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(54) **Electrophotographic process for forming a visible image.**

(57) Electrophotographic process in which a charge pattern is formed on a photoconductive element comprising a charge generating pigment-binder layer and a smooth charge-conveying top layer and the charge pattern is developed with a one-component developing powder of which the particles have a specific resistance exceeding 10^{11} Ohm.m. Preferably the electrophotographic process is performed on a photoconductive element comprising a charge generating pigment-binder layer which is composed of a dispersion of an azo dye in a charge-transfer-complex of a polyvinyl carbazole and a nitrated fluorene derivative.

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Electrophotographic Process for Forming a Visible Image.

This invention relates to a process for forming a visible image in which a photoconductive element with a charge-generating layer, and a smooth charge-conveying top layer is provided with a charge pattern, and the charge pattern is developed with a one-component developing
5 powder of which the particles have a specific resistance exceeding 10^{11} Ohm.m.

According to electrophotographic processes applied in practice, charge patterns are generally developed with a binary developing powder composed of a mixture of two components. One component is a toner
10 powder which is deposited on the charge pattern and consists mainly of a resin into which a suitable dye, normally being black, is incorporated. The other component is a carrier consisting of a material against which the former component is triboelectrically charged by continuous movement of the developing powder. If magnetic brush development is applied, the
15 carrier consists of fine particles of a magnetisable material such as iron, magnetite or a ferrite.

The binary developing powders have the disadvantage that due to the consumption of the toner powder the ratio between the toner powder and carrier powder as well as the properties of the carrier powder which is
20 not consumed, are changed. This has the consequence that toner powder has to be added at regular intervals and the carrier powder has to be replenished from time to time. Latter measure implies that, frequently, some kilograms of a black powder, that strongly contaminates the environment, have to be thrown away.

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A binary developing powder has the additional disadvantage that it has a rather strong abrasive action on the substrate, usually a photoconductive element, bearing the charge pattern, which has the consequence that useful life of this photoconductive element is limited.

5 Several electrophotographic processes, in which a charge pattern is developed with a developing powder composed of only one component, have been proposed to overcome the above-mentioned disadvantages.

If the developing powder is applied to the charge pattern by means of a magnetic roll, the powder for example consists of resin particles in which
10 extremely fine, magnetisable material has been dispersed. The magnetisable, one-component developing powders proposed in the prior art falls into two groups. One group does not contain substantial amounts of electrically conductive material, and has a specific resistance exceeding 10^{11} Ohm.m. The other group has been made electrically conductive by the addition of
15 a conductive material, such as carbon black, and generally has a specific resistance in the range of approx. 10^3 to 10^{10} Ohm.m. If a charge pattern is developed with an electrically conductive developing powder, this developing powder is charged by induction and deposited on the charge pattern. In that case a potential difference of about 10 Volt will
20 still be developed. This is disadvantageous to the useful life of the photoconductive element, because minimal damages and scratches will become visible on the copies made, the useful life of the photoconductive element thus being limited again, notwithstanding the comparatively low abrasive action of the one-component developing powder. In addition, by the use of
25 an electrically conductive toner powder there are produced images of hard gradation, as a result of which continuous tones can hardly be reproduced. Further, the transfer of the developed image onto plain paper by means of an electric field meets with great difficulties.

For the above-mentioned reasons a process in which a charge pattern is
30 developed with a one-component developing powder containing no or hardly any electrically conductive material is preferred.

As the toner powder is not pre-charged, the powder particles only carry a small amount of charge but the powder is nevertheless deposited imagewise on a charge pattern. Various charging and developing mechanisms have been
35 suggested but in fact it is not known how the powder particles become charged and why an insulating developing powder, carrying little or even no charge, is yett active as a developer.

Processes in which a charge pattern on a photoconductive surface is

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developed with the aid of an electrically insulating developing powder consisting of one component, are known.

According to British Patent Specification 1 481 332 a charge pattern on a photoconductive zinc oxide-binder layer is developed with such a developing powder.

