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PROCESS FOR PREPARING A PLANOGRAPHIC PRINTING PLATE

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U.S. Cl. 96—1 7 Claims

ABSTRACT OF THE DISCLOSURE

A planographic printing plate is prepared by xerographically developing a latent electrostatic image on a xerographic layer using an inorganic photoconductor adapted to provide zinc ions, the image being developed with a developing composition forming a hydrophobic deposit on the xerographic layer in the image areas. The resultant xerographically developed layer is treated with an aqueous solution containing a hydrophilic zinc chelate or a compound capable of forming such a chelate with zinc ions.

This invention relates to a process for the preparation of a planographic printing plate and to the printing plate obtained therewith.

Planographic printing is based on the physical property of repellence of greasy materials for water. The printing surface which is substantially flat contains the pattern of the image to be printed in terms of a differentiation in water-repellency. In the ordinary lithographic or planographic printing processes a printing plate is prepared by affixing to a water-attractive, hydrophilic surface, a water-repellent hydrophobic image, usually greasy, resinous or waxy in nature.

There are several methods known for preparing a lithographic printing plate. According to one of them use is made of a photoconductive insulating material such as an electrophotographic recording layer containing photoconductive zinc oxide dispersed in an electrically insulating binder. To prepare the printing surface said layer is electrostatically charged and image-wise exposed.

The electrostatic image according to the electrical sign of the electrostatically attractable developer particles in respect of the applied charge, may be developed as a negative or a positive of the original to be reproduced. According to a common technique the electrostatic image is rendered visible by applying a developer powder, which is held electrostatically to the charged areas of the sheet. The powder image preferably composed of hydrophobic fusible powder particles may be fixed by heating. Normally the difference in hydrophobicity between the developed image parts and the non-covered areas of the recording layer is not high enough for high quality planographic printing and has to be increased. Therefore it has been proposed to chemically treat the recording layer in the undeveloped areas in order to make the said areas highly water-receptive.

It is known from the United States patent specification 2,952,536 to image-wise hydrophilize a photoconductive insulating recording layer comprising an electrically insulating binder having suspended therein a finely divided photoconductive pigment by means of an aqueous solution providing hydrophilic anions forming insoluble compounds with said pigment, and which anions are provided by a solid organic acid at least as strong as acetic acid.

It has now been found that a photoconductive insulating recording layer comprising an electrically insulating binder having suspended therein an inorganic photoconductive substance which can provide zinc ions such as photoconductive zinc oxide, can be provided with an improved hydrophility by treating it with a compound capable of forming an hydrophilic chelate therewith, or by treating it with an already formed hydrophilic zinc chelate.

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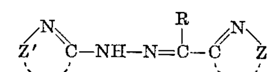
The water-solubility of the chelating compound can be improved by introducing one or more water-solubilizing group(s) in its structure.

The compound may be a non-metal containing chelating compound, or a water-soluble metal chelate, for example formed by reaction of a non-metal containing chelating compound with a metal salt, e.g. a copper(II) or cobalt(II) salt.

Preferably used compounds capable of forming a hydrophilic zinc chelate are represented by the following general formula:



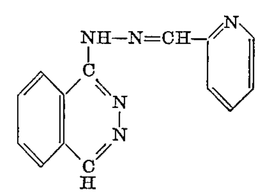
wherein:

R represents a hydrogen atom, an alkyl radical e.g. an alkyl radical having from 1 to 5 carbon atoms and

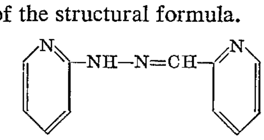
each of Z and Z′ represents the atoms necessary for completing a nitrogen-containing ring or ring system preferably containing one or more water-solubilizing substituents e.g. a carboxylic or sulphonic acid group in order to improve the water-solubility.

Compounds according to said general formula which have proved to be particularly useful are listed in the following table:

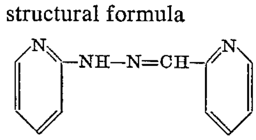
TABLE



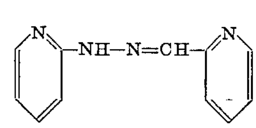
(2) The zinc chelate derived from $ZnSO_4.7H_2O$ and a compound of the structural formula.



