching resistance, whereas the material produced according to the invention has good developer and etching resistance.

EXAMPLE 13

The procedure is the same as in Example 7 but, instead of 1 g of gelatin, 2 g of polyacrylic acid (mean molecular weight 10,000) are used. The necessary exposure time is 3 minutes. The material obtained according to the invention has a sufficient developer and etching resistance. With a material produced without the content of 2-mercapto-benzothiazole, no development with water is possible and also no etching since the copying layer is damaged by water.

EXAMPLE 14

The procedure is the same as in Example 7 but a bimetal plate of steel and copper is coated and a coating solution is used which, instead of the 3 g of diazo mixed condensate, contains 3 g of diazo resin obtained by condensation in an acid medium (sulfuric acid) from p-diazo-diphenylamine and formaldehyde. The light-sensitive material obtained is exposed for 3 minutes under a negative and developed with water. It then can be easily etched with the etching solution indicated in Example 2.

In contradistinction thereto, a material produced in the same manner but without the content of 2-mercapto-benzothiazole cannot be etched.

Similarly, good results are obtained when a plate of aluminum and copper is coated with the same solution, in accordance with the invention. In this case, the etching solution described in Example 3 is used.

EXAMPLE 15

The aqueous light-sensitive solution described in Example 14 is whirl-coated onto the cleaned copper surface of a copper laminated plate of insulating material, viz. a commercial plate of several paper layers impregnated with resin and coated with a copper layer, and dried. After exposure and development with water, the plate is etched with the etching solution described in Example 3. The material thus obtained can be easily etched whereas a comparative material produced without the content of 2-mercapto-benzothiazole in the layer does not withstand etching.

EXAMPLE 16

The procedure is the same as in Example 7 but, instead of 1 g of gelatin, 2 g of polyacrylic acid (as in Example 13) are used and, instead of 3 g of the diazo mixed condensate, there are used 3 g of the water-soluble crude diazo condensate obtained by adding to 17 parts by weight of 85 per cent phosphoric acid, 1.3 parts by weight of paraformaldehyde and 10.4 parts by weight of 3-methoxydiphenylamine-4-diazonium chloride and heating to 40° C. for 35 hours with stirring.

The light-sensitive bimetal plate obtained is exposed for 3 minutes and then developed with water. The adhesion of the stencil to the copper surface is good; with a plate produced without the content of 2-mercapto-benzothiazole, it is completely insufficient.

EXAMPLE 17

The procedure is the same as in Example 16 but, in-

stead of the crude diazo condensate, an equal quantity of 4,4'-diazidostilbenedisulfonic acid (as disodium salt) is used.

The light-sensitive bimetal plate obtained is exposed for 3 minutes under a negative and then developed with water. The adhesion of the fully exposed stencil to the copper is again good; with a plate produced without the content of 2-mercapto-benzothiazole, it is completely insufficient since the stencil is damaged during development with water.

EXAMPLE 18

A copper-laminated plate of insulating material is coated as in Example 14, but with the aqueous solution described in Example 7.

The light-sensitive material obtained is exposed for 3 minutes under a negative original and then developed with water. The stencil on the copper is resistant to water and can be easily etched with the etching solution described in Example 2. A stencil of a plate produced without the content of 2-mercapto-benzothiazole has a very poor adhesion to the copper and thus cannot be etched.

EXAMPLE 19

After cleaning with dilute H₂SO₄, the copper surface of a bimetal plate of steel and copper is coated with the following aqueous solution:

- 2.0 g of polyvinyl alcohol containing acetyl groups (saponified to about 88 percent; viscosity about 25 cp at 20° C. in a 4 percent aqueous solution)
- 3.0 g of ammonium bichromate
- 0.01 g of wetting agent as in Example 7
- 0.1 g of crystal violet
- 0.1 g of 2-mercapto-benzothiazole, dissolved in 3 ml of isopropanol, and
- 100 ml of water.

