The present invention relates to a process for the preparation of printing plates, wherein the water-accepting surface of a support is coated with a covering layer onto which a powder image is transferred and fixed by heat; the covering layer is then removed. The invention also relates to a material for carrying out this process.

Printing plates with water-accepting surfaces are known. The water-accepting property in the non-printing areas is of great importance, since it renders these areas repellent to greasy ink. The printing areas on the other hand accept the ink, thus producing the print image.

According to the prior art, water-accepting surfaces are produced by providing supports, i.e., mechanically resistant bases the surface of which is not water-accepting, particularly paper, which is the most important material, and plastic materials, with a coating consisting, for example, of carboxymethyl cellulose. Powder images produced by a known electrophotographic process are transferred onto printing plates prepared in this way.

The necessary fixing of the powder image is carried out with the aid of solvent vapor which partly dissolves the resinous powder substance and makes it adhere to the water-accepting surface. It has, however, proved to be a disadvantage, during the subsequent printing process with a printing plate obtained in this manner, that the anchoring of the resin areas which are supposed to print is not very satisfactory. Even with medium-long runs, portions of the image areas come off.

A firm anchoring of the powder image to the mechanically stable support through fixing by heat is not possible, since the resulting heat causes faults, i.e., cracks and shrinking, to appear in the water-accepting layer. During the subsequent printing process, the layer tends to accept ink in these cracks, which has a disturbing effect on the print image and may even render it unrecognizable.

Furthermore, it is a disturbing factor with all fixing processes that those toner particles which adhere in an undesirable manner to the non-image areas during the transfer of the powder image, are bonded to the support during the heat-fixing process and therefore print during the subsequent printing process, thus producing a disturbing so-called image background. It has proved to be uneconomical for normal requirements to do away with the coatings and to replace the originally hydrophobic supports by hydrophilic materials, such as aluminum plates. Even then, the disadvantages mentioned above still apply.

The present invention achieves a firm and mechanically stable anchoring of the powder image to the support without damaging the hydrophilic layer, particularly when using inexpensive paper supports provided with a hydrophilic layer. Furthermore, it is intended to obtain print images which are practically free of background when transferring a powder image onto any kind of support.

The present invention provides a process for preparing printing plates by transferring a powder image and using a support having a hydrophilic surface. In this process, the hydrophilic surface is provided with a covering layer, which is soluble in a solvent which does not dissolve the material of the hydrophilic surface, the powder image to be reproduced is transferred onto the covering layer, fixed thermally by burning-in, and the covering layer is then removed with a solvent which does not dissolve the hydrophilic surface, thus decoating the latter.

The present invention also provides a material for carrying out the above process. The material comprises superimposed layers which are linked together, i.e., a support with a hydrophilic surface, on top of which there is a covering layer which is soluble in a solvent which does not dissolve the hydrophilic surface.

By the present invention a printing plate is obtained which produces very long runs of prints which are practically free of background. The anchoring of the printing areas to the support is very firm due to the burning-in process and is not damaged even during very long runs. By removing the covering layer with water or dilute aqueous acids or, if desired, with aqueous alkaline solvents, the unaffected hydrophilic surface is decoated in the non-printing areas. The hydrophilic surface is not attacked by the solvent removing the covering layer, since the two coatings have different solubilities. The decoated, smooth, and undamaged surface has perfect water-accepting properties, so that images which are practically free of background are obtained. Individual toner particles which might have been deposited on the covering layer during the transfer process of the powder image are almost completely removed together with the covering layer, so that they have no adverse influence later.

Cellulose products, such as paper which is commercially available for printing purposes and which has a sufficient mechanical and dimensional stability, are suitable as supports. It is, however, also possible to use plastic foils, for example thermoplastic materials such as polystyrene, including polyethylene and propylene; or polyacrylates; or polyamides; or thermosetting plastics, for example phenol-formaldehyde resins, or modified natural resins, if these have a sufficiently high mechanical stability. Any other insulating materials may advantageously be used as supports, since the powder image to be reproduced is not produced on the printing plate itself but by transfer of a powder image. Metal foils, such as aluminum, zinc or copper plates may also be used. Metal foils have an inherent hydrophilic surface. If materials are used having a surface which is not hydrophilic, the supports must be provided with a hydrophilic coating; coatings of this nature are known. Substances which are particularly suitable for this purpose are gum arabic, mesquite gum, karaya gum, guar gum and similar malleable latices, ammonium algininate and potassium alginates. Of the proteins, casein, soya bean protein, zein, gelatin, egg albumin and blood albumin are suitable. The following synthetic, hydrophilic colloidal substances are also suitable: carboxymethyl cellulose, potassium polyacrylate, carboxyl derivatives of polys tyrenes which have been rendered soluble by the addition of a suitable alkali, hydroxy ethyl cellulose and polyvinyl alcohol. Other suitable water-accepting, i.e., hydrophilic colloidal substances are starch, dextrin, gelatin and its derivatives, including fibrous potassium pectate.

