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The present invention relates to a light-sensitive recording material composed of an electrically conductive layer support suitable for the production of a printing form or printed circuit and of a photoconductive layer system containing a photoconductor, binder, sensitizing dye and conventional additives, and to its use in a process for the production of a printing form or printed circuit.

Processes have been disclosed which exploit the high light sensitivity of electrophotographic systems for the production of images. A particular advantage here is that the image can be produced by laser exposure or projection exposure. A film original is not necessary.

The production of planographic printing plates by electrophotographic means has been disclosed by German Patent 1,117,391, corresponding to British Patent 944,126. The printing plates used here are provided with a coating which, in addition to a suitable binder and an appropriate sensitizing dye, contains an organic photoconductor. A latent charge image, which is rendered visible by means of a dry or liquid developer, is produced on this layer by electrostatic charging and imagewise exposure. The toner image obtained is fixed, for example by heating the plate, so that, in the final decoating step, the toner image areas are protected from attack by the decoating solution.

However, such a process still has disadvantages. Thus, the fixed toner must either be washed off the printing

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plates surface by means of a solvent, or an increased number of waste sheets at the start of printing must be accepted, when the toner only "runs off" in the printing machine. On the other hand, the achievable resolution is limited, since baking of the toner, leads to undesirable shifts in total value. Moreover, the temperature in the baking phase must be kept within the optimum range, with considerable expense on controls.

Finally, relatively long runs are not even obtained, since the printing image areas do not withstand mechanical stress for a prolonged period.

Attempts have already been made to combine the advantages of the electrophotographic process described with those conventional positive or negative working systems. German Patent 1,447,008, corresponding to British Patent 996,315, has disclosed the production of a planographic printing plate which was coated with a mixture of organic photoconductors and the constituents of conventionally operating positive layers based on o-quinone-diazide. The toner image produced electrophotographically on this layer was used as a photomask in a further exposure step with actinic light. The differentiation of solubility between the image areas and non-image areas was induced via the photochemical reaction of the exposed o-quinone-diazide. The disadvantage in this case, however, is that the conductivity of this coating in the dark is high and that the solubility differences

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between the image areas and non-image areas are limited because of the relatively high photoconductor content.

A negative-working photoconductor layer has been disclosed by German Patent 1,811,209, corresponding to British Patent 1,274,296. In this case, a recording material is used which, in the photoconductive layer, contains a photoconductor capable of photopolymerization, from the group comprising the vinyloxazoles and vinylcarbazoles. The disadvantage is that, even with high photoconductor content of the layer, the hardening of the areas not covered by toner still does not meet more stringent requirements, in spite of a relatively high light intensity.

In order to avoid the disadvantages of these processes, attempts have also already been made to apply a photoconductor layer to the light-sensitive layer. Such double layers are described in German Patent 1,071,478, corresponding to U.S. patent 2,939,787, in EP-A 0,053,362 and in German Offenlegungsschrift 3,310,804, corresponding to GB-A 2,121,201. In all cases, a photoconductor layer is applied as a covering layer to a conventionally positive-working or negative-working light-sensitive coating. Such a procedure corresponds to the electrophotographic procedure, because the toner image can then be produced on the surface of the photoconductor layer.

This combination of the layers has, however, a number of disadvantages. On the one hand, there is an increa-

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sed risk of halations, since the photoconductor mask formed by the toner image and the light-sensitive base layer are separated from one another by the photoconductor layer. The photoconductor layer must therefore be as thin as possible. On the other hand, the layer may contain only those photoconductors and sensitizer dyes which are transparent to radiation of those wavelengths which are suitable for a photoreaction in the light-sensitive layer. Moreover, when the photoconductor layer and a negative-working layer are combined, the photoconductor layer is also removed from the image areas on decoating. It is therefore no longer available for the further processing steps. This also applies to the combination of photoconductor layer and a positive-working layer, if the applied toner image is not fixed. On the other hand, however, fixing leads to the undesired toner run-off at the start of printing, as already mentioned above. A final disadvantage is that, in cases where the photoconductor layer and light-sensitive layer form a not completely uniform interface between them, a layer of varying thickness is obtained after stripping, and this can lead to premature wear of the printing form produced or to a non-uniform reproduction of halftone originals.

It was therefore the object of the present invention to avoid the described disadvantages of the known processes and to combine the advantages of electrophotographic and conventionally light-sensitive coating in an optimum manner and to provide a recording material

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which is capable of meeting the technical demands with respect to length of run, light sensitivity, resolution and easy handling to a high degree.

The achievement of this object starts from a light-sensitive recording material composed of an electrically conductive layer support suitable for the production of a printing form or printed circuit and of a photoconductive layer system containing a photoconductor, binder, sensitizing dye and conventional additives, wherein the photoconductive system comprises a photoconductive layer applied to the layer support and a light-sensitive covering layer which contains at least one photochemically reactive compound. Preferably, the photochemically reactive compound present in the light-sensitive covering layer is a compound or a combination of compounds, the solubility of which in alkaline-aqueous and/or alcoholic solvent systems is reduced by actinic radiation, if a positive-working material is desired. If, on the other hand, a negative-working material is intended, the photochemically reactive compound present in the light-sensitive covering layer is a compound or a combination of compounds, the solubility of which in alkaline-aqueous and/or alcoholic solvent systems is increased by actinic radiation.

