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[54] **PREPARATION OF PRINTING PLATES
EMPLOYING ORGANIC POLYMERIZABLE
PHOTOCONDUCTOR**
6 Claims, No Drawings

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ABSTRACT: A process for the preparation of printing plates from electrophotographic reproduction material, having a support suitable for printing purposes and a photoconductive layer thereon, by charging, imagewise exposure to light, developing the latent electrostatic image on the layer with a finely divided toner, subsequent heating, and removal of the photoconductive layer in the nonimage areas. The latent electrostatic image is produced on a layer which contains at least one known polymerizable organic photoconductor containing or forming during heating olefinic double bonds, and the image is made visible by means of a developer which, at least partially, consists of one or more finely divided solid substances forming radicals when heated. The reproduction material with the developed image thereon is heated to a temperature between 50° and 300° C., preferably to a temperature between 100° and 200° C., and finally the organic photoconductive layer is removed, in known manner, in the nonimage areas by dissolving it away.

PREPARATION OF PRINTING PLATES EMPLOYING ORGANIC POLYMERIZABLE PHOTOCONDUCTOR

It is known to use photoconductive organic compounds in the photoconductive layers of of electrophotographic reproduction materials. Furthermore, it is known to process electrophotographic reproduction materials containing organic photoconductors into printing plates. These latter have supports suitable for printing purposes. In the unprocessed state, they also are called electrophotographic materials. An electrophotographic material is known, for example, the photoconductive layer of which consists of a monomolecular photoconductor and high-molecular weight alkali-soluble substances. This material is charged, exposed to light, and developed with dyed resin powder in the usual manner. The resin powder is fixed by burning in, the layer is then treated with an alkaline solution to remove the nonimage areas, and a planographic printing plate results. The disadvantage of this process is that, when treating with the alkaline solution, comparatively small image areas are easily undermined and sometimes even washed away.

Furthermore, an electrophotographic material is known the photoconductive layer of which contains zinc oxide finely distributed in a cross-linkable binding agent. A method is known for the processing thereof where for developing the latent electrostatic image, a substance catalyzing cross-linking of the binding agent is used in a finely distributed solid form. When burning in the developer, the image areas become difficultly soluble or insoluble in certain solvents in which the nonimage areas, which are not cross-linked, are readily soluble. For the preparation of a printing plate, the photoconductive layer is dissolved away in the nonimage areas. Here, too, the already mentioned effect of undermining the image areas occurs since cross-linking of the layer does not uniformly penetrate to the support because of the incorporated zinc oxide. In order to overcome this drawback, in a variation of the process, electrophotographic printing materials are used which, between the support and the photoconductive layer, additionally contain a metal chromate or phosphate intermediate layer which increases adhesion. Undermining of the image areas is considerably reduced by this measure but the process still has the disadvantage that organic solvents must be used for removing the nonimage areas.

The present invention provides a process for the electrophotographic preparation of printing plates which meet high requirements regarding dissolving ability and length of printing run and the nonimage areas of which preferably can be removed by means of an aqueous solution.

According to the present process, a planographic printing plate is obtained which may be converted, by means of one of the known processes, into a relief printing plate or, if desired, also into an intaglio printing plate, if the support material is appropriate.

The essence of the invention is that a polymerizable monomeric photoconductor is imagewise polymerized by radical initiation, the imagewise distribution of the radical donor being achieved by its use as a developer substance.

The electrophotographic material serving as starting material in the process is known in principle. The use of a photoconductive organic substance having an olefinic double bond is known. The use thereof in printing plates is not expressly described, but it is known from German Pat. No. 1,117,391, that they are, in principle, useful in this field.

In the process according to the invention, there may be used photoconductors having vinyl or vinylidene groups as well as those in which three of all four hydrogens of the ethylene group are substituted. Suitable polymerizable compounds also include photoconductive stilbene and styrene derivatives.

Compounds carrying vinyl groups preferably are employed. Vinylcarbazole, substituted vinylcarbazole, substituted vinyloxazoles, substituted vinyltriazoles, and vinylbibenzofuran have proved particularly suitable. Suitable compounds which do not form the vinyl group before heating are the substituted hydroxyethyl-diphenyltriazoles. They split off water during heating, whereby a vinyl group is formed.

A very suitable compound including the vinylidene group is acenaphthylene.