(3) The copper chelate derived from $CuSO_4$ and a compound of the structural formula



(4) The cobalt chelate derived from $CoCl_2$ and a compound of the structural formula.



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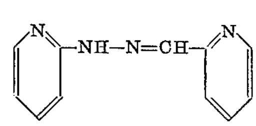

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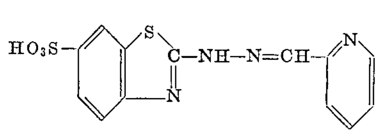

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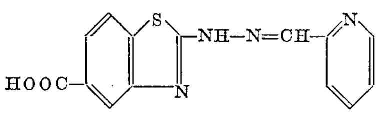


The preparation of compounds according to the above general formula is described in the United Kingdom patent specification No. 16,336/65.

The compounds capable of forming a chelate are preferably used in an aqueous acidic medium and form a coloured zinc chelate so that the hydrophilization of the white zinc oxide can be easily followed.

According to a preferred embodiment the image-wise hydrophilization is carried out by treating the portions of the recording layer, which are not covered by the hydrophobic developing substance, with an aqueous liquid containing said chelating compound or chelate in dissolved form in a concentration comprised between 2 and 20 g. per liter.

It is evident that the chelating compounds and chelates used in the present invention may be combined with other known zinc oxide hydrophilizing compounds such as, e.g., water-soluble cyanoferrates(III) and water-soluble cyanoferrates(II) and mineral and organic acids forming a hydrophilic zinc salt precipitate in aqueous medium e.g. orthophosphoric acid and water-soluble salts thereof, citric acid and tartaric acid.

The resistance to wear of the hydrophilized portions of the recording layer, which resistance is important for obtaining printing plates suitable for long runs, can be increased by the use in combination with the chelating compounds of hydrophilic colloids which may be applied together or after the treatment with said compounds. Suitable hydrophilic colloids for that purpose are e.g. gum arabic, alginic acid, water-soluble alginates e.g. ammonium alginate, caseinates, gelatin, polyacrylic acid esters, polystyrene sulphonic acid, polyvinyl alcohol, and carboxymethylcellulose. A treatment with hydrophilic precipitating or hardening agents for these colloids has proved to be advantageous; so, use can be made of formaldehyde as protein hardener and heavy metal salts forming a precipitate e.g. with alginates.

To keep the printing properties of the planographic plate intact even after months of storage the hydrophilized areas may be treated with a hygroscopic substance e.g. an hygroscopic salt or organic compound containing a great amount of hydrophilic groups e.g. as is the case in polyols such as glycerine.

The hydrophilizing action of the hydrophilizing agent may be improved by a pre-treatment of the developed and fixed recording layer with a softening or swelling agent for the binder occasionally in combination with a wetting agent improving the penetrating power of the hydrophilizing agent in the recording layer. In this way much more zinc oxide grains are reached by the hydrophilizing agent and hydrophilized.

As swelling agents preferably water-miscible compounds such as acetone and methylethylketone are used.

In order to decrease the interfacial tension between the hydrophilic areas and the aqueous phase applied on printing, the aqueous phase of the printing ink or the liquid of the damping system, may contain lower (C_1–C_3) aliphatic alcohols.

In order to regulate the pH of the hydrophilizing liquid which has preferably a pH between 3 and 6, for liberating zinc ions from the zinc oxide photoconductor, water-soluble mineral and organic acids can be used e.g. nitric acid, sulphuric acid, hydrogen chloride, boric acid, acetic acid and lactic acid.

According to a preferred embodiment the electrophotographic recording layer is rendered water-receptive on the areas to be hydrophilized after the printing master has been mounted on the press, thus obviating any separate immersion treatment. The hydrophilizing treatment of the said layer may be carried out by means of an absorbent pad impregnated with the aqueous chelating compound solution.