5 With that process excellent copies can be prepared, but due to the very limited useful life of a photoconductive element based on zinc oxide, the photoconductive element must often be exchanged. The same British patent specification also describes that a photoconductive element comprising a conductive substrate, an evaporated selenium layer functioning as a
10 charge-generating layer, and a smooth charge-conveying layer based on polyvinyl carbazole, a polycarbonate and a xylene resin can be developed with a developing powder consisting of resin particles in which magnetisable iron oxide powder and nigrosine have been dispersed. In that case, the resin particles consist of a mixture of a styrene type resin and a maleic acid
15 resin modified with a natural resin. The application of this process makes it possible to obtain a very long useful life of the photoconductive element, a contributing factor being the smooth surface of the top layer which becomes hardly filthy, as opposed to a rough zinc oxide-binder layer. On the other hand, however, the application of the aforesaid smooth
20 photoconductive element has the disadvantage that edge effect will occur, i.e. images will be developed almost exclusively at the edges of the image areas.

The object of the present invention is to provide an electrophotographic process which does not show the foregoing disadvantages, and combines all
25 the advantages mentioned above. The process according to the invention is a process as described in the opening paragraph of this application, characterized in that the image is formed on a photoconductive element of which the charge-generating layer comprises a pigment that generates charges in light, said pigment being dispersed in a charge-conveying binder,

30 It has appeared that application of the process according to the invention results on the one hand in a long useful life of the photoconductive element and, on the other, notwithstanding the smooth surface of the photoconductive element, in a solid area development of the image areas without edge effects. The content of pigment in the charge-generating layer
35 may range from 5 to 50% by weight, but the limits are not critical. At contents of pigment lower than 5% an increasing edge effect is observable, and at contents higher than 50% the formation of a uniform dispersion becomes more difficult.

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An optimum image quality is obtained if the content of charge-generating pigment ranges from 10 to 35% by weight.

To ensure that the photoconductive element will have the desired smooth surface, a charge-generating pigment having a particle size between 0.1 and 3 μm is preferably chosen, but to guarantee that a smooth surface is obtained in all events, a particle size less than 1 μm is particularly preferred. The thickness of the charge-generating layer is not critical either, and may be chosen between 0.2 and some tens of micrometers, for example, but at a thickness between approximately 0.5 and 3 μm the results obtained with the photoconductive element are optimal.

10 Among the charge-generating pigments, especially the pigments which, under the influence of an electric field, have a substantial charge-generating capacity in the dark, prove to be particularly suitable. Generally, blue photoconductive pigments are concerned such as phthalocyanines and azo pigments, the latter group giving the best image quality.

15 Suitable charge-generating pigments are the bisazo pigments mentioned in British Patent Specification 1 370 197, of which Fenelac Blue, also known under the name Diane Blue (C.I. 21180), is a proper representative. This dye is also designated by the more systematic name 3,3' - dimethoxy- 4,4' - bis (2'' -hydroxy - 3'' -anilinocarbonyl naphthylazo)-biphenyl. Copies

20 showing still sounder image areas and that when the photoconductive element is used for a longer time, are obtained if the element combines the stilbene bisazo pigments disclosed in the British Patent Specification 1,520,590. Very suitable representatives of this group are 3,3' -dichloro- 4,4' -bis(2'' -hydroxy-3'' -anilinocarbonyl naphthylazo)-stilbene and 4,4' - 25 bis (2'' -hydroxy- 3'' -isopropylaminocarbonyl naphthylazo)-stilbene.

In addition to the blue photoconductive pigment, which may be a mixture of such blue pigments, a red or orange photoconductive pigment may be added for the purpose of improving the spectral sensitivity.

The polyxylenediylidene dyes described in the East-German Patent 30 Specification 75 233 and, more particularly, the dimethoxy- substituted poly- α - cyanoxylenediylidene, which is obtained by polycondensation of 1,4 -phenylene diacetonitrile with 2,5 - dimethoxy terephthalaldehyde, are very suitable.

In the process according to the invention this polycondensation product, 35 together with one of the two stilbene bisazo pigments referred to before, produces an exceptionally beautiful image.