The aforementioned supports which do not have an inherent water-accepting surface are coated with the water-accepting substances in known manner, generally from a solution, and dried. The resulting supports with water-accepting surfaces are inexpensive and commercially available in various forms.

For the covering layer, compounds having satisfactory water- or acid-solubility, sufficient stability to heat, and useful layer-forming properties are suitable. If uncoated metal supports are used, these compounds may also be alkali-soluble.

The following water-soluble compounds are, for example, suitable for the covering layer: alkali salts and alkaline-earth metal salts of organic mono- or oligosulfonic acids, particularly with aromatic or heterocyclic
nuclei, for example the potassium salt of 1,3-dihydroxy-naphthalene -5,7-disulfonic acid, the sodium salt of benzzenesulfonic acid, and the sodium salt of furancarboxylic acid; organic, preferably aromatic, carboxylic acids, such as the sodium salt of 4-chlorobenzoic acid, the ammonium salt of 4-hydroxybenzoic acid, the sodium salt of 4-hydroxy-toluene-2-carboxylic acid, and the postassium salt of naphthenalene-1,8-dicarboxylic acid.

Regarding compounds which are soluble in dilute acids, the following are preferably used according to the present invention: amino compounds, such as 1-amino-5-naphthol, 1,2-diaminobenzene, 3-amino-4-hydroxy-toluene, imidazole compounds, such as 2-methylbenzimidazol, 2-phenylbenzimidazol, and 2-styrene-benzimidazol, and pyridine or quinoline compounds, for example 4-aminoypyridine, and 6-hydroxy-quinoline.

Other compounds are also suitable if they have the properties required, i.e., water- or acid-solubility and sufficient stability to heat as well as suitable layer-forming properties.

If the powder images are transferred onto metal foils, for example aluminum foils, the aluminum foils may also be coated with alkali-insoluble compounds, for example polymeric, isocyclic or aromatic heterocyclic sulfonylic acids and carboxylic acids, such as benzoic acid, amino benzoic acid, picolinic acid, naphthoic acid, benzene sulfonic acid, naphthalene-disulfonic acids, and quinoline-6-sulfonic acid; compounds containing hydroxyl groups, such as resorcinol, 2,3-dihydroxynaphthalene, 1,2,3-tri-hydroxyquinoline, and phloroglucinol; acid anhydrides, such as phthalic acid anhydride, and naphthalic dicarboxylic acid anhydride; sulfonamides, such as naphthalene - 1 - sulfanilide, phenylsulfanilide, 5-(p-tolyl)-sulfonamide)-acacenaphthene, and sulfonimidic, such as benzoic acid, sulfonic acid imide, and benzenedisulfonic acid imides (1,2) - imide. The aforementioned compounds which are used for the covering layer may also be applied in admixture with resins up to approximately 50% by weight. In this case, however, it is advantageous to add small quantities of organic solvents, for example, isopropyl alcohol, isopropyl alcohol, glycolmonoethyl ether, or mixtures of such solvents. Mixtures of such substances with small quantities of other substances, such as pigments or fillers may also be used for forming the covering layer.

As resins, the following compounds are, for example, suitable natural resins, such as balsam resins, colophony, shellac, modified synthetic resins, such as colophony-modified phenol resins and other resins with a higher colophony content, and plastic materials, such as camphor resin and indene resins; in particular resins which are readily soluble in solvents, for example ketone resins, maleinates resins, maleic acid-colophony mixed esters of alcohols of high molecular weight, and phenol-formalddehyde condensates. For covering layers on metal supports, which may also be coated with the aid of alcoholic solutions, it is advantageous to use alkali-insoluble resins, for example mixed polymers of styrene and maleic acid anhydride, maleinate resins and phenolic resins.