As a result, a recording material can be made available which is distinguished by very long print runs and high light sensitivity. Its structure makes it possible to effect the imaging and the differentiation of solubility

by irradiation with actinic light in separate working steps and without use of a vacuum frame, each under optimum conditions. The reproduction of tonal values in half-tone originals can also be controlled as a function of the duration of irradiation. In addition, uncontrolled halations are avoided, since the toner image is arranged on the light-sensitive covering layer. Fixing of the toner image serving as a photomask is not necessary. This has the advantage that falsification of the toner image fixing is avoided and, on the other hand, corrections are facilitated and easy removal of the toner particles is possible. On decoating of the material according to the invention, the layer thickness in the areas not dissolved away is fully preserved in all cases. In the event that post-curing of the decoated material by application of heat is desired, the latter acts in particular on the surface of the coating, which is exposed to the most severe stress during the printing process.

The recording material according to the invention is shown in a diagrammatic representation in the attached figure A, in which 1 marks the photoconductive layer, 2 marks the light-sensitive covering layer and 3 marks the electrically conductive support.

According to the invention, the photoconductive layer 1 is composed of materials, such as are conventionally used for electrophotographic purposes, for example those known from German Patent 2,526,720, corresponding to U.S. Patent 4,063,948. It is composed essentially of a photo-

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conductor, binder and sensitizing dye, and these can be arranged as a dispersion in on layer or separately in a charge-generating layer and a charge-transporting layer. The photoconductive layer can be chargeable either positively or negatively.

Examples of suitable photoconductors are inorganic materials, such as Se or zinc oxide, or organic materials, such as anthracene, perylene, tetracene or derivatives of carbazole, acylhydrazone, oxadiazole, pyrazoline, imidazole, benzimidazole, benzoxazole or benzothiazole, or organic pigments, such as indigo, phthalocyanine, metal phthalocyanines or perylene pigments, or organic polymeric compounds, such as poly-N-vinylcarbazole, and mixtures thereof, if appropriate.

Highly sensitive compounds which are particularly suitable in practice are metal-free phthalocyanines, metal phthalocyanines and derivatives of oxadiazole, oxazole, hydrazone and pyrazoline.

The use of photoconductive, in particular organic, substances in photoconductive layers and their use for the production of printing forms is known, for example, from the publications cited as state of the art.

Those photoconductors can here be used with particular advantage which represent aromatic, carbocyclic or heterocyclic compounds which are substituted by one or more dialkylamino groups.

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In this connection, compounds such as the said oxadiazole derivatives should be mentioned, which are disclosed by German Patent 1,058,836, corresponding to U.S. Patent 3,189,447, in particular 2,5-bis-(4'-dialkylaminophenyl)-1,3,4-oxadiazole. Examples of further suitable photoconductors are triphenylamine derivatives, more highly fused aromatic compounds such as anthracene, benzofused heterocycles and derivatives of pyrazoline or imidazole. Derivatives of triazole and oxazole, such as are known from German Patent 1,060,260, corresponding to U.S. Patent 3,112,197, and German Patent 1,120,875, corresponding to U.S. Patent 3,257,203, are also included here. Vinylaromatic polymers, such as polyvinylanthracene, polyacenaphthylene, poly-N-vinylcarbazole and copolymers of these compounds are also suitable. Polycondensates of aromatic amines and aldehydes, such as are known from German Auslegungsschrift 1,197,325, corresponding to U.S. Patent 3,244,517, are also included. In addition to these compounds indicated, which predominantly are of p-conducting character, n-conducting compounds are also employed. These so-called electron acceptors are known, for example, from German Patent 1,127,218, corresponding to U.S. Patent 3,287,123.

With respect to film-forming properties and adhesive strength, natural and synthetic resins are suitable as binders. In selecting these, solubility properties play above all a particular role, in addition to the film-forming and electrical properties and those of adhesive strength to the support. For practical purposes, those

resin binders are particularly suitable which are soluble in aqueous or alcoholic solvent systems, if appropriate with an addition of acid or alkali. For physiological and safety reasons, aromatic or aliphatic, highly inflammable solvents are to be rejected. Advantageous resin binders are high-molecular substances which carry groups conferring solubility in alkali. Examples of such groups are acid anhydride, carboxyl, phenol, sulfonic acid, sulfonamide and sulfonimide groups. Preferably, resin binders with high acid numbers are used, since these are particularly readily, soluble in alkaline-aqueous-alcoholic solvent systems. Copolymers with anhydride groups can be used particularly successfully since, due to the absence of free acid groups, the conductivity of the photoconductive layer in the dark is low, in spite of good solubility in alkali.

Copolymers of styrene and maleic acid anhydride, and also phenolic resins or reaction products of polymers containing hydroxyl groups with sulfonyl isocyanates according to European Patent 0,048,876 (corresponding to U.S. Patent 4,387,151) are very particularly suitable.