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In general, the charge-conveying binder is a photoconductive binder which presents no or a relatively low sensitivity to visible light with respect to the pigment. Generally, these substances also have a charge-generating capacity, but as a rule this is lower than that of a charge-

5 generating pigment. Examples of suitable charge-conveying binders are: polyvinyl naphthalene, poly-9-vinyl anthracene, polyvinyl carbazole (PVK), substituted PVK such as chlorinated, bromated or iodated PVK, polyvinyl pyrene or halogen-substituted polyvinyl pyrene. The charge-conveying binder need not necessarily consist of a polymeric photo-

10 conductive substance. It is also possible to use electrically insulating polymers into which a non-polymeric charge-conveying substance has been incorporated. Examples of such non-polymeric substances are N-alkyl carbazoles such as N-ethyl carbazole or N-isopropyl carbazole; 2,5 -bis (4-aminophenyl)- 1,3,4, -oxadiazole; 2,5 -bis (4-diethylaminophenyl)-1,3,4-

15 oxadiazole and triphenylmethane diamines such as bis (4-diethylamino- 2 - methyl phenyl)(phenyl) methane.

Charge-conveying binders that transport negative or positive charge carriers predominantly, are suitable binders for the charge-generating layer, but for attaining optimum results a charge-transfer complex of an

20 electron donor and of an electron acceptor, which complexes can transport both positive and negative charge carriers in approximately the same degree, is preferred. Charge-transfer complexes in which one of the charge-conveying binders referred to in the preceding paragraph function as electron donor and a nitrated fluorene derivative as an electron acceptor, are very useful.

25 Very suitable combinations are, inter alia, PVK with one of the following electron acceptors:

2,4,5,7- tetranitrofluoren -9-one
 2,4,7- trinitrofluoren -9-one
 9-oxo-4,5,7-trinitrofluorene -2-carboxylic acid, methyl ester
 30 9-oxo-4,5,7-trinitrofluorene -2-carboxylic acid, n-butyl ester
 2- bromo-4,5,7-trinitrofluoren -9- one
 α,α,α - trifluoro -N-2,4,7- trinitrofluoren -9- ylidene -p- toluidine.
 N- 2,4,7- trinitrofluoren -9- ylidine aniline or one of the aniline derivatives described in the British Patent Specification 1,462,687.

35 The molar ratio between electron donor and electron acceptor may vary from 20:1 to 1:1, but optimum results are obtained at ratios between 10:1 and 3:1. (If the donor is a polymer, the molar ratio is based on the monomeric units thereof).

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The smooth charge-conveying top layer may consist of one of the charge-conveying binders applied in the charge-generating layer. To keep the absorption of light in the charge-conveying top layer as low as possible, the use of a colourless, transparent charge-conveying substance is preferred. Preferably, the same charge-conveying substance as present in the charge-generating layer, but without the addition of an electron acceptor, is used. Small quantities of an electron acceptor may indeed be found in the charge-conveying layer, since the charge-generating layer may partially dissolve in the solution of the charge-conveying layer applied over it during coating. The thickness of the charge-conveying top layer is not critical. Layer thicknesses of 1 to 50 μm , e.g., are applicable, but in the cases where the photoconductive element should remain properly flexible, a thickness of 1 to 6 μm is preferably applied. To promote the flexibility, a suitable softener may be added as well.

The charge-generating layer may be coated on a support that is conventionally used for photoconductive elements. Very suitable are, for example, the smooth aluminium-coated plastic supports, and the slightly rough conductive supports consisting of electrochemically roughened aluminium. In addition, a thin anchoring layer or barrier layer may be applied between the charge-generating layer and the support.

In a way usual in electrophotography the photoconductive element can be charged with a corona or a scorotron limiting the charging current. By doing so, in order to avoid undesired impurities, it is possible to guide a hot air flow along the photoconductive element by means of a blowing or suction device and an adequate heating element. After imagewise exposure, the one-component developing powder is contacted with the photoconductive element by means of a supplying member which may be, for example, a rotatable cylinder in which stationary magnets are arranged.

The developing powder has a specific resistance exceeding $10^{11} \Omega \cdot \text{cm}$. Such a high specific resistance can be obtained by non-incorporating electrically conductive substances into the developing powder. Preferably, the developing powder contains approximately 40 to 65 parts by weight of an electrically insulating magnetisable material such as magnetite or a ferrite. The rest of the developing powder consists for the vast majority of a synthetic resin, that is customary for developing powders. Suitable synthetic resins include epoxy resins, modified epoxy

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resins, polyester resins and styrene-acrylate copolymers.

