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## (54) COPYING PROCESS


(71) We, HOECHST AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-


The present invention relates to an electro-photographic copying process, and more especially to a process in which a latent image produced on a chargeable imaging surface by electrostatic charging and exposure is developed with aqueous ink and transferred onto a receiving material and the imaging surface is then cleaned. The invention also relates to the developer liquid and the cleaning liquid used in the process.

In plain paper copying machines, photoconductive copying drums or webs are used. The charge images produced on the photoconductor by electrostatic charging and imagewise exposure are made visible by means of a dry toner or liquid toner, and the toner image is then transferred onto the copying paper.

Dry toners consist essentially of colored polymer powders, which have to be fixed on the copying paper by an energy-consuming fusing step.

Liquid toners are normally polymer-coated pigment particles dispersed in binder-containing, electrically insulating liquids, preferably in aliphatic hydrocarbons. No energy or only very little energy is required to fix them on the copying paper, but considerable quantities of hydrocarbons penetrate the copying paper and are released into the surrounding air.

Therefore, attempts have been made to use water-based toner liquids which are ecologically harmless. These attempts were successful, to some extent, in the development of latent images on zinc oxide/binder layers (see German Auslegeschrifts No. 1,219,328 and No. 1,293,593), in particular because of the relatively rough surface structure of such layers.

On smooth photoconductive layers, however, which are normally used in copying machines adapted for cyclic operation, electrostatic charge images would be erased immediately by electrically conductive aqueous inks. Therefore, development by contact with such inks is impossible.

Latent charge images on smooth photoconductor layers can only be made visible with aqueous inks if a direct contact between ink and photoconductor layer is avoided. Two methods for this have been proposed. According to the first of these methods, the charge image is covered with a thin layer of an insulating liquid before it is contacted with the aqueous developer, as is disclosed in German Offenlegungsschriften No. 1,927,210 and No. 2,226,479. The applied ink adheres to the areas corresponding to the charge image.

According to the second method, which is described in U.S. Patent No. 3,084,043, the ink is applied to the charge image from the depressions of a structured applicator element. Only the raised portions of the applicator element, from which the ink has been removed by a wiper, come into contact with the photoconductor layer. Under the influence of the charge image the electroconductive ink is polarized and migrates from the depressions onto the photoconductor surface. After transfer of the ink from the photoconductor layer to the receiving material, the photoconductor layer must be cleaned and dried, and is then ready for the next copying cycle.

By another cleaning method, disclosed in German Offenlegungsschrift No. 20 61 530, the ink-stained photoconductor layer is treated with a cleaning liquid which is compatible with

the ink and is then dried with an absorbent cloth. According to still another method, which is disclosed in German Offenlegungsschriften No. 2,052,535 and No. 2,056,546, the ink-stained photoconductor layer is dusted with an absorbent powder after transfer of the ink-developed image, and the powder is then wiped off with a cloth, together with the traces of ink.

When photoconductive selenium layers - which are the only layers used in practice for cyclic copying with ink - are cleaned with ink-dissolving aqueous mixtures and then dried with an absorbent cloth, an annoying residue composed of ink and cleaning liquid remains. This residual film weakens the charge of the selenium layer and causes an increased transverse conductivity and, consequently, reduced sharpness of the copies (see German Offenlegungsschrift No. 2,032,652). With an increased intensity of drying, for example when a web of absorbent cloth is used, mechanical damage to the photoconductor layer is increased (German Offenlegungsschrift No. 2,032,652). Also, if the photoconductor layer is dusted over with a fine powder and then brushed off, the photoconductor layer is rapidly damaged. Although the copying processes described above generally require a high expenditure on equipment, they still tend to cause soiling of the copying machines. These deficiencies have hitherto prevented a wider use of cyclic copying with ink.

The present invention is concerned with providing a process for the production of electrophotographic copies with aqueous inks, the process being free from the above-described disadvantages and using a system including a smooth, chargeable imaging surface, especially a photoconductor layer, an aqueous ink, and a cleaning liquid, and by which it is possible to completely remove residues of ink and of cleaning liquid during cyclic operation without causing damage to the imaging surface. These conditions are important for long runs.