As the sensitizing dyes which represent dyes which are soluble or dispersible in organic solvents or represent pigments, those are employed which have also been used hitherto for this purpose. Suitable sensitizers are known from, for example, Belgian Patent 558,078 or German Patent 2,526,720, corresponding to U.S. Patent 4,063,948. Suitable pigments, such as phthalocyanines, azo pigments,

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disazo pigments, perylene pigments, quinacridone pigments and benzimidazole pigments are to be found, for example, in German Patent 2,904,183, corresponding to British Patent 2,104,748. The sensitizing dyes are usually present in small amounts of about 0.001 to 1 %, and the pigments are present, depending on the case, in quantities of up to 50 %, relative to the photoconductor fraction.

The layer thickness of the photoconductive layer can be up to about 50 μm . Preferably, it is within the range from about 2 to 10 μm .

The photoconductive layer can contain conventional additives, such as flow leveling agents and plasticizers and/or adhesion promoters between the layer support and the photoconductive layer, in order to improve the surface structure, the flexibility and the adhesion.

The light-sensitive covering layer which contains at least one photochemically reactive compound is described below.

In the case where this is a compound or a combination of compounds, the solubility of which in alkaline-aqueous and/or alcoholic solvent systems is increased by actinic radiation, that is to say where the provision of a positively working covering layer is ensured, the light-sensitive compound is applied alone or in combination with a soluble resin to the photoconductive layer.

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For example, o-quinone-diazides, such as are described, for example, in German Patent 1,447,008, corresponding to British Patent 996,315, can be used as the light-sensitive compounds.

It is also possible to use radiation-depolymerisable compounds or resins.

For this purpose, those compositions are suitable, for example, which contain a polymer with at least one C-O-C bond, which can be cleaved by acid, and a compound which forms a strong acid on irradiation and, if appropriate, a suitable binder, as described in EP-A 0,082,463. Examples of suitable acid-cleavable compounds are monomeric or polymeric orthocarboxylic acid derivatives, specifically an ester thereof, monomeric or polymeric acetals, enol ethers or N-acyliminocarbonates or mixtures thereof. As the radiation-sensitive components which preferably form a liberate strong acids, a large number of known compounds are suitable, such as, for example diazonium, phosphonium, sulfonium and iodonium salts, o-quinone-diazide sulfochlorides, halogen compounds and metal-organic halogen compounds.

A further material which can be used for positive working systems contains, as the light-sensitive compound, a copolymer of styrene and maleic acid or maleic acid anhydride, which is wholly or partially esterified with o-nitrobenzyl alcohol. An additional binder is not absolutely necessary.

Suitable alkali-soluble binders are the binders described

above for the photoconductive layer, in a quantity of about 50 to 85 % by weight of the light-sensitive covering layer.

The positive-working light-sensitive covering layer is applied in a quantity of about 0.1 to 50 g/m², corresponding to a layer thickness of about 0.1 to 50 µm, preferably from about 1 to about 25 µm.

In the case of a negative-working covering layer, the latter contains a compound or a combination of compounds, the solubility of which in alkaline-aqueous and/or alcoholic solvent systems is reduced on actinic irradiation. This light-sensitive layer can additionally contain alkali-soluble binders.

Examples of suitable light-sensitive compounds are diazonium salt polycondensation products, such as are obtained, for example, by reacting diphenylamine-4-diazonium salts with aldehydes, preferably with formaldehyde.

Preferably, cocondensates are used which, in addition to diazonium salt units, also contain other units which are not light-sensitive and which are derived from compounds capable of condensation, in particular aromatic amines, phenols, phenol ethers, aromatic thioethers, aromatic hydrocarbons, aromatic heterocyclic compounds and organic acid amides. Such condensation products are described in German Offenlegungsschrift 2,024,244, corresponding to British Patent 1,312,925. Those diazonium salt polycon-

densation products described in German Offenlegungsschrift 2,739,774, corresponding to U.S. Patent 4,186,017, are also suitable. Further suitable light-sensitive compounds are low-molecular or high-molecular organic acids, but in particular low-molecular aromatic azido compounds which contain at least two azido groups. Examples of suitable compounds are 4,4'-diazido-stilbene, 4,4'-diazido-stilbene-2,2'-disulfonic acid, 4,4'-diazido-benzophenone, 4,4'-diazido-diphenylmethane and others. Further examples are the azidostyryl compounds mentioned in British Patent 790,131, the azido-imidazolyl compounds mentioned in German Patent 950,618, corresponding to British Patent 765,909, and the diazido stilbene compounds mentioned in U.S. Patent 2,848,328.

The negative-working covering layers according to the invention contain in general 5 to 90, preferably 20 to 70, per cent by weight of diazonium or azido compounds and 95 to 10 %, preferably 80 to 30 %, of an alkali-soluble or swellable binder. Examples of suitable binders are the polymers described for the photoconductor layer.

To stabilize the light-sensitive diazonium salt or azido compounds, it is advantageous to add a compound having acidic character. Particularly suitable acids are phosphoric and phosphonic acids.

Furthermore, additives, such as plasticizers, adhesion promoters, surface-active substances, dyes, pigments, color formers and small quantities of other resins can be

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added to the light-sensitive mixtures, described above, for the light-sensitive covering layer. These also include, for example, condensed melamine/formaldehyde resins which facilitate thermal post-curing. The nature and quantity of these additives depend on the envisaged field of use.