Electrophotographic recording materials which are especially suited to be used in the preparation of a planographic printing plate are e.g. described in the published Dutch patent applications 6608814 and 6608815.

Any known process for forming the electrostatic latent image and hydrophobic image may be used.

According to a common technique the hydrophobic image is formed by the subsequent steps of producing an electrostatic image on a photoconductive zinc oxide/hydrophobic binder layer by integrally electrostatically charging that layer, subsequently image-wise exposing and developing the latter with a hydrophobic developer powder which is fixed to the recording layer e.g. by heating.

The powder image can be formed by the known dry "carrier-toner development" or by a liquid development based on electrophoresis wherein charged hydrophobic particles are attracted from an electrically insulating liquid to the charged areas of the recording layer. Such development technique is e.g. described in the United Kingdom patent specification 755,486.

According to a developing technique described in the United Kingdom patent specifications 987,766, No. 1,020,505, No. 1,020,503, Ser. No. 1,033,419 and Ser. No. 1,033,420 an aqueous liquid is image-wise applied to an electrostatic charge pattern present in a zinc oxide containing recording layer.

Said aqueous liquid can be an aqueous dispersion of hydrophobic material which after evaporating the aqueous liquid forms a hydrophobic deposit in correspondence with the printing parts.

According to a special embodiment the hydrophilizing chelating compounds used in the present invention can be applied in the aqueous liquid of the damping system of a planographic printing device or in the hydrophilic liquid phase of a planographic printing ink consisting of an emulsion of a lipophilic liquid phase in a hydrophilic liquid phase. Results obtained according to that embodiment are better than those obtained by a common hydrophilizing pretreatment of the plate, in other words the reproducibility of the quality of the copies is improved and the amount of copies of good quality which can be produced without substantial degrading of the printing plate is increased.

The following examples illustrate the present invention without, however, limiting it thereto.

EXAMPLE 1

A layer of photoconductive material consisting of photoconductive zinc oxide dispersed in an insulating binder (3 parts by weight of zinc oxide to one part by weight of resin binder) was coated on a sheet of aluminium foil laminated to a paper support. The resin binder contained on a weight basis 80% of styrene-butadiene copolymer (80/20), 20% of silicon resin (Silicon Resin SR–82 supplied by General Electric—Silicone Products Department, Waterford, N.Y., U.S.A.). The recording layer was charged with a negative corona with a tension of −6000 v. on the corona wires and exposed through a graphic original. Development was carried out using the magnetic brush technique with iron particles as carrier and gilsonite as fusible toner. The powder image was fixed to the layer by heating for 90 seconds at 140° C.

A cotton pad was impregnated with a solution containing the following ingredients:

compound 1 of the table—0.4 g.
a 85% aqueous solution of orthophosphoric acid—10 ccs.
water—90 ccs.

The plate was rubbed lightly with the cotton pad while on the press, and printing started. The quality of prints was very good.

On using 0.3% by weight of compound 1 together with an acid for maintaining the pH to 5 in the liquid of the damping system of an offset printing device up till 5000 of excellent sharp copies were obtained.

EXAMPLE 2

Example 1 was repeated excepting that instead of the chelating compound 1, compound 2 of the table was used. Plate quality was fully equivalent to that of Example 1.

EXAMPLE 3

Example 1 was repeated excepting that instead of the chelating compound 1 compound 3 was used.

Plate quality was fully equivalent to that of Example 1.

EXAMPLE 4

Example 1 was repeated excepting that instead of the chelating compound 1 compound 4 was used.

Plate quality was fully equivalent to that of Example 1.

EXAMPLE 5

Example 1 was repeated excepting that instead of the chelating compound 1 compound 5 was used.

Plate quality was equivalent to that of Example 1.

EXAMPLE 6

A layer of photo-conductive material consisting of photoconductive zinc oxide dispersed in an insulating binder (6 parts by weight of zinc oxide to one part by weight of binder) was coated on a flexible aluminium foil.