After drying the layer, the material is exposed for 3 minutes under a negative and developed with water. The developed stencil has a good adhesion to the copper background. The copying layer of a material produced in the same manner but without the content of 2-mercapto-benzothiazole has an insufficient adhesion to the copper so that it is impossible to develop and obtain an undamaged stencil.

EXAMPLE 20

After cleaning with 3 percent H₂SO₄, a bimetal plate of steel and copper is coated on the copper side thereof with the following aqueous solution:

- 1.0 g of gelatin
- 3.0 g of diazo resin as in Example 14
- 0.01 g of wetting agent as in Example 7
- 0.1 g of crystal violet
- 0.2 g of N,N'-diphenylthiourea, dissolved in 3 ml of isopropanol, and
- 100 ml of water.

After drying the layer, the bimetal plate is exposed for 3 minutes under an original, developed with water and etched with the aqueous etching solution described in Example 14. A flawless printing plate results therefrom. A comparative material produced in the same manner but without the content of diphenylthiourea is useless because of the insufficient resistance of the exposed parts of the copying layer to water.

EXAMPLE 21

The copper surface of a bimetal plate of steel and copper is coated with the aqueous solution described in Example 7, in which the 0.2 g of 2-mercapto-benzothiazole is replaced by 0.15 g of 2-mercapto-6-methyl-benzthiazole. An etchable bimetal plate is obtained.

EXAMPLE 22

The copper surface of a bimetal plate of steel and copper is coated with the aqueous light-sensitive solution described in Example 7, in which the 0.2 g of 2-mercapto-benzothiazole is replaced by 0.15 g of 2-mercapto-4-methyl-benzothiazole. An etchable bimetal plate is obtained. Similarly, good results are obtained with only 0.1 g of 2-mercapto-6-ethoxy-benzothiazole in the layer.

EXAMPLE 23

After pretreatment with dilute H_2SO_4 , the copper surface of a bimetal plate of steel and copper is coated with the aqueous solution described in Example 7, in which the 0.2 g of 2-mercaptobenzthiazole is replaced by 0.2 g of diphenylthio-carbazone. A bimetal plate is obtained which, after exposure for 3 minutes and development with water, easily can be etched with the etching solution described in Example 15.

EXAMPLE 24

The procedure is the same as in Example 2 but the 0.25 g of 2-mercapto-benzothiazole is replaced by 0.1 g of 2,5-dimercapto-1,3,4-thiadiazole. The developer resistance of the material obtained is 7 minutes. No undercutting occurs upon etching with the copper etching solution described in Example 14.

EXAMPLE 25

The procedure is the same as in Example 2 but the 0.25 g of 2-mercapto-benzothiazole is replaced by 0.4 g of 2,5-dimercapto-1,3,4-thiadiazole. A light-sensitive bimetal plate is obtained which has a developer resistance of 8½ minutes; etchability is very good.

EXAMPLE 26

The procedure is the same as in Example 2 but the 0.25 g of 2-mercapto-benzothiazole is replaced by 0.2 g of 5-mercapto-1-phenyl-1,2,3,4-tetrazole. The developer resistance of the material obtained is 6½ minutes. No undercutting occurs upon etching.

EXAMPLE 27

The procedure is the same as in Example 2 but the 0.25 g of 2-mercapto-benzothiazole is replaced by 0.2 g of 2-mercapto-1-methylimidazole. The developer resistance of the material obtained is 4 minutes. Only slight undercutting occurs upon etching with the aqueous etching solution described in Example 14. A comparative material with a layer without the above-mentioned mercapto compound is damaged considerably upon etching.

EXAMPLE 28

The procedure is the same as in Example 2 but the 0.25 g of 2-mercapto-benzothiazole is replaced by 0.25 g of 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione. The developer resistance of the material obtained is 5½ minutes. No undercutting occurs upon etching with the etching solution described in Example 14.