Care must be taken here to ensure that the added substances neither affect the photoconductive properties of the arrangement nor impede the light reaction during the actinic irradiation.

In addition, the covering layer may contain dyes or pigments which are able to increase the layer strength and enhance the contrast after irradiation. Dyes, such as are listed, for example, in U.S. Patents 3,218,167 and 3,884,693, are suitable. Victoria Pure Blue FGA (C.I. Basic Blue 81), Victoria Pure Blue (C.I. 44,045), Rhodamines and Orasol Blue GN are particularly suitable.

The image contrast after irradiation can be enhanced by the addition of Metanil Yellow (C.I. 13,065) or phenylazodiphenylamine.

However, photopolymerizable compositions can also be used for the light-sensitive, negative-working layer. Such compositions as a rule contain binders, one or more addition-polymerizable compounds and a photopolymerization initiator.

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Examples of suitable binders are methyl acrylate or methylemethacrylate/acrylic or methacrylic acid copolymers, benzyl acrylate or benzylemethacrylate/acrylic or methacrylic acid copolymers, benzyl acrylate or benzylemethacrylate/itaconic acid copolymers, styrene/itaconic acid copolymers, half-esters or half-amides of styrene/maleic acid anhydride copolymers, terpolymers of acrylic or methacrylic acid/styrene/alkyl acrylate or alkylemethacrylate, and vinyl acetate/crotonic acid copolymers.

Compounds with one, and preferably with several, unsaturated groups are suitable as addition-polymerizable monomers. Preferred examples are ethylene glycol diacrylate and dimethacrylate, polyethylene glycol diacrylate and dimethacrylate, trimethylolethane triacrylate and trimethacrylate, trimethylolpropane triacrylate and trimethacrylate, neopentyl glycol diacrylate and dimethacrylate, pentaerythritol or dipentaerythritol tri-, tetra- or hexa-acrylate or -methacrylate and epoxydi-acrylate or -methacrylate, oligo-acrylates (Japanese Published Application 7,361/77) and acrylic urethane resins or acrylic urethane oligomers (Japanese Published Application 41,708/73).

Examples of suitable photopolymerization initiators are vicinal polyketaldonyl compounds (U.S. Patent 2,367,660), α -carbonyl compounds (U.S. Patents 2,367,661 and 2,367,670), acyloin ethers (U.S. Patent 2,448,828), aromatic acyloin compounds which are substituted with an α -hydrocarbon (U.S. Patent 2,722,512), polynuclear quinone

compounds (U.S. Patents 3,046,127 and 2,951,758), combinations of triallylimidazole dimer and p-aminophenyl ketone (U.S. Patent 3,549,367), benzothiazole compounds (Japanese Published Application 48,516/76), benzothiazole compounds/trihalogenomethyl-s-triazine compounds (Japanese Laid-Open Application 74,887/79 and German Offenlegungsschrift 3,038,605, corresponding to U.S. Patent 4,421,844), and acridine and phenazine compounds (U.S. patent 3,751,259).

Thermal polymerization inhibitors, such as are known from German Offenlegungsschrift 3,310,804, corresponding to GB-A 2,121,201, such as hydroquinone, benzoquinone or p-methoxyphenol, are preferably used in addition to the materials mentioned. In some cases, dyes, pigments or pH indicators can also be added in order to increase the image contrast.

The tickness of the negative-working covering layer can vary within wide limits and can assume values within the range from 0.1 to 50 μm . If diazonium salt polycondensates are used, thicknesses of about 0.2 to 3 μm will in general be selected and, if photopolymerizable compounds are used, thicknesses in the range from about 5 to 50 μm will be selected.

The light-sensitive covering layer used can also be a material which - depending on the processing method - is positive- or negative-working. Such a process and a corresponding material are described, for example, in EP-A 0,082,463.

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The photoconductive coating can be applied to the layer support in accordance with the known methods, by coating, dipping or spraying.

The light-sensitive covering layer is preferably applied by lamination or spraying, in order to avoid damage to the photoconductive layer.

Lamination can be carried out by means of a commercially available laminator. In this case, the light-sensitive layer is first applied to a temporary support, for example a polyester film of 20 to 50 μm thickness, by coating, dipping or spraying, and is transferred from this temporary support to the photoconductive layer by applying pressure and heat. The temporary support can be readily removed immediately after cooling, or only before processing of the material.

If the light-sensitive covering layer is applied by spraying, the solvent composition and the coating conditions must be selected such that the photoconductor layer is not incipiently dissolved and a uniform, continuous film is formed.

If the covering layer is applied by coating, this is done by curtain-coating, since mixing of the two layers cannot be excluded if spin-coating or related methods are used.

The layer support used can be all the materials known for this purpose, such as, for example, aluminum, zinc, mag-

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nesium, chromium or copper plates, the surfaces of which can have been pretreated, and also metallized cellulose products, such as films of cellulose hydrate, cellulose acetate or cellulose butyrate. Paper which has been rendered superficially hydrophilic and electrically conductive or plastic films as well as composite materials of paper or film and metal can also be used. Multi-metal support material is also suitable.

The preferred support material used for printing forms is mechanically or electrochemically roughened aluminum which may have been provided with a superficial oxide layer and posttreated with substances which render it hydrophilic, such as polyvinylphosphonic acid.