Insofar as the polymerizable organic photoconductors are sufficiently film forming themselves, they may be directly applied to a suitable support and processed according to the process of the invention. Since this usually is not the case to a sufficient extent, it has proved advantageous to employ a material the layer of which, in accordance with German Pat. No. 1,117,391, in addition to the organic photoconductor, contains resins which are soluble in aqueous alkali. Suitable resins are high molecular weight substances carrying alkali-solubilizing groups. Such groups, for example, are acid anhydride, carboxylic, sulfonic, sulfonamide, or sulfonamide groups. Preferably employed are resins having high acid numbers since they are especially soluble in aqueous alkaline solutions. Copolymers having anhydride groups can be used particularly successfully since, by the absence of free acid groups, the conductivity in the dark of electrophotographic layers is low despite the good alkali-solubility thereof. Copolymers of styrene and maleic anhydride have proved particularly suitable.

A preferred embodiment of the process according to the invention therefore is to produce the latent electrophotographic image on a layer containing at least one polymerizable organic photoconductive compound having a vinyl group, and an alkali-soluble binding agent. After development and heating, the imagefree areas of the photoconductive layer are removed in known manner by treatment with an aqueous alkaline liquid, if desired containing an organic solvent. Suitable alkaline liquids are described in the German Pat. No. 1,117,391.

The layer of the electrophotographic starting material also may contain sensitizers, in known manner. These are added to the reproduction layer in small quantities, about 0.00001 to about 0.1 percent, calculated on the weight of photoconductor. Suitable sensitizers, generally dyestuffs, are known from Belgian Pat. No. 558,078, for example.

Furthermore, the light-sensitivity of the layer may be increased, in known manner, by the addition of so-called activators. These are electron acceptors which form molecular complexes with the photoconductors, which generally are electron donors. Particulars are disclosed in German Pat. No. 1,127,218.

As layer supports for use in the electrophotographic starting material, all materials known for this purpose may be used, e.g. aluminum, zinc, magnesium, or copper plates, and also cellulose products, such as special papers, cellulose hydrate, cellulose acetate, or cellulose butyrate films, the latter particularly in a partially saponified form. To a certain extent, plastic materials, such as polyamides in the form of films, also are suitable as supports.

For the performance of the process of the invention, an electrophotographic material of the above-described type is corona-charged in the usual manner. Positive or negative charges optionally may be sprayed thereon. A latent electrostatic charge image then is produced on the charged layer by means of imagewise exposure to light. Contact exposure, or diascopic or episcopic exposure is possible. It is also possible to employ a contact or glass-engraved screen. The latent image then is made visible by means of a developer which at least contains substances which decompose into radicals when heated.

Suitable developers are all available solid compounds which find use in radical-initiated polymerization of olefins. In the present case, the following have proved particularly advantageous: benzoyl peroxide, dichlorobenzoyl peroxide, succinyl peroxide, azoisobutyric nitrile, tetraphenyl hydrazine, dehydrolophine, diazodistilbene, and sodium trichloroacetate. These substances may be used for development either in the dry state or dispersed in the form of a liquid developer.

The invention, therefore, also provides a dry finely divided developer powder for the performance of the process of the invention, which consists entirely or partially of one or more substances which form radicals when heated.

Generally, only the pure radical-forming substance is employed as a developer. If, however, the image is to be made distinctly visible, a normal resin-containing toner may be mixed therewith. The proportion of radical-forming substance in the dry developer should, however, not be below 20 percent by weight. Furthermore, it has proved advantageous to pulverize the radical-forming substances to a particle size less than 10μ .

In most cases, the developer substance is applied to the layer to be developed by means of a support. A mixture with iron filings used in the known magnetic brush or magnetic roll leads to favorable results.

Due to clean working and high-dissolving power, liquid development has proved particularly advantageous in the present invention. The invention, therefore, also provides a liquid developer containing a highly resistant liquid phase and a finely divided solid phase dispersed therein, the solid phase entirely or partially consisting of one or more substances forming radicals when heated. Here, too, the preferably employed solid substance is a pure radical-forming substance. Sometimes, however, it is of advantage when the solid phase includes a dyestuff. The particle size also should be below 10μ . The solid substance usually is ground in a ball mill.

As dispersing agents, there are employed liquids which do not dissolve the solid phase. Suitable are, for example, some hydrocarbon halides, particularly, however, higher molecular weight, liquid aliphatic hydrocarbons, such as the product known under the name Shellsol T (registered trademark). The charge nature of the dispersed solid phase depends upon the properties of the radical-forming substance itself as well as upon the specific solvent used. When dispersed in Shellsol, the radical-forming substances exhibit the following nature of charge: diazodistilbene and sodium trichloroacetate are given negative charges; all the other substances, however, are given positive charges.