EXAMPLE 29

The cleaned copper surface of a bimetal plate of steel and copper is coated with the aqueous light-sensitive solution described in Example 7, in which the 0.2 g of 2-mercapto-benzothiazole is replaced by 0.2 g of the sodium salt of 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione. After drying, the layer is exposed for 3 minutes under a negative, developed with water and etched with the etching solution described in Example 14. The stencil is resistant to etching.

EXAMPLE 30

The cleaned copper surface of a bimetal plate of steel and copper is coated with the following light-sensitive solution:

3.0 g of the diazo compound described in the following

2.0 g of polystyrene resin as in Example 1

0.5 g of polyvinyl acetate (viscosity about 20 cp at 20° C. in a 20 percent ethyl acetate solution)

0.2 g of crystal violet

0.2 g of 2-mercapto-benzothiazole, and

100 ml of ethylene glycol monomethyl ether.

The diazo compound used is obtained by reacting 6 parts by weight of naphthoquinone-(1,2)-diazide-(2)-4-sulfochloride with 4.5 parts by weight of 1-methyl-2-(2'-hydroxy-phenyl)-benzimidazole in solution in dioxane at 20° to 30° C. by dropwise addition of dilute soda solution with stirring (see also German Published Patent Application No. 1,047,622).

The material obtained after drying of the layer is exposed for 3 minutes under a negative and then developed with the developer described in Example 1. Etching is performed with the aqueous etching solution described in Example 14, which is performed without undercuttings.

A comparative material produced without the content of 2-mercapto-benzothiazole in the copying layer has a poor layer adhesion and is attacked considerably upon etching.

EXAMPLE 31

The procedure is the same as in Example 30 but the diazo compound employed there is replaced by the diazo compound described in the following and the quantity of the 2-mercapto-benzothiazole is 0.3 g instead of 0.2 g. The diazo compound used is benzoquinone-(1,4)-diazide-(4)-2-sulfonanilide. Production thereof is described in Example 1 of German Patent Specification No. 960,335. The plate obtained is resistant to etching and has a good layer adhesion. A comparative material produced without the content of 2-mercapto-benzothiazole in the layer has a very poor adhesion of the layer and cannot be etched.

EXAMPLE 32

The procedure is the same as in Example 31 but, instead of 3.0 g, 4.0 g of the benzoquinone-(1,4)-diazide-(4)-2-sulfonanilide are used and 2.0 g of a product obtained by condensation of chloroacetic acid with a novolak resin (preparation is described in Example 5 of German Patent Specification No. 1,053,930) are used instead of the 2.0 g of polystyrene resin.

The stencil obtained has a good adhesion to the copper surface. The adhesion of the layer in a material produced without the content of 2-mercapto-

benzothiazole in the layer is so poor that the layer separates from the copper surface during development.

EXAMPLE 33

After cleaning with 3 percent sulfuric acid, the copper surface of a plate of steel and copper is coated with the following light-sensitive solution:

- 4.0 g of styryl-N-phenyl-nitrone
($C_6H_5CH:CH:CH:[NO]C_6H_5$ obtained by reaction of cinnamic aldehyde with phenylhydroxylamine)
- 2.0 g of polystyrene resin as in Example 1
- 0.5 g of polyvinyl acetate as in Example 1
- 0.2 g of crystal violet
- 0.4 g of 2-mercapto-benzothiazole, and
- 100 ml of ethylene glycol monomethyl ether.

The light-sensitive bimetal plate obtained after drying of the layer is exposed for 4 minutes under a negative, then developed with the developer described in Example 1, and then etched with the etching solution described in Example 14. A good adhesion of the stencil to the copper is obtained; flawless etching being obtained thereby.

After an accelerated storage of 1 hour, the developer resistance is 2 minutes, that of a comparative material produced without the content of 2-mercapto-benzothiazole is only 1 minute.