The aforementioned compounds for the covering layer are applied in solution onto hydrophilic surface of the support. This may be performed in known manner by spraying, spreading, roller application, dipping, etc., as a solution, or application onto the support while rotating. The material is then dried at an elevated temperature. For the production of powder images on the material according to the present invention, a mirror image of an original is produced in known manner on an electrophotographic material, such as selenium, zinc oxide or an organic coating, by contact with the original or preferably by episcopic or dioscopic projection. This invisible image is developed by contacting it with a developer comprising a toner, for example a resin-carbon black mixture. Preferably, developed mixtures are used which are described in Belgian Patents Nos. 594,137; 594,397; 606,518; and 626,060. A powder image corresponding to the original is obtained.

The material of the present invention is placed onto this powder image with its covering layer and placed in the field of a corona discharge which causes the powder image to be transferred from the photosensitive-conductive layer onto the covering layer of the material of the present invention. Images corresponding to the original are thus obtained.

The images are then fixed by heating to 100-170°C., preferably to 120-150°C; this may be performed for example, with an infra-red radiator. It is also possible to partially dissolve the powder image by treatment with solvent vapors and to fix it by pressure. When converting the fixed images into a printing plate, the covering layer is removed from the non-image areas. When removing the water-soluble compounds mentioned above as suitable for the preparation of the covering layer, wiping over with pure water will be sufficient. When removing acid-soluble compounds, this being particularly important with paper printing foils, weak aqueous solutions of acids, such as phosphoric acid, hydrochloric acid, and acetic acid, are used in concentrations up to 5% by weight. Up to 50% by weight of organic solvents, such as methyl and/or ethyl alcohol, isopropyl alcohol, and glycolmonoethyl ether may also be added to these aqueous acid solutions. With this treatment, the water-accepting surface is decorated in the non-image areas, but not damaged. The areas covered by the fixed powder are not attacked.

If an alkaline medium is required for removing the covering layer comprising the aforementioned alkali-soluble compounds, up to 5% by weight aqueous solutions of alkali or alkaline earth hydroxides are suitable, for example, solutions of sodium, potassium and calcium hydroxide and alkali phosphates, in particular those containing phosphates and alkali polyphosphates which exhibit an alkaline reaction in an aqueous solution, for instance, sodium polyphosphate; also water-soluble silicates, such as sodium silicate. Organic basic substances may also be used for this purpose. The following organic basic substances are suitable: primary, secondary and tertiary saturated amines of low molecular weight, such as trimethylamine, diethylamine, diethylethylamine, diethylamine, and propylamine; amino alcohols, for example ethanolamine, diethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, diamines and polyamines, such as ethylenediamine, diethylenetriamine, and triethylenetetramine; and substituted amides of low molecular weight, for example dimethylformamide.

These organic basic substances may partly be undiluted. In most cases, however, it is advisable to use them in dilution, particularly with stronger bases. Preferably, solutions of 0.01 to 5% by weight, particularly of 1.0 to 5.0% are used. Suitable solvents are water and/or organic solvents, such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and ethylenglycol monomethyl ester; mixtures of different solvents may also be used. Furthermore, it is often advantageous to add thickening agents to the acid as well as the alkaline liquids in order to increase the viscosity thereof. The following substances may be used, for example, as thickening agents: polyvinyl-alcohol, cellulose products, such as carboxymethyl cellulose or alkyl cellulose, or soluble starch products. After the treatment with the liquids which remove the coating from the non-image areas, it is necessary, but not necessary to rinse the printing plate with water and to increase the hydrophilic properties thereof even further by wiping the plate with a dilute solution of phosphoric acid. After inking up with greasy ink, printing may be performed in known manner.