The binder is prepared from a mixture of EPOK X–1772 (ammoniacal alkyd resin salt marketed as a 66 to 68% (by weight) aqueous solution by British Resin Products) and EPOK–W–9801 (a 72 to 75% aqueous solution of a melamine-formaldehyde resin marketed by British Resin Products). The coated layer is dried for 24 h. at room temperature and cured for 1 min. at 100° C.

The cured recording layer is charged with a negative corona with a tension of −6000 v. on the corona-wires and exposed to a line-copy.

The electrostatic image is electrophoretically developed by means of an electrophoretic developer obtained by diluting the hereinafter described concentrated developer composition in a ratio of 15/1000 by means of Shellsol T (trade name)

carbon black (average particle size 20 nm.)—30 g.
zinc monotridecyl phosphate—1.5 g.
Shellsol T (trade name)—750 ccs.
fixing agent composition prepared as described hereinafter—150 g.

The fixing agent composition is prepared as follows: 500 g. of Alkydal L67 (trade name of Farbenfabriken Bayer AG, Leverkusen, Germany, for a linseed oil (67% by weight) modified alkyd resin) and 500 ccs. of white spirit containing 11% by weight of aromatic compounds are heated at 60° C. till a clear solution is obtained and cooled.

Hydrophilization of the developed plate occurs as described in Example 1. On printing with a fatty lithographic ink very sharp prints are obtained.

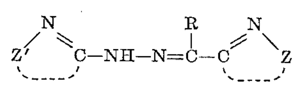
EXAMPLE 7

A layer of photoconductive material consisting of photoconductive zinc oxide dispersed in a ratio of 8 to 1 by weight in Alkydal V10 (trade name of Farbenfabriken

Bayer AG, Leverkusen, Germany for a 43% by weight solution of a styrolated alkyd resin modified with 35% by weight of a drying vegetable oil) as binding agent is coated onto a baryta-coated paper of 135 g./sq. m. Said. recording layer is suited for the powder development described in Example 1 and for the electrophoretic development in Example 6. Hydrophilization on the press after development is carried out as described in Example 1. With the obtained offset-master 500 high quality prints were produced.

What we claim is:

1. Process for preparing a planographic printing plate comprising the steps of developing a latent electrostatic image on a photoconductive insulating recording layer containing an inorganic photoconductive substance which can provide zinc ions, the developing being carried out with a developing composition forming an image-wise hydrophobic deposit on said layer, fixing said image-wise hydrophobic deposit and treating the portions of the recording layer free of hydrophobic deposit with an aqueous solution containing a hydrophilic zinc chelate or a compound capable of forming a hydrophilic zinc chelate with said zinc ions, said chelate being of zinc and a compound represented by the general formula



wherein:

R is hydrogen, or an alkyl radical having from 1 to 5 carbon atoms, and

each of Z and Z′ represents the atoms necessary for completing a nitrogen-containing ring or ring system.

2. Process for preparing a planographic printing plate according to claim 1, wherein the said compound capable of forming said chelate or said zinc chelate is applied to the printing plate after mounting the printing plate on a printing press.

3. Process for preparing a planographic printing plate according to claim 2, wherein the said compound capable of forming said chelate or said zinc chelate is incorporated into the aqueous liquid of a damping system of a planographic printing device.

4. Process for preparing a planographic printing plate according to claim 1, wherein the said compound capable of forming said chelate or said zinc chelate is incorporated into the aqueous phase of a planographic printing ink composed of a lipophilic phase dispersed in a hydrophilic phase.

5. Process for preparing a planographic printing plate according to claim 1, wherein the said compound capable of forming said chelate or said zinc chelate is used in dissolved form in an aqueous liquid in a concentration of 2 to 20 g. per liter of said liquid.

6. Process for preparing a planographic printing plate according to claim 1, wherein the said compound capable of forming said chelate is used in the form of a water-soluble metal chelate other than a zinc chelate.

7. Process for preparing a planographic printing plate according to claim 1, wherein the said compound capable of forming said chelate or said zinc chelate is used in combination with a water-soluble acid bringing the pH of the aqueous treating liquid in the range of 3 to 6.

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