The present invention provides a copying process wherein an electrostatic charge image is produced on a smooth, hydrophobic chargeable imaging surface, developed by applying to the surface with an applicator an aqueous ink, and the developed image is transferred to a receiving surface, the chargeable surface subsequently being cleaned with a liquid that detaches the ink residue and has a contact angle with the surface of greater than 90°.

Photoconductor layers are especially suitable as the chargeable imaging surfaces. Preferably, organic photoconductors are used. Surfaces to which charge images are applied, e.g. by image-wise charging or by transfer of a charge image, are also designated as chargeable imaging surfaces.

The organic photoconductor layers preferably used are more strongly hydrophobic, i.e., less easily wettable by aqueous inks, than, for example, a selenium layer. The hydrophobic properties of a layer may be easily ascertained by comparative wetting tests, using liquids with different surface tensions.

The organic photoconductor layer is on a conductive support; preferably, an imaging surface is used which contains or consists of poly-N-vinyl carbazole and trinitro-fluorenone. An imaging surface which contains a condensation product of 3-bromopyrene and formaldehyde has also proved advantageous. Alternatively, the chargeable imaging surface may be in the form of a photoconductive double layer, comprising a charge carrier-producing layer with a hydrophobic charge carrier-transporting layer coated thereon, as described in, for example, German Offenlegungsschrift No. 2,237,539.

Photoconductor films provided with a very smooth hydrophobic protective layer, as described, e.g., in German Offenlegungsschrift No. 2,452,623, may be used with particular advantage.

The photoconductor layer is employed in the normal manner as the chargeable imaging surface in the copying machine, e.g., in the form of a cover on a seam-less drum, or as a flexible web. Flexible photoconductor materials may be stretched over or cemented on a copying drum or used in the form of endless belts.

Suitable aqueous inks are aqueous dye solutions containing at least one dye, or aqueous pigment dispersions, which are easily detached by the cleaning liquid by which the photoconductor layer is not wetted and which, in concentrations below about 0.15%, do not diminish the surface tension of the cleaning liquid to such an extent that the hydrophobic chargeable imaging surface is wetted. Combinations of dye solutions and pigment dispersions may also be used. It is possible, according to the invention, for the aqueous ink to wet the imaging surface, but preferably an ink is used which does not wet the imaging surface.

If the ink does not wet the surface it is possible to use the same solution as the aqueous ink and as the cleaning liquid. In this case, the troughs for the aqueous ink and for the cleaning liquid provided in the copying machine may be connected with each other. In this manner, it is possible to avoid an undesirable concentration of the dye or pigment in the cleaning station, if the evaporation losses occurring during copying are compensated by adding fresh solvent, e.g., fresh water, to the cleaning liquid. The solution can only be used

as the cleaning liquid, however, if it does not tend to foam in the cleaning station. In the cleaning station, the cleaning liquid is normally applied to the soiled photoconductor layer by means of a rotating foam roller. The foaming tendency may be overcome, or reduced, by adding an anti-foaming agent.

As a rule, aqueous dye solutions meet the requirements better than do aqueous pigment dispersions containing wetting-promoting dispersing agents. Therefore, it is preferred to use an aqueous solution containing at least one dye. The following specific black and blue dyes, whose names in some cases are registered trade-marks, may especially be used: Paper Deep Black AGX, a product of Bayer AG., Ink Blue BITN (Color Index No. 42,780). Supranol Blue B (C.I. No. 42,645). AstraViolet 3 R extra (C.I. No. 49,013), and Benzo Deep Black E (C.I. No. 30,235) and Patent Blue AE (C.I. No. 42,090).

Although it is possible to use aqueous dispersions of, e.g., carbon black or organic pigments the surface tension of the cleaning liquid is relatively quickly reduced, e.g. by the dispersing agent, so that the cleaning liquid has to be frequently replaced by fresh liquid.