If desired, a charge-controlling agent may be added to the developing powder, for the purpose of suppressing slight edge effects, but the developing results with and without charge-controlling agents only show small differences. Also substances, such as hydrophobic silica, improving the flow behaviour, may be added. As usual in electrophotography, developing powders of which the particles are as spherical as possible and their diameter as uniform as possible are preferred.

In a way usual in electrophotography the developed powder image may be transferred onto a suitable receiving material, such as paper, and be fixed thereon. The transfer onto paper can occur direct by means of an electric field, but can also be performed via a silicone rubber intermediate.

The present invention is further explained with reference to the following examples.

15 Example 1

A polyethylene terephthalate foil, to which a smooth coating of aluminium had been applied by vaporization, was successively provided with an extremely thin anchoring layer, a charge-generating layer having a thickness of 1 μm , and a charge-conveying layer of 2 μm in thickness. The thickness of the layer was measured with a capacitive thickness gauge, which was calibrated for a dielectric constant = 3 (Fischer C-Scope). The anchoring layer was applied by dip-coating in a one per cent by weight solution of a vinyl chloride vinyl acetate maleic anhydride terpolymer in butyl acetate. The terpolymer marketed by Union Carbide Corp., U.S.A., under the name Bakelite VMCH, contains the above-mentioned components in the weight ratio of 86:13:1.

The charge-conveying layer was formed from a dispersion of the following composition:

1.56 g of 3,3'-dichloro -4,4'-bis (2''-hydroxy -3''-anilino-carbonyl naphthylazo) -stilbene
5.6 g of polyvinyl carbazole (Luvican M170 of B.A.S.F., Germany)
36 ml of chlorobenzene
2.2 g of 2,4,7-trinitrofluoren -9-one
17.5 ml of tetrahydrofuran

35 Before formation of the layer the dispersion was ground until the diameter of the pigment particles was smaller than 1 μm .

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The transparency of the formed layer was 30%.

After drying, the charge-conveying layer was applied with a solution of 5 g of polyvinyl carbazole (Luvican M170) in 100 ml of chlorobenzene.

To remove remainders of the solvent the product was dried at 105°C to obtain a constant weight. The resulting photoconductive element had a smooth glossy surface.

The photoconductive element was charged with a negative corona to -360 Volt and imagewise exposed with a quantity of light of $4\mu\text{J per cm}^2$ of a halogen bulb, in which process the potential of the fully exposed areas dropped to -80 Volt. The potential of the unexposed areas, measured 1 second after charging, was -300 Volt.

The charge pattern was developed with a magnetic brush developing device which comprised no means for charging the developing powder, and which was provided with a one-component developing powder obtained as follows :

A mixture of 50 g of epoxy resin (Epikote 1004 from Shell, Netherlands) and 50 g of magnetite powder was homogenized via extrusion and then ground.

In the presence of a small quantity of hydrophobic silica (Aerosil 972) the particles were rounded by heat-treatment and the particles that were smaller than 8 μm and larger than 30 μm in diameter were removed by sifting.

The specific resistance of the powder was $2 \times 10^{14} \text{ Ohm.m}$.

The powder image obtained by development was transferred onto paper via a silicone rubber intermediate. The background of the image formed on the paper was entirely free from developing powder, and the reproduction of the black image areas of the original was sharp and uniform in density without edge effects. The photoconductive element did not show memory effect when it was repeatedly charged and exposed at a cycling time of 6 seconds. The resistance to wear and other mechanical defects was excellent. An endless belt formed of the photoconductive element was still utilisable well after it had been traversed 100,000 times along the developing station and the silicone rubber intermediate of a copier.

Example 2

The process according to Example 1 was repeated, but instead of the developing powder used in that example for the development there was used a developing powder which, as against the developing powder of Example 1, could be

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positively charged by triboelectric action. The developing powder, which was likewise composed of 50% by weight of magnetite and 50% by weight of resin, contained as the resin a mixture of an epoxy resin (Epikote 828) stabilized with 4- α , α -dimethylbenzylphenol, an epoxy resin (Epikote 1004 from Shell) and the reaction product of an epoxy resin (Epikote 1001 from Shell) with 2-methylaminoethanol. The copies obtained according to this process were equal to those obtained according to Example 1.