It is possible, however, to change or stabilize the nature of the charge in a known manner by means of additives. Suitable additives are naphthenates, for example, and they are particularly advantageously employed together with a small quantity of binding agent, such as linseed oil. Their technical effect is known from German Pat. (DAS) No. 1,047,516.

Application of the liquid developer may be performed in a known manner, e.g. by immersion or roller application. Preference is given, however, to roller application because of higher uniformity achieved therewith.

After development of the latent electrostatic image with one of the aforementioned developers of the invention, the radical-forming substance loosely adheres imagewise to the polymerizable layer. Polymerization then is initiated by heating. Polymerization is effected, as already stated, in the temperature range between 100 and 200°C . The specific temperature advantageously depends upon the decomposition temperature of the radical-forming substance employed. Heating preferably performed in an oven heated to the required temperature. Infrared radiators of sufficient intensity also are suitable; when employing them, it is advisable, however, to use a dyed developer in order to increase the energy reception of the developed image areas. The duration of the heat treatment depends upon the photoconductor to be polymerized, the radical-forming substance which initiates polymerization, the temperature employed, and the thickness of the layer to be polymerized. Sometimes, heating for 30 seconds is sufficient to polymerize the layer; sometimes, however, several minutes are required. The extreme duration of heating is 5 minutes.

The image areas polymerized by heating become insoluble in suitable solvents, i.e. in the preferred embodiment they are insoluble in aqueous alkaline solutions.

The solutions are applied to the layer, e.g. by means of a cotton pad. It also is possible to immerse the plates directly into the liquid. Also suitable for removing the nonimage areas are appropriately constructed devices, e.g. those with application rollers for the liquid. Differentiation into hydrophilic and oleophilic areas, which is desired in offset printing, is thereby

obtained, the polymerized organic photoconductive layer yielding the oleophilic areas and the support surface yielding the hydrophilic areas.

After treatment with the alkaline liquid, the printing plate advantageously is aftertreated with water and, if desired, the hydrophilic properties are further enhanced by wiping over with dilute phosphoric acid solution. After inking up with greasy ink, prints can be made therefrom in planographic printing machines in known manner.

It also is possible to produce printing plates for relief and, if desired, also for intaglio printing by subsequent etching of the bared support. The etching is performed in known one-step or multistep etching machines.

The printing plates prepared in accordance with the invention using one of the described developers produce long runs. The photoconductive layer, which generally has a thickness of only a few microns is completely polymerized to the depth of the support and is firmly anchored therewith. Undermining during removal of the nonimage areas does not occur. Since the organic photoconductive layers are homogeneous, grainless layers, the finest screen dots easily can be truly reproduced. The process of the invention, therefore, also preferably is employed in the preparation of printing plates of very finely screened halftone originals. This field hitherto has been substantially foreclosed to electrophotographic printing plates.

The invention will be further illustrated by the following examples:

EXAMPLE 1

A superficially roughened about 100μ thick aluminum foil is coated with a solution of 2 g. of N-dimethylvinylcarbazole, 2 g. of a polystyrene synthetic resin (Lytron 820 of Monsanto), and 4 mg. of Rhodamine B in 40 g. of glycol monomethylether, and dried. The coated material is positively charged to about 300 volts by means of a corona discharge. Then, exposure is performed under a positive screened film original in a vacuum frame. When using a 200 watt incandescent lamp at a distance of 75 cm., the exposure time is 2 seconds. The charge image produced on the photoconductor layer then is developed in a developer bath which contains 10 g. of finely distributed sodium trichloroacetate per 100 g. of a high-boiling hydrocarbon (Shellsol T). After evaporation of excess dispersing agent adhering to the layer, the resulting white image of sodium trichloroacetate is heated for 3 minutes to 200°C ., the sodium trichloroacetate being thereby decomposed. The radicals resulting during decomposition polymerize the photoconductor layer of N-dimethylvinylcarbazole in the image areas. The layer is removed in the nonimage areas by bathing it for 2 minutes in a solution of 5 g. of sodium metasilicate in 100 ml. of water, 40 ml. of methanol, 35 ml. of glycol, and 20 ml. of glycerol, and is subsequently is wiped with a sponge. A printing plate is thus obtained by means of which very long run of several ten thousands of prints can be achieved in the offset printing process.