If an ink employing a dye only is used, the quantity of the dye or dye mixture present may vary within wide limits. It was found, however, than no advantage is obtained by using a concentration above 15%, calculated on the total weight of the aqueous ink. Solutions containing from about 0.5 to about 10 per cent by weight of dye are advantageously used.

If a pigment is used, the pigment may be present in a quantity between about 1 and 40 per cent by weight, based on the total weight of the ink.

A pigment in an aqueous dispersion which has proved particularly advantageous is "Hostatint"(R) Black 6 R, a pigment paste without a binder, produced by Hoechst Aktiengesellschaft.

If a mixture of dye and dispersed pigment is used, the quantity of dye which may be added to the aqueous dispersion may vary within wide limits. As a rule, no further advantage is achieved by adding more than 5 per cent by weight, calculated on the total weight of the developer to be used. Preferably, about 0.5 to about 5 per cent by weight are added.

Suitable dyestuffs of good water-solubility are found among various classes of dyes, e.g., among acid, basic, directly absorbed and reactive dyestuffs. Substantive dyes have the advantage that they are directly absorbed by the cellulose fibres of copying paper and thus are fixed thereon. If it is desired to produce water-resistant copies, it is frequently possible to convert the dyes into sparingly soluble salts in the copying paper. In this case, the paper must contain the fixing component. According to another fixing method, binders may be added which become insoluble in the copying paper. For example, it is possible to use acid resins and polymers dissolved in water to which volatile bases have been added. The pH value of the aqueous inks must be high enough that any ink dried in the copying machine may be re-dissolved in fresh ink.

Generally, water-soluble binders, thickeners, humectants etc. may be added to the aqueous inks.

By varying their concentration or by adding, for example, thickeners, the viscosity of the aqueous inks may be adapted to the tool by which they are applied. Of the various applicator elements, each one requires a specific viscosity. Suitable applicator elements, e.g., are rollers or endless belts provided with tiny cups, grooves or nubs, or belts or drum covers made of a mono-filament fabric. The applicator element is structured, in some way in each case, a structured element being one which has a plurality of first portions and a plurality of portions depressed below the first portions.

After having been filled with the aqueous ink, the applicator element is thoroughly wiped off, so that the raised areas are free from liquid when they are contacted with the surface carrying the charge image. Suitable wipers are, e.g., mechanical devices such as elastic doctor blades or doctor rolls, and also air brushes.

In order to ensure uniform development, either the photoconductor material or the applicator element, or both, should be elastic. Preferably, endless flexible photoconductor belts supported on rubber rollers are used in combination with rigid applicator elements, e.g., applicator rolls.

The cleaning liquid used for removing traces of aqueous ink remaining on the imaging surface, e.g., the photoconductor layer, after transfer of the developed image to the receiving material, e.g, paper, does not wet the imaging surface according to the invention. It detaches however, slightly dried or still wet ink that had not been transferred.

For most aqueous inks, water is best suited and is thus preferred according to the invention. Desalted water is more advantageous than normal water, because, among other advantages, chalk stains are thus avoided. In the case of aqueous inks containing acid binders, it may be of advantage to add to the cleaning liquid a weak base, e.g., dilute ammonia solution or sodium carbonate solution. The concentration of the base must be so low that no wetting of the imaging surface occurs.

The cleaning liquid may contain organic liquids which only slightly reduce the surface tension, e.g., formamide or triethylene glycol. Care must be taken, however, that the organic additives do not attack the imaging surface.

The cleaning liquid may be applied to the soiled imaging surface in any desired manner. Advantageously, rotating rollers covered with soft sponge rubber may be used. By using water-filled soft rubber rollers, traces of ink may be wiped off without undesirably damaging the imaging surface.

A simple, sharp-edged doctor blade made of rubber or rubber-like materials suffices for removing the drops of cleaning liquid present on the cleaned imaging surface. Various elastomers may be used for this purpose, e.g., polyurethanes or polychloroprenes. The doctor blade may be mounted in a fixed position or oscillate transversely to the web; alternatively, it may be in the form of a revolving endless belt. An even gentler wiping is possible by using an air brush.