For the production of printed circuits, metallized plastic supports in the form of sheets or boards are used, in which case the metal layer can be applied by vapor deposition, lamination or by chemical deposition or electro-deposition. In this case, the support surface laid bare by decoating is etched or reinforced by electroplating in these areas.

The invention also relates to a process for the production of a printing form or printed circuit by electrophotographic means, in which a recording material composed of an electrically conductive layer support and a photoconductive layer system located thereon is electrostatically charged and exposed imagewise, and the resulting charge image is rendered visible by means of a finely particulate toner and subsequently the whole area is

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subjected to actinic radiation and then to decoating. The process comprises using, as the photoconductive layer system, a double layer which, as reviewed from the support, is composed of a photoconductive coating and a light-sensitive covering layer which is differentiated by actinic radiation with respect to its solubility. As desired, those areas of the light-sensitive covering layer which are not covered by toner are dissolved away together with the photoconductive layer constituents located below or those areas of the light-sensitive covering layer which are covered by toner are dissolved away together with the photoconductive layer constituents located below, depending on whether a positive or a negative reproduction is intended.

The process according to the invention is shown in principle in a diagrammatic representation in the attached figures.

In Figure A, the recording material according to the invention is shown, where 1 is the photoconductive layer, 2 is the light-sensitive covering layer and 3 is the layer support, here shown as a metal plate. As indicated in Figure L, however, it can also represent, for example, a film or plastic sheet 7 which is provided with an electrically conductive layer 3. An organic photoconductor is preferably used in the photoconductive layer 1. The light-sensitive covering layer contains at least one compound which confers solubility in the particular decoating agent on irradiation, or at least one compound

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which confers insolubility in the particular decoating agent on irradiation.

Figure B illustrates the electrostatic charge, generated, for example, by corona-charging, of the recording material according to the invention, which charge, as shown, can be negative or positive. Figure C diagrammatically shows the imagewise exposure ($h \cdot \nu_1$) of the charged material, which exposure can be effected by a lens system by projection or directly by means of laser beams. Figure D illustrates how the resulting charge image is rendered visible by means of an electrostatic developer. This can be carried out either with a liquid developer or with a dry developer. A toner of opposite charge can be used, as shown here, but the image can also be rendered visible by reversal development with a toner charged in the same sense as the electrostatic charge. The toner image formed can be fixed by the process according to the invention, that is to say baked or consolidated by solvent vapors. Preferably, however, because of the subsequent removal of the toner image, it is advantageous not to fix the toner image and merely to leave it in the developed state, corresponding to the existing electrostatic and adhesive forces.

Figures E and F illustrate the irradiation with actinic light ($h \cdot \nu_2$). For example, metal halide/mercury vapor lamps, which emit a high spectral fraction in the near ultraviolet region, are suitable for this purpose.

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The irradiation can serve, on the one hand, for converting the areas 4 not covered by toner into the soluble state, or for rendering insoluble the areas 5 which are not covered by toner; a positive process results under G, and a negative process results under H.

Figure G illustrates the printing plate freed from toner according to E, and Figure H illustrates the printing plate freed from toner according to F, and these plates are then subjected to the decoating process. The composition of suitable decoating solutions is known per se from German Patent 1,117,391 corresponding to British Patent 944,126. As decoating solutions suitable for the present process, alcohol mixtures are used to which alkali is added in the form of sodium metasilicate or ethanolamine. Preferably, a decoating agent which represents an alkaline-aqueous solution, which may contain a wetting agent, is used for dissolving away. If possible, the toner removed can be re-used. The removal of toner and the decoating can also take place in one step, and this is preferred. The layer constituents remaining after the decoating process, that is to say after dissolving away, can be subjected to thermal post-curing. This results in the finished printing forms according to Figure I or K respectively, as positive or negative printing plates.

In the case where the support, as mentioned at the outset, is composed of a metalized plastic plate 3,7, the material according to Figure I can be subjected to

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etching, whereby the metal image exposed by the decoating is removed (Figure L). After detachment (stripping) of the remaining layer constituents, a printed circuit according to Figure L₁ results. However, the material according to Figure I can also be subjected to an electroplating bath and the exposed metal areas can thus be reinforced by electroplating, with application of a further metal layer 8, as shown in Figure I₁. After stripping, a finished circuit board 2 is obtained.

Process steps corresponding to these shown, starting from a material I, can also be carried out with a material as shown under Figure K.

According to the invention, it is also possible, when using an appropriate material for the light-sensitive covering layer, to adjust a positive-working material to negative-working, if required, by inserting further process steps, such as heating and repeated irradiation.

The process according to the invention has the following advantages:

Due to the high light sensitivity of the electrophotographic double-layer system, the imagewise exposure can be effected by projection of the image original or also directly by a laser of, for example, low power. In the case of projection exposure, any desired number of printing plates or circuit images can be produced from one original, without the latter coming into contact with

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the light-sensitive material. The original is therefore not subjected to any wear.

It is not even necessary to fix the toner image produced by electrophotographic means. The toner mask can therefore, in a simple manner, be corrected or completely removed before or during decoating. There is therefore no interference, due to the presence of toner, with processing steps carried out later and, in particular, the problem of "toner run-off" at the start of printing, known from conventional electrophotographic printing plates with a fixed toner image, does not arise.