EXAMPLE 34

The copper surface of a plate of steel and copper which has been cleaned in the usual manner is coated with the following solution:

- 12.0 g of a prepolymer of diallyl-isophthalate, soluble in xylene (e.g., that commercially available under the trade name Dapon M, registered trade mark of Ciba) dissolved in
- 55.0 g of xylene filtered and mixed with a solution of
- 0.1 g of benzil
- 0.1 g of Michler's ketone
- 0.4 g of xanthone, and
- 0.2 g of 2-mercapto-benzothiazole

in 33.0 g of 4-methoxy-4-methyl-2-pentanone. For drying of the layer, the plate of steel and copper is first left in the open, then heated for 5 minutes to 52° C. in a drying cabinet in order to completely remove the solvent.

The material obtained is exposed for 3 minutes under a negative to a xenon lamp of 5,000 watts and developed for 1 to 2 minutes with 1,1,1-trichlorethane, fresh trichlorethane being finally used for rinsing the plate. After drying, the plate is etched with the etching solution described in Example 14. Etching is good without undercuttings. A comparative material produced without the content of mercapto-benzothiazole cannot be etched.

EXAMPLE 35

After cleaning with dilute sulfuric acid, the copper surface of a plate of steel and copper is coated with the following light-sensitive solution:

- 1.4 g of a copolymer of methyl methacrylate and methacrylic acid, having a mean molecular weight of 40,000 and an acid number of 60
- 1.4 g of trimethylol ethane triacrylate
- 0.05 g of 2-mercapto-benzothiazole
- 0.05 g of benzacridine
- 0.02 g of Supranol Blue GL (Colour Index 50,335)
- 0.2 g of 1,6-dihydroxy-ethoxy-hexane, and

13.0 g of ethylene glycol monoethyl ether and dried. The layer is then exposed for 1 minute under a negative to a xenon lamp of 5,000 watts at a distance of 80 cm and developed for 15 seconds with the developer described in Example 1, rinsed with water, and dried. The bimetal plate can be etched within 3 minutes with the aqueous etching solution described in Example 1, no undercuttings occurring thereby.

The layer of a comparative material produced without the content of 2-mercapto-benzothiazole has a poor adhesion to the copper and is attacked during development.

EXAMPLE 36

The cleaned copper surface of a plate of steel and copper is coated with the following light-sensitive solution:

- 5.0 g of diazidostilbene disulfonic acid (as disodium salt)
- 3.0 g of polyamide from hexamethylene diamine/adipic acid, caprolactam and bis-p-aminocyclohexylmethane (Ultramid 1C, registered trade mark of Badische Anilin- & Soda-Fabrik, Ludwigshafen, Germany)
- 0.15 g of 2-mercapto-benzothiazole, and
- 100 ml of 90 percent methanol (remainder water).

After drying the layer, the material obtained is exposed for 3½ minutes under a negative; a bimetal plate with a good contrast is obtained. The plate is developed for 1 to 1½ minutes with methanol, dried, and then etched with the etching solution described in Example 14. The layer is resistant to etching, whereas a comparative material produced without the content of 2-mercapto-benzothiazole in the layer is damaged during development.

EXAMPLE 37

After cleaning with dilute H_2SO_4 , a plate of steel and copper is immersed for 2 minutes into a 1 percent solution of 2-mercapto-benzothiazole in isopropanol, then drained and dried. The copper surface of the thus pretreated plate is coated with the aqueous solution described in Example 7 but without the content of 2-mercapto-benzothiazole.

After exposure of the material obtained under a negative, a bimetal plate is obtained the layer adhesion of which to the copper is very good so that a long resistance during development with water is achieved and particularly the etching resistance, e.g., as regards the etching solution described in Example 14, is very good.

When pretreatment of the copper surface is performed with a 1 per cent solution of the sodium salt of 2-mercapto-benzothiazole, similarly good results are obtained.