Example 3

The process according to Example 1 was repeated once more, but now with a developing powder that, as against the developing powder according to Example 1, could be negatively charged by triboelectric action. As the resin this developing powder contained a polyester with an acid value =12 (Atlac 382E form Atlas, U.S.A.)

Just as in example 1 the magnetite content of the developing powder was equal to 50% by weight. Also in this case the image quality of the copies was almost equal to that obtained according to Example 1.

There was only a slight edge effect visible as a result of the fact that the developing powder deposited to a greater degree at the edges of the image areas.

Example 4

The process according to Example 1 was repeated, but now with a photoconductive element in which the charge-generating pigment had been replaced by 4,4'-bis (2"-hydroxy -3"-isopropylaminocarbonyl -naphthylazo) stilbene. The light sensitivity of the resulting element was equal to that of the photoconductive element according to Example 1. The copies obtained with the process showed the same image quality as that according to Example 1. Upon frequent copying the image quality could longer be maintained constant than in the process according to Example 1.

Example 5

The process according to Example 1 was repeated, but half the charge-generating pigment in the photoconductive element was replaced by the red poly- α -cyanoxylenediylidene obtainable by polycondensation of 1,4-phenylenediacetonitrile with 2,5-dimethoxyterephthalaldehyde. The light-sensitivity and the useful life of the photoconductive element were then equal to those according to Example 1. The spectral sensitivity had changed, the grey reproduction of coloured originals on the copies thus being improved.

C L A I M S

1. A process for forming a visible image in which a photoconductive element with a charge-generating layer, and a smooth charge-conveying top layer is provided with a charge pattern, and the charge pattern is developed with a one-component developing powder of which the particles have a specific resistance exceeding 10^{11} Ohm.m.,
5 c h a r a c t e r i z e d in that the image is formed on a photoconductive element of which the charge-generating layer comprises a pigment that generates charges in light, said pigment being dispersed in a charge-conveying binder.
2. A process according to claim 1, c h a r a c t e r i z e d in
10 that a charge-generating layer containing 10 to 35% by weight of a charge-generating pigment is used.
3. A process according to claim 1 or 2, c h a r a c t e r i z e d in that a charge-generating layer having a thickness between 0.5 and $3\mu\text{m}$ in which the average diameter of the charge-generating pigment
15 particles ranges from 0.1 to $3\mu\text{m}$ is used.
4. A process according to any one of the preceding claims, c h a r a c t e r i z e d in that a charge-generating layer containing as charge-generating pigment an azo dye and as charge-conveying binder a charge-transfer complex of an electron donor and of an electron acceptor,
20 is used.
5. A process according to claim 4, c h a r a c t e r i z e d in that a charge -generating layer containing as charge-conveying binder a charge-transfer complex of a polyvinyl carbazole and a nitrated fluorene derivative, is used.
- 25 6. A process according to claim 5, c h a r a c t e r i z e d in that a charge-generating layer containing as charge-conveying binder a charge-transfer complex of a polyvinyl carbazole and a nitrated fluorene derivative in a molar ratio between 3:1 and 10:1, is used.
7. A process according to any one of the preceding claims
30 c h a r a c t e r i z e d in that a charge -generating layer containing as charge-generating pigment a stilbene bisazo dye, is used.
8. A process according to claim 7, c h a r a c t e r i z e d in that a charge-generating layer containing 4,4'-bis (2''-hydroxy -3''-isopropylaminocarbonyl-naphthylazo)-stilbene as a charge-generating

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pigment, is used.

9. A process according to claim 8, characterized in that a charge-generating layer containing as charge-generating pigment a mixture of 4,4'-bis(2-hydroxy-3-isopropylaminocarbonyl-5-naphthylazo)-stilbene and the polycondensation product of 1,4-phenylene diacetonitrile with 2,5-dimethoxy terephthalaldehyde, is used.