A further advantage is that the toner image is produced directly on the light-sensitive covering layer. When the whole area is irradiated, there are therefore no uncontrolled halations, such as are frequently the case, when the film originals are used, due to air occlusions between the film and the light-sensitive layer. The irradiation can therefore be carried out without the use of a vacuum printing frame, that is to say even during the transport of the plate, and this gives a time saving.

A coloring of the light-sensitive covering layer produces a color change directly during the irradiation, is that irradiated plates and not yet irradiated plates can be distinguished even if the toner image has already been removed. In addition, the image areas can be distinguished from the non-image areas.

The reproduction of tonal values in halftone originals

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can be influenced by the selection of the irradiation conditions, as is known from conventional positive- or negative-working printing plates. The increase in tonal value, which occurs in the press in offset printing, can at least partially be compensated in this way.

In decoating by dissolving away, only the more readily soluble non-image areas are removed, and the double-layer arrangement is fully preserved in the image areas.

It is possible to post-cure the layer areas remaining after stripping by applying heat, whereby the resistance of the surface to chemicals or to mechanical stress can be further improved.

A further special advantage of the process is its versatile applicability, depending on the starting material and the process steps.

Thus, a positive-negative reversal can, for example, be achieved by appropriate charging of the electrophotographic double layer and toner, by the selection of a positive- or negative-working covering layer or even a covering layer which, depending on the processing, alternatively works positively or negatively.

Since fixing of the toner image is not necessary, the charging and the application of toner can be repeated if required, or the entire process sequence can be carried out in several cycles with different image originals.

The Examples which follow are intended to describe the present invention in more detail, without restricting it thereto.

Example 1

The following coating solution:

50	parts by weight	of a copolymer of styrene and maleic acid anhydride (Scripset [®] 540, Monsato),
(p.b.w.)		
42	p.b.w.	of 2-vinyl-4-(4'-diethylaminophenyl)-5-(2'-chlorphenyl)-oxazole,
0.2	p.b.w.	of Rhodamine FB (C.I. 45,170),
360	p.b.w.	of ethylene glycol monomethyl ether,
		and
550	p.b.w.	of tetrahydrofuran

was applied to an electrochemically roughened and anodically oxidized, 0.03 mm thick aluminum plate which had been posttreated with polyvinylphosphonic acid according to German Offenlegungsschrift 1,621,478 corresponding to British Patent 1,230,447.

After drying, the layer weight was 3.0 g/m^2 . To this photoconductive layer, a light-sensitive covering layer of 2.0 g/m^2 was applied by spray-coating with the following solution:

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- 0.8 p.b.w. of the esterification product obtained from 1 mol of 2,3,4-trihydroxybenzophenone and 3 mol of 1,2-naphthoquinone-2-diazide-5-sulfonic acid chloride,
- 0.40 p.b.w. of the esterification product obtained from 1 mol of 2,2'-dihydroxy-1,1'-dinaphthyl-methane and 2 mol of 1,2-naphthoquinone-2-diazide-5-sulfonic acid chloride,
- 6.00 p.b.w. of a cresol-formaldehyde novolak having a softening point of 120 to 135 °C and a mean molecular weight of 1,500,
- 0.60 p.b.w. of 1,2-naphthoquinone-2-diazide-4-sulfonic acid chloride and
- 0.30 p.b.w. of crysatl violet (C.I. 42,555) in
- 40.00 p.b.w. of ethylene glycol monomethyl ether and
- 50.00 p.b.w. of tetrahydrofuran.

The two-layer combination thus obtained was provided with a negative charge by means of a corona discharge in a commercially available machine for the production of electrophotographic printing forms, and was exposed image-wise for 20 seconds by projection, and the latent charge image was developed with a commercially available electrophotographic dry developer.

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The aluminum plate with applied toner was then irradiated for 1.0 minute with a 5 kW metal halide lamp.

Finally, a stripper decoating solution of sodium silicate, glycerol, water, ethylene glycol and ethanol according to European Patent 0,034,317, corresponding to U.S. Patent 4,388,391, was applied to the plate with a cotton pad. This solution completely dissolved the toner-free layer constituents of the covering layer, together with the photoconductor layer located below. The non-fixed toner was at the same time washed off the image areas of the aluminum plate. The layer constituents located below remained unaffected.

By selecting a correspondingly longer irradiation time, it was possible to sharpen the plate, and this led to a more open reproduction of tonal values. A run of 150,000 copies was obtained from the plate, and this could be increased to 180,000 by thermal post-curing of the remaining layer before printing (5 minutes, 220 °C).

Example 2

A photoconductor layer having a weight of about 4.5 g/m² was applied to a printing plate support, as described in Example 1.