EXAMPLE 38

A bimetal plate of steel and copper is pretreated with a 1 percent solution of 2,5-dimercapto-1,3,4-thiadiazole in isopropanol as in Example 37. The light-sensitive layer according to Example 7 but without the content of 2-mercapto-benzothiazole adheres excellently to the thus pretreated plate and is resistant to etching. Similarly effective is the pretreatment of a plate of steel and copper with a 1 percent aqueous solution of the potassium salt of 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione.

EXAMPLE 39

Several bimetal plates of steel and coper are pre-treated according to Example 37 at different tempera-
tures and for different times. Immediately upon pre-
treatment, the plates are coated with the aqueous light-
sensitive solution described in Example 14 (but without
the content of 2-mercapto-benzothiazole) and etched
with the etching solution described in Example 14. The
results are given in the following table. All are resistant
to etching.

2-mercapto-benzthiazole sodium salt in aqueous solution, per cent	Duration of pre-treatment	Temper- ature °C.	Adhesion
0.5	2 minutes	20	good
1.0	2 minutes	20	good
0.5	30 seconds	50	very good
1.0	30 seconds	50	very good
0.5	2 minutes	50	very good
1.0	2 minutes	50	very good

EXAMPLE 40

After cleaning with dilute H₂SO₄, two plates of steel
and copper are pretreated for 2 minutes with a 0.1 per-
cent aqueous solution of the sodium salt of 2-mercapto-
benzothiazole at 80° C. One of them is coated immedi-
ately and the other one after 30 minutes, with the solu-
tion described in Example 2 but without he content of
2-mercapto-bensothiazole. Despite the very thin pre-
treatment solution, the plate of steel and copper need
not be coated immediately but also can be coated after
30 minutes. In the case of the immediately coated bi-
metal plate, the resistance to the developer described
in Example 2 is 4½ minutes, and 4 minutes in the case
of the plate coated after 30 minutes.

EXAMPLE 41

After cleaning with 3 per cent sulfuric acid, two
plates of steel and copper are treated for 2 minutes with
a 1 percent solution of 2-mercapto-benzothiazole in
isopropanol at 20° C., then drained and dried. One of
them is coated immediately, the other one after 1 hour,
with the light-sensitive solution described in Example
2 but without the content of 2-mercapto-benzothiazole.

The resistance to a developer of 50 percent by vol-
ume of ethylene glycol monoethyl ether and 50 percent
by volume of 10 percent phosphoric acid is 7 minutes
in the case of the immediately coated plate and 5 min-
utes in the case of the other plate.

EXAMPLE 42

Two plates of steel and copper are pretreated under
the same conditions as in Example 41 but with the use
of a 1 percent aqueous solution of the sodium salt of
2-mercapto-benzothiazole. The plates are coated with
the light-sensitive solution described in Example 41 in
the one case immediately and in the other case after 1
hour. The resistances to the developer indicated in Ex-
ample 41 are 6½ and 5 minutes.

EXAMPLE 43

A brass plate is cleaned with 3 percent sulfuric acid,
rinsed with water and then with acetone, and whirl-
coated with the aqueous light-sensitive solution de-

scribed in Example 14 and containing, inter alia, 0.2 g
of 2-mercapto-benzothiazole and dried. The thus ob-
tained light-sensitive plate is exposed under a negative
and developed with water. The tencil adheres firmly to
the brass support. In this manner, it is possible to pro-
duce signals, warning plates and the like.

Solutions in which the light-sensitive composition is
dissolved in an organic solvent, as the solution de-
scribed in Example 2, which contains 0.25 g of
2-mercapto-benzothiazole, also have a good adhesion
to brass surfaces.

The layer of a comparative material produced with-
out the content of mercapto-benzothiazole in the layer
has an insufficient adhesion only.