With the material of the present invention, high quality printing plates which are completely free of background and produce long runs, are obtained by the transfer method.
The invention will be further illustrated by reference to the following specific examples:

**Example 1**

<table>
<thead>
<tr>
<th>Parts by wt.</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide (&quot;Zinkoxyd besonders rein, Sorte A&quot; of the Zinkweiss-Handelsgesellschaft Oberhausen, Germany)</td>
<td>95.0</td>
</tr>
<tr>
<td>Silicone resin K, 50% solution in toluene, produced by Wacker-Chemie Burghausen, Germany</td>
<td>80.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>100.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>25.0</td>
</tr>
<tr>
<td>Rhodamine B extra</td>
<td>0.01-0.05</td>
</tr>
</tbody>
</table>

are homogenized three times in a colloid mill or in a high-speed mixer. The ready-to-brush-on suspension is applied in known manner to a paper foil, which is backed with a thin aluminum foil, and dried. For producing images on the electropainting material produced in this manner, the coating is provided with a negative charge by means of a corona discharge, and is then exposed in the cassette of a vertical reproduction camera with a "root" mirror for 5-30 seconds, depending on the reproduction scale, at stop 9. Eight Nitrophot bulbs of 500 watts each are used as a light source. A line drawing printed on both sides is used as an original. The laterally reversed electrostatic image of the original resulting on the zinc oxide coating is made visible by dusting with a double toned consisting of a resin powder (toner) dyed with carbon black, and kieselguhr. The toner consists of a low melting point polysulphide-polysulphide mixture to which carbon black and preferably also the organic dye Nigrosin spirit-soluble (Schultze Farbstofffabellen, No. 983) have been added. The constituents are melted together, ground and then separated into fractions by air sieving, since a uniform particle size is desirable for producing the images. A toner with particle sizes ranging from 8-15 µ is very suitable, for example, this toner is mixed with kieselguhr preferably in the proportion of 1:2 by weight.

The power image which was produced in this manner is transferred onto a paper printing foil. The paper printing foil consists of a paper base which is coated with a hydrophilic colloid, for example gelatin, casein, carboxymethyl cellulose, or polyvinyl alcohol, which, as a filler, is finely distributed. The hydrophilic coating is coated with a solution consisting of 100.0 parts by volume of ethylene glycol and glycol-monomethyl ether, 5.0 parts by weight of 2-methylbenzimidazol and 4.0 parts by weight of a ketone resin (Kunstharz EM, made by Rheinpreussen G.m.b.H., Homburg/Niederrhein, Germany) and then dried. The thus prepared paper printing foil is placed onto the electrostatic powder image with its coated side and subjected to the electric field of a corona discharge whereby the powder image is transferred onto the paper printing foil. Then, the two foils are separated and the powder image is fixed by heating for 30 seconds in a drying cupboard at approximately 160°C.

The obtained image is converted into a printing plate by wiping it over with a 2.0% by weight solution of phosphoric acid. The areas not covered by the toner are thereby removed, so that the water-accepting layer is exposed. Images which are completely free of background are obtained. The printing plate can then be used for printing in an offset printing machine.

**Example 2**

A paper foil is coated with a zinc oxide suspension, as described in Example 1 and after drying of the coating, an electrophotographic image is produced as described in Example 1. The powder image is transferred onto an aluminum foil previously coated with a solution consisting of 100.0 parts by volume of ethylene glycol monomethyl ether, 5.0 parts by weight of naphthalene-1,8-di-carboxylic acid (naphthalic acid), and 2.0 parts by weight of a styrene copolymer containing carbonyl groups, having a decomposition range of 200-210°C and a specific gravity of 1.15-1.16 (Lustrex 820) and then dried. The powder image is transferred onto this material as described in Example 1, and is fixed by heating to approximately 180°C. For conversion into a printing plate, the image is wiped over with a solution containing, by weight, 40.0% methanol, 10.0% glycerin, 45.0% glycol and 5.0% sodium silicate. The areas of the coating which are not covered by the toner are removed. The water-accepting layer is thus exposed, whereas the printing areas, i.e., the so-called image areas, accept great ink, so that the printing plate thus obtained can be used for printing in an offset machine.

**Example 3**

5.0 parts by weight of 2,5-bis-(4'-diethylamino-phenyl-(1'))-1,3,4-oxadiazole, 5.0 parts by weight of a phenol-modified synthetic resin (Rhenophen 140) and 0.01 g of Rhodamine B are dissolved in 100.0 parts by volume of benzene, and a mechanically roughened aluminum foil is coated with the solution. After drying, the coating is provided with a negative electric charge by means of a corona discharge. An electrophotographic image is obtained as described in Example 1.