To this layer, a light-sensitive coating of the following composition was applied in such a way that the layer weight after drying was about 1.5 g/m²:

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97.0 p.b.w. of a binder obtained by reacting 11.3 p.b.w. of a polyvinyl butyral having a molecular weight of 70,000 to 80,000 with 5.11 p.b.w. of propenylsulfonyl isocyanate corresponding to German Auslegungsschrift 2,053,363 or U.S. Patent 3,732,106),

48.3 p.b.w. of a diazonium salt polycondensation product prepared from 1 mol of 3-methoxy-diphenylamine-4-diazonium sulfate and 1 mol of 4,4'-bismethoxydiphenyl ether in 85 % strength phosphoric acid and isolated as the mesitylene sulfonate,

4.5 p.b.w. of phosphoric acid and

3.5 p.b.w. of Victorian Pure Blue FGA (C.I. Basic Blue 81) in

3,500 p.b.w. of ethylene glycol monomethyl ether and
1,035 p.b.w. of tetrahydrofuran.

As described in Example 1, the double layer thus obtained was electrostatically charged and exposed, the resulting charge image was developed with a liquid developer adjusted for positive development and then irradiated for 2 minutes under a metal halide lamp of 5 kW power.

To remove the layer constituents with applied toner, an aqueous solution of

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5 p.b.w. of sodium octyl-sulfate,
2 p.b.w. of sodium metasilicate pentahydrate,
1 p.b.w. of trisodium phosphate and
1 p.b.w. of phenoxyethanol

was used.

The treatment time was 90 seconds. Within this time, both the toner constituents and the layer constituents located below were completely detached.

The toner-free layer constituents of the double layer were completely preserved and, on printing, gave a negative image of the exposure original.

Since the toner image showed an increase in tonal value as compared with the original, the increase in tonal value to be observed in negative layers was at least partially compensated.

Example 3

As described in Example 2, a double layer comprising a photoconductor layer with 2,5-bis-(4'-diethylaminophenyl)-1,3,4-oxadiazole as the photoconductor and a negative-working covering layer was produced on a 100 μ m thick aluminum printing plate support with mechanically grained surface. Instead of the reaction product of polyvinyl butyral and propenylsulfonyl isocyanate, a copolymer of

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styrene and maleic acid anhydride (Scripset[®] 540, Monsato) was used as the binder in the covering layer. The decoating solution mentioned in Example 2 was used for decoating this plate.

This gave a printing plate, from which perfect prints could be prepared right from the start of printing, and a longer run was achieved than a conventional electrophotographic printing plate.

Example 4

The photoconductive layer described in Example 1 was applied in a layer weight of 6 g/m^2 to a $35 \text{ }\mu\text{m}$ thick copper foil which was free from oxide layers and which was laminated to a 1.5 mm thick laminated phenoplast sheet.

A coating solution according to EP-A 0,082,463 of the following composition:

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|-----|---|
| 40 | p.b.w . of methyl ethyl ketone, |
| 15 | p.b.w. of ethylene glycol ethyl ether acetate, |
| 5 | p.b.w. of diethylene glycol monoethyl ether, |
| 28 | p.b.w. of a cresol/formaldehyde novolak having a softening range from 105 to 120 °C by the DIN 53,181 capillary method, |
| 3.5 | p.b.w. of polyvinyl ethyl ether (Lutanol A 25), |
| 8.3 | p.b.w. of the polyacetal of 2-ethylbutyraldehyde |

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and triethylene glycol,
0.2 p.b.w. of 2-(6-methoxy-naphth-2-yl)-4,6-bis-tri-
chlormethyl-s-triazine and
0.01 p.b.w. of crystal violet base

was spin-coated onto a 50 μm thick polyester film as a temporary support, and the dried solution was then used as a dry resist material.

The layer thickness after drying was 25 μm .

In a laminator used for processing dry resist material, this resist material was transferred as the light-sensitive covering layer to the surface of the photoconductor layer, with application of pressure and at a temperature of 130 °C. The polyester film used as the temporary support was then peeled off at room temperature.

The copper base was earthened and the double layer was negatively charged by means of a corona, exposed image-wise and developed with a commercially available dry developer, and the plate was post-treated for 10 minutes at 80 °C. The whole area was then irradiated for 0.5 minute with a 5 kW metal halide lamp through the toner mask.

If a correction is necessary, the toner can be removed by wiping and the irradiation step can be repeated.

Decoating could be carried out alternatively in two

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steps, with quick working, using an aqueous solution of 5 p.b.w. of sodium metasilicate x 9 H₂O, 3 p.b.w. of trisodium phosphate x 12 H₂O and then with the solution described in Example 2, or in one step with a solution which contained 6 p.b.w. of diethylene glycol monoethyl ether, 5 p.b.w. of propanol, 0,7 p.b.w. of sodium metasilicate, 2,5 p.b.w. of trisodium phosphate and 85 p.b.w. of water.

In both cases, the toner-free layer constituents of the double layer were completely dissolved away, whereas the image areas were preserved and, on these, only the toner was washed off.

The bared copper layer was then etched away and the etch resist, that is to say the layer constituents present, were stripped with solvents, such as acetone or methylglycol.

A printed circuit with exact track boundaries was obtained in this way.

Example 5

The procedure followed was as in Example 4, with the difference that, after the irradiation, the toner image was removed by wiping, the plate was heated for 30 minutes to 120 °C and the plate, cooled to room temperature, was then irradiated once more under a metal halide/mercury

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vapor lamp. Subsequently, decoating was carried out and, as distinct from Example 4, a negative image of the image original was obtained. The production of a printed circuit was continued as described in Example 4.