EXAMPLE 44

An exposed pigment paper which has been made
light-sensitive 1 day before by moving it for 2½ minutes
in a potassium bichromate solution into which, per 100
ml, a solution of 0.15 g of 2-mercapto-benzothiazole in
2.5 ml of isopropanol has been stirred in, is transferred
to a copper gravure cylinder after copper plating of the
jacket thereof. After the transfer of the pigment paper
and development with water at 40° C., a remarkably
firmly adhering copy is obtained which yields a well
etched material with a particularly smooth etching pro-
cedure.

Instead of adding the mercapto-benzothiazole solu-
tion to the potassium bichromate solution, it is also pos-
sible, after conventional wiping with wet whiting and
rinsing with water, to treat the copper plated gravure
cylinder with a 2 percent aqueous solution of the so-
dium salt of 2-mercapto-benzothiazole for 1 to 2 min-
utes at 30° to 35° C. After the transfer of the pigment
paper and development, a remarkably firmly adhering
copy is obtained in this case also.

EXAMPLE 45

A Monel metal plate with a copper content of 32 per-
cent is cleaned with an aqueous pumice slurry, then
briefly treated with 3 percent sulfuric acid, rinsed with
water and then with acetone. Onto the thus cleaned
plate, there is whirl-coated a negative-working coating
solution according to Example 2. After drying, the
plate is exposed under a negative original and then de-
veloped with the developer described in Example 2.
The stencil obtained has a good adhesion to the Monel
metal background.

According to the same working method but without
the content of 2-mercapto-benzothiazole in the coating
solution, a layer with a very poor developer resistance
is obtained so that the image is damaged during devel-
opment.

Analogous results are achieved when plates of tom-
bac, carbobronze or bronze are coated in the same
manner and the light-sensitive materials obtained are
used in the same manner.

It will be obvious to those skilled in the art that many
modifications may be made within the scope of the
present invention without departing from the spirit
thereof, and the invention includes all such modifica-
tions.

What is claimed is:

1. A presensitized negative-working copying material
comprising a copper-containing support and a layer
thereon, said layer including a compound selected from
the group consisting of tetramethylthiuram disulfide

and a sulfur-containing organic compound having at least one mercapto group, and, superposed on it or coated simultaneously with it, a light-sensitive compound selected from the group consisting of diazonium salts, diazo resins, aromatic azido compounds, nitro compounds, photopolymerizable compounds, and bichromate-containing colloids.

2. A copying material according to claim 1 in which the sulfur-containing compound and the light-sensitive compound are in the same layer.

3. A copying material according to claim 1 in which the sulfur-containing compound and the light-sensitive compound are in separate layers, with the former compound being intermediate the support and the latter compound.

4. A copying material according to claim 1 in which the sulfur-containing compound is 2-mercapto-benzothiazole.

5. A copying material according to claim 1 in which the sulfur-containing compound is N,N'-diphenylthiourea.

6. A copying material according to claim 1 in which the sulfur-containing compound is 2-mercapto-benzimidazole.

7. A copying material according to claim 1 in which the sulfur-containing compound is 2-mercapto-

benzoxazole

8. A copying material according to claim 1 in which the sulfur-containing compound is thiourea.

9. A copying material according to claim 1 in which the sulfur-containing compound is 5-mercapto-1-phenyl-1,2,3,4-tetrazole.

10. A copying material according to claim 1 in which the sulfur-containing compound is 2-mercapto-1-methyl-imidazole.

11. A copying material according to claim 1 in which the sulfur-containing compound is 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione.

12. A process for improving the adhesiveness of a negative-working copying layer to a copper-containing support which comprises coating said support with a layer containing

a compound selected from the group consisting of tetramethylthiuram disulfide and an organic compound having at least one mercapto group.

13. A process according to claim 12 in which a light-sensitive compound is coated over the sulfur compound-containing layer.

14. A process according to claim 12 in which a light-sensitive compound is contained in the sulfur compound-containing layer.

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