EXAMPLE 2

Instead of the solution of N-dimethylvinylcarbazole used in example 1, a solution of a corresponding quantity of 2-vinyl-4-(o-chlorophenyl)-5-(p-diethylaminophenyl)-oxazole is used for coating an aluminum foil. The layer is negatively charged to 400 volts by means of a corona device. Exposure is carried out under a contact screen and a diapositive, the exposure time depending upon the specific source of light used and the enlargement scale. Usually, it is in the range of several seconds. The exposed plate is developed with a liquid developer which contains 6 g. of finely distributed pure tetraphenyl hydrazine in 1,000 g. of a high-boiling hydrocarbon (Shellsol T). The remainder of the process is as in example 1. A screened printing plate is obtained.

EXAMPLE 3

An etchable zinc plate is coated with a solution of 10.5 g. of 2-vinyl-4-(o-chlorophenyl)-5-(p-diethylaminophenyl)-oxazole, 25 g. of a novolak (Alnovol 429 K), 20 g. of a polyvinyl

acetate (Mowilith CT 5), and 120 mg. of Rhodamine B in 300 g. of glycol monoethyl ether, and dried. The thickness of the dry photoconductive layer should be about 10 to 12 μ . It is negatively charged to about 400 volts by means of a corona device. Exposure may be performed in a contact reproduction frame, as described in example 1. The latent charge image produced by exposure is developed with a dispersion of 10 g. of dehydrolophine in 1,000 g. of a high-boiling hydrocarbon (Shellsol T), and is then heated to 200° C. and decoated. The zinc bared by decoating in the nonimage areas then may be deep-etched by means of commercial etching media. A relief printing plate is thus obtained.

EXAMPLE 4

A superficially roughened aluminum foil is coated with a solution of 5 g. of 1-hydroxyethyl-2,5-bis-(1-diethylamino-phenyl)-1,3,4-triazole, 5 g. of polystyrene synthetic resin (Lytron 820 of Monsanto), and 10 mg. of Rhodamine B in 100 g. of glycol monoethyl ether. The layer is negatively charged to 400 volts. Exposure is performed with a reproduction camera having eight 500 watt incandescent lamps. The original is a halftone photograph. Exposure is carried out under a glass-engraved screen and the plate, which has been exposed to light for 60 seconds, is developed in the manner described above with a dispersion of 20 g. of benzoyl peroxide in 1,000 g. of a high-boiling hydrocarbon (Shellsol T). Heating is performed for about 5 minutes, a somewhat longer period than is usual with vinyl compounds since water first has to be split from the hydroxyethyl group. After decorating the nonimage areas, a printing plate for offset printing is obtained.

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 modifications.

What is claimed is:

1. A process for the preparation of a printing plate which

comprises exposing an electrostatically charged, supported photoconductive insulating layer to light under a master, the layer comprising a monomeric polymerizable organic photoconductor containing an olefinic bond, developing the resulting latent electrostatic image by contacting it with a finely divided material which forms free radicals when heated, heating the layer to a temperature in the range of about 50–300° C. to polymerize the photoconductor, and removing the photoconductive layer from the support in the nonimage areas.

2. A process according to claim 1 in which the photoconductive insulating layer comprises a polymerizable organic photoconductor containing vinyl groups in admixture with an alkali-soluble binding agent, and the photoconductive layer is removed from the support in the nonimage areas by treatment with an aqueous alkaline liquid.

3. A process according to claim 1 in which the finely divided material which forms radicals when heated is contacted with the latent electrostatic image in the form of a dry powder.

4. A process according to claim 1 in which the finely divided material which forms radicals when heated is contacted with the latent electrostatic image in the form of a dispersion in a dielectric liquid.

5. A process according to claim 1 in which the polymerizable organic photoconductor is selected from the group consisting of vinylcarbazoles, vinyloxazoles, vinyltriazoles, vinyl-dibenzofuran, and hydroxyethyl-diphenyltriazoles.

6. A process according to claim 1 in which the finely divided material which forms radicals when heated is selected from the group consisting of benzoyl peroxide, dichlorobenzoyl peroxide, succinyl peroxide, azoisobutyric nitrile, tetraphenyl hydrazine, dehydrolophine, diazidostilbene, and sodium trichloroacetate.

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