Example 6

The procedure followed was as in Example 4, with the difference that a negative-working material was laminated as the light-sensitive covering layer to the photoconductor layer.

For this purpose, the following formulation was applied to polyester film as a temporary support, as described in Example 4:

- 6.5 p.b.w. of a terpolymer of n-hexyl methacrylate, methacrylic acid and styrene (60:30:10 parts by weight) having a mean molecular weight of 35,000 (according to German Auslegungsschrift 2,363,806, corresponding to U.S. Patent 3,930,865),
- 5.0 p.b.w. of an unsaturated polyurethane synthesized from 3 mol of 2,2,4-trimethylhexamethylene diisocyanate and 2 mol of triethylene glycol (1st reaction stage) and then 2 mol of hydroxyethyl methacrylate (2nd reaction stage),
- 2.8 p.b.w. of 2-ethylhexyl 4-hydroxybenzoate,

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0.2 p.b.w. of 9-phenylacridine,
0.1 p.b.w. of 3-mercaptopropionic acid 2,4-dichloro-
anilide and
0.025 p.b.w. of the dye "Disperse Red" (C.I. 179), in
25 p.b.w. of methyl ethyl ketone and
2 p.b.w. of ethanol.

As described in Example 4, the double layer obtained was electrophotographically treated and developed, and irradiated for 1 minute with a 5 kW metal halide lamp.

Decoating was carried out with the following solution:

4 p.b.w. of sodium lauryl-sulfate,
1 p.b.w. of sodium carbonate,
2 p.b.w. of trisodium phosphate x 12 H₂O,
2 p.b.w. of sodium metasilicate x 5 H₂O,
1 p.b.w. of phenoxyethanol, and
90 p.b.w. of water.

This gave a negative image of the original, which could be used as a printed circuit board.



Patent claims

1. A light-sensitive recording material composed of an electrically conductive layer support suitable for the production of printing forms or printed circuits, and a photoconductive layer system containing a photoconductor, binder, sensitizing dye and conventional additives, wherein the photoconductive system comprises a photoconductive single layer or multiple layer applied to the support and a light-sensitive covering layer which contains at least one photochemically reactive compound.

2. The recording material as claimed in claim 1, wherein the photochemically reactive compound present in the light-sensitive covering layer is a compound or a combination of compounds, the solubility of which in alkaline aqueous and/or alcoholic solvent systems is reduced by actinic irradiation.

3. The recording material as claimed in claim 1, wherein the photochemically reactive compound present in the light-sensitive covering layer is a compound or a combination of compounds, the solubility of which in alkaline aqueous and/or alcoholic solvent systems is increased by actinic irradiation.

4. The recording material as claimed in claims 1 and 2, wherein at least one o-quinone-diazide is present as the photochemically reactive compound.



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5. The recording material as claimed in claims 1 and 3, wherein at least one diazonium salt polycondensation product is present as the photochemically reactive compound.

6. The recording material as claimed in claims 1 to 5, wherein the layer areas which are more readily soluble after actinic irradiation are dissolved in an alkaline aqueous solvent which may contain a wetting agent.

7. The recording material as claimed in claim 1, wherein the layer thickness of the light-sensitive covering layer is within the range from about 0.1 to about 50 μm .

8. The recording material as claimed in claim 7, wherein the layer thickness of the light-sensitive covering layer is within the range from about 1 to about 25 μm .

9. The recording material as claimed in claim 1, wherein the layer thickness of the photoconductive layer is within the range from about 2 to about 10 μm .

10. A process for the production of a printing form or printed circuit by electrophotographic means, in which a recording material composed of an electrically conductive support and a photoconductive layer system located thereon is electrocally charged and exposed image-wise, and the resulting charge image is rendered visible by means of



a finely particulate toner and subsequently the whole area is subjected to actinic irradiation and then to decoating, which comprises using, as the photoconductive layer system, a double layer which, as viewed from the support, is composed of a photoconductive coating and a light-sensitive covering layer which is differentiated by actinic radiation with respect to its solubility.

11. The process as claimed in claim 10, wherein those areas of the light-sensitive covering layer which are not covered by toner are dissolved away together with the photoconductive layer constituents located below.

12. The process as claimed in claim 10, wherein those areas of the light-sensitive covering layer which are covered by toner are dissolved away together with the photoconductive layer constituents located below.

13. The process as claimed in claims 10 to 12, wherein the decoating agent used for dissolving away is an alkaline aqueous solution which may contain a wetting agent.

14. The process as claimed in claims 10 or 13, wherein an organic photoconductor is used in the photoconductive layer.

15. The process as claimed in claim 10 or 11, wherein at least one compound which confers solubility in the particular decoating agent on irradiation is used in the light-sensitive covering layer.



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16. The process as claimed in claim 10 or 12, wherein at least one compound which confers insolubility in the particular decoating agent on irradiation is used in the light-sensitive layer.

17. The process as claimed in claims 10 to 16, wherein the layer constituents remaining after the dissolving-away are subjected to thermal post-curing.

18. The process as claimed in claims 10 to 16, wherein, after dissolving away, the bared support surface is etched or strengthened by electroplating and, if appropriate, the remaining layer constituents are removed by detaching (stripping).