The powder image is transferred onto a paper printing foil in an electric field. The paper printing foil, which has a hydrophilic coating, is provided with a covering layer before transferring the image. For this purpose, a solution consisting of 100.0 parts by volume of water and 8.0 parts by weight of the sodium salt of 2,3-di-hydroxynaphthalene 6-sulfonic acid is applied to the water-accepting coating of the paper printing foil on a whirl-coater and then dried.

The powder image transferred onto the coating is fixed at approximately 180°C and may be converted into a printing plate by wiping the coating over with water. The coating consisting of the sodium salt of 2,3-di-hydroxy-naphthalene-6-sulfonic acid, is thus removed from the areas not covered by toner together with the kieselguhr which adheres to it loosely.

In order to increase the water-accepting properties of the non-image areas further, the image is wiped over with an 0.5% solution of phosphoric acid. The printing plate thus obtained can be used for printing in an offset machine.

**Example 4**

A reversed positive electrostatic charge image is obtained on an aluminum foil, which was vapor treated with selenium in known manner, and is made visible by a developer consisting of a toner and glass balls covered with a synthetic resin. The powder image is transferred onto a paper printing foil, thus producing a correct image of the original. The paper printing foil which is intended for transfer purposes, is provided with a coating prepared as follows: 50.0 g of 2-(p-aminophenyl)-5-amino-benzimidazol and 40.0 g of synthetic resin EM are dissolved in 1000.0 parts by volume of ethylene glycol monomethyl ether. A hydrophilic coating on the paper printing foil is coated with this solution by machine application and dried.

After transferring the powder image onto the material, the image is fixed by heating at 180°C for 30 seconds. Then, it may be converted into a printing plate by wiping over with a 2% by weight, solution of phosphoric acid.

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 preparing a printing plate which comprises forming a fusible powder image on an electrophotographic plate, transferring the powder image electrically into a printing layer which is stable to heat and is on a support having a hydrophilic surface, fusing the image by heat treatment, and removing the covering layer in the non-
3,315,600

image areas by treatment with an aqueous solvent which does not dissolve the hydrophilic surface on the fused powder image.

2. A process according to claim 1 in which the support is paper.

3. A process according to claim 1 in which the support is metal.

4. A process according to claim 1 in which the support is aluminum.

5. A process according to claim 1 in which the hydrophilic surface is a coating of a hydrophilic colloid.

6. A process according to claim 1 in which the solvent is an aqueous solution of phosphoric acid and the covering layer is soluble in an acid solution.

7. A process according to claim 1 in which the solvent is water and the layer is soluble in water.

8. A process according to claim 1 in which the covering layer comprises 2-methyl-benzimidazole and a ketone resin.

9. A process according to claim 1 in which the covering layer comprises naphthalene-1,8-dicarboxylic acid and a styrene copolymer containing carbonyl groups.

10. A process according to claim 1 in which the covering layer comprises the sodium salt of 2,3-dihydroxy-naphthalene-6-sulfonic acid.

11. A process according to claim 1 in which the covering layer comprises 2-(p-aminostyrene)-5-aminobenzimidazole and a synthetic resin.

12. A transfer material for use in the preparation of planographic printing plates which comprises a support having a hydrophilic surface, and a covering layer which is stable to heat on the hydrophilic surface, the covering layer being soluble in an aqueous solvent which does not dissolve the hydrophilic surface.

13. A transfer material according to claim 12 in which the support is paper.

14. A transfer material according to claim 12 in which the support is metal.

15. A transfer material according to claim 12 in which the support is aluminum.

16. A transfer material according to claim 12 in which the hydrophilic surface is a coating of a hydrophilic colloid.

17. A transfer material according to claim 12 in which the solvent is an aqueous solution of phosphoric acid and the covering layer is soluble in an acid solution.

18. A transfer material according to claim 12 in which the solvent is water and the layer is soluble in water.

19. A transfer material according to claim 12 in which the covering layer comprises 2-methyl-benzimidazole and a ketone resin.

20. A transfer material according to claim 12 in which the covering layer comprises naphthalene-1,8-dicarboxylic acid and a styrene copolymer containing carbonyl groups.

21. A transfer material according to claim 12 in which the covering layer comprises the sodium salt of 2,3-dihydroxy-naphthalene-6-sulfonic acid.

22. A transfer material according to claim 12 in which the covering layer comprises 2-(p-aminostyrene)-5-aminobenzimidazole and a synthetic resin.

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DAVID KLEIN, Primary Examiner.