In order to remove the last traces of dampness, the cleaned imaging surface may be after-dried in known manner with cold or, preferably, warm air before the next cycle begins; this is particularly advisable in the case of high web feed speeds, of about 10 m/min. or more. In a copying machine having an endless photoconductor web installed therein, it is also possible to form a relatively wide loop in a well ventilated zone. During passage of this loop, the last traces of dampness escape from the web.

The system comprising a very smooth hydrophobic imaging surface with a preferably organic photoconductor, readily soluble aqueous inks, cleaning liquids which do not wet the imaging surface, and gentle wipers for cleaning, ensures a gentle, but satisfactory cleaning of the copying layer. After completion of the copying cycle, so little moisture is left on the layer that the next cycle is not appreciably affected. Long runs may be printed before the photoconductor shows any sign of damage.

No annoying or physiologically hazardous gases escape from the copying machine during the copying operation, and the copies produced are odorless. The aqueous inks preferably used can be produced much more easily than the conventionally employed dry or liquid electrophotographic toners.

The following examples describe the invention.

*Examples:*

As a rule, an electrophotographic copying machine comprising a revolving endless photoconductor web was used for the tests. The stations used for electostatic charging, image-wise exposure, development, transfer, and cleaning were arranged, in this order, about the web.

The developing station consisted of an applicator roller, i.e., a brass roller of 8 cm diameter to which a film provided with screen-like elevations had been cemented. The screened film was produced as follows:

A 25 µ thick, negative-working dry resist film marketed by KALLE Niederlassung der Hoechst AG under the designation "T 25" was laminated in a laminator to the aluminum surface of a 100 µm thick polyester film provided on one side with a vapor-deposited aluminum layer. Subsequently, the material was exposed under a smooth point screen with 60 points per centimeter and a tonal value of 85% and was then completely developed with 0.8% sodium carbonate solution. The aluminum surface under the non-exposed areas was thereby bared.

During operation, photoconductor web and surface of the applicator roller moved at the same speed of about 10 m/min. and in the same direction. The aqueous ink used in each case was taken from a trough by a system composed of two rubber rollers and applied to the applicator roll. The applicator roll was doctored off by means of an air brush. The cleaning station consisted of a soft foam roller which rotated during operation and dipped shortly into water with its lower portion, while its upper portion was in light contact with the photo-conductor web. Immediately following the foam roller, a doctor blade was fixedly mounted which consisted of polyurethane of a Shore hardness of 65°.

*Examples 1 to 12:*

| Example No. | Photoconductor | Aqueous Ink Per Cent by Weight in Water | Aqueous Ink Dye or Pigment | Cleaning Liquid |
|---|---|---|---|---|
| 1 | I | 2 | Ink Blue BITN (C.I. 42,780) | $H_2O$ |
| 2 | II | 6 | Ink Blue BITN (C.I. 42,780) | $H_2O$ |
| 3 | III | 4 | Ink Blue BITN (C.I. 42,780) | $H_2O$ |
| 4 | IV | 5 | In Blue BITN (C.I. 42,780) | $H_2O$ |
| 5 | II | 4 | Ink Blue BITN (C.I. 42,780) | aqueous dye |
| 6 | II | 3.5 | Paper Deep Black AGX (Bayer) | $H_2O$ |
| 7 | II | 3.5 | Paper Deep Black AGX (Bayer) | aqueous dye + 0.01% of anti-foaming agent[1] |
| 8 | IV | 4 | Supranol Blue B (C.I. 42,645) | $H_2O$ |
| 9 | IV | 3.5 | Astra Violet 3R extra (C.I. 48013) | $H_2O$ |
| 10 | II | 5 | Patent Blue AE (C.I. 42,090) | $H_2O$ |
| 11 | II | 5 | Benzoe Deep Black E (C.I. 30235) | $H_2O$ |
| 12 | II | 2 + 10 | Paper Deep Black AGX Hostatint Black GR[2] | $H_2O$ |

The following photoconductors were used for the chargeable imaging surface in the Examples:

I. A layer of poly-N-vinyl carbazole and trinitrofluorenone, as disclosed in German Auslegeschrift No. 1,572,347;

II. a layer of poly-N-vinyl carbazol and trinitrofluorenone covered with a nitrocellulose top layer, as disclosed in German Offenlegungsschrift No. 2,452,623;

III. a layer containing a condensation product of 3-bromo-pyrene and formaldehyde, as disclosed in German Offenlegungsschrift No. 2,137,288; and

IV. a photoconductive double layer as disclosed in German Offenlegungsschrift No. 2,237,539, comprising an N,N'-dimethyl-perylene-3,4,9,10-tetracarboxylic acid diimide layer coated with a layer composed of 2 parts by weight of 2,5-bis-(p-diethylaminophenyl)-oxadiazole-1,3,4, 1 part by weight of a vinyl acetate/vinylchloride copolymer, and 1 part by weight of polyester.

1. The anti-foaming agent used was Nopco NDW, a product of Nopco Chemical Co., USA.

2. A binder-free pigment paste marketed by Hoechst AG.

WHAT WE CLAIM IS:-

1. A copying process wherein an electrostatic charge image is produced on a smooth hydrophobic chargeable imaging surface, developed by applying to the surface with an

applicator an aqueous ink and the developed image is transferred to a receiving surface, the chargeable surface subsequently being cleaned with a liquid that detaches the ink residue and has a contact angle with the surface of greater than 90°.

2. A process as claimed in claim 1, wherein the surface material contains an organic photoconductor.

3. A process as claimed in claim 1, wherein the surface material comprises polyvinyl carbazole and trinitrofluorenone.

4. A process as claimed in claim 1, wherein the surface material comprises a condensation product of 3-bromopyrene and formaldehyde.

5. A process as claimed in claim 1, wherein the imaging surface is a photoconductive double layer composed of a charge carrier-producing layer and a charge carrier-transporting layer.

6. A process as claimed in any one of claims 1 to 5, wherein the imaging surface comprises an organic photoconductor layer covered by a hydrophobic protective layer.

7. A process as claimed in any one of claims 1 to 6, wherein the surface is flexible.

8. A process as claimed in any one of claims 1 to 7, wherein the aqueous ink is an aqueous solution of at least one dye.

9. A process as claimed in claim 8, wherein the aqueous dye is a solution of Paper Deep Black AGX.

10. A process as claimed in any one of claims 1 to 7, wherein the aqueous ink is an aqueous dispersion of a pigment.

11. A process as claimed in claim 10, wherein the aqueous pigment dispersion contains at least one water-soluble dye.

12. A process as claimed in any one of claims 1 to 11, wherein an ink is used which is readily detached by the cleaning liquid.

13. A process as claimed in any one of claims 1 to 12, wherein the ink contains a thickener.

14. A process as claimed in any one of claims 1 to 13, wherein the cleaning liquid used is salt water.

15. A process as claimed in claim 14, wherein the cleaing liquid consists of salt water and a weak base.

16. A process as claimed in any one of claims 1 to 15, wherein the cleaning liquid also contains an organic liquid by which its surface tension is only slightly reduced, compared with an otherwise identical composition with the organic liquid absent.

17. A process as claimed in claim 16, wherein the organic liquid is formamide.

18. A process as claimed in any one of claims 1 to 17, wherein the aqueous ink does not wet the imaging surface.

19. A process as claimed in any one of claims 1 to 18, wherein the cleaning liquid is a non-wetting liquid ink which is also used as the aqueous ink.

20. A process as claimed in claim 19, wherein the ink contains an anti-foaming agent.

21. A process as claimed in claim 1, substantially as described in any one of the examples herein.

22. A copying process wherein a latent image produced on a chargeable image surface by electrostatic charging and exposure is developed by means of an aqueous dye and the developed image is transferred onto a receiving material and the imaging surface is then cleaned, wherein the imaging surface has a dead-smooth, hydrophobic surface which may be wetted by the aqueous dye applied by means of a known structured applicator element and that the cleaning liquid used to absorb residual dye still present after transfer can be easily wiped off and forms a wetting angle of more than 90° with the imaging surface.

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