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DEVELOPER COMPOSITION FOR ELECTROSTATIC IMAGES AND METHOD OF UTILIZING SAME

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20 Claims. (Cl. 252—62.1)

Electrophotographic material usually consists of a support on which there is a coating of a photoconductor, this coating being provided in the absence of light with an electrostatic charge. Then, the material is exposed to light behind a master by the contact process, or an episcopic image is projected thereon, so that an electrostatic image is formed which corresponds to the master.

The image is developed by being briefly contacted with a resin powder, whereupon a visible image is formed which is fixed by heating or by the action of solvents. In this way, an image of the master, which is resistant to abrasion, is obtained electrophotographically.

The present invention relates to developers of a special kind for such electrophotographic processes.

The developers normally consist of a mixture of a carrier the material used may be grains of inorganic materials such as fine glass balls or iron filings, or crystals of inorganic salts such as common salt or potassium chloride. In the case of the toner, the material used may be a resin powder containing dyestuffs or pigments, e.g., carbon black.

When using the developer, the toner acquires a charge opposite to that of the carrier material as a result of frictional electricity. Thus, all the powder is loosely held by the carrier material so that the two components do not separate. When the developer is scattered over an electrostatic image, the toner particles are attracted to the image being developed, if it has a charge of the opposite polarity to that of the toner. If the electrostatic image and the toner have charges of the same polarity, the toner particles accumulate on the discharged portions of the electrophotographic material.

The known developers contain, in addition to the carrier, either a toner which acquires a charge which is positive with respect to the carrier material or one which acquires a charge which is negative with respect to the carrier. Thus, depending upon the polarity of the photoconductor coating and that of the toner, either the charged or the uncharged portions are developed.

Now a developer for electrophotographic purposes has been found consisting of a carrier and two distinguishable toners, one of which acquires a positive charge with respect to the carrier and one of which acquires a negative charge with respect to the carrier.

By stating that the two toners are distinguishable we mean that they have characteristics such that the portions of the developed image to which the toners respectively adhere will be distinguishable. Thus the toners may differ in color or shade, or one toner may be glossy, while the other has a mat appearance, especially after fixing. Alternatively, one of the toners may be fluorescent and thus distinguish from the other.

If, for example, a negatively charged electrostatic image is treated with a developer of this type, the positively charged toner will be attracted by the negatively charged image portions and the negative toner in the developer will adhere to the non-charged parts. If the positive and negative toners of the developer in accordance with the invention are pigmented differently, multicolored images, or images which otherwise differ from the background,

are obtained. If a number of differently pigmented negative toners and/or a number of differently pigmented positive toners are mixed together, the corresponding mixtures of the colors of the various toners of similar polarity will be obtained in the image portions and image-free portions respectively.

The carriers used for the developers in accordance with the invention may consist of grains of inorganic materials, e.g., tiny glass or quartz balls, or fine particles of metals, e.g., iron, copper, and brass, or crystals of inorganic salts such as potassium sulfate, potassium chloride, sodium chloride, copper sulfate, or grains of organic materials, e.g., polystyrene and carboxymethyl cellulose; glass balls covered with organic resins, or crystals of organic compounds such as oxalic acid, adipic acid or phthalic anhydride. Glass balls and also iron powder have proved particularly suitable as carrier materials for the developer in question because of their high density and their mechanical stability.

The carriers generally have a particle size in the range of about 100 to about 600μ. Smaller or larger carrier particles may be used, but carriers with the larger portion of the particles in the range mentioned, preferably from about 200 to 400μ, have proved advantageous.

Materials suitable as positive toners for the developer in accordance with the invention, if one of the preferred materials, i.e., glass or iron, is used as the carrier, include natural and synthetic resins, e.g., colophony, copals, dammar resin, asphalt, colophony-modified phenol resins, ketone resins, maleic resins, coumarone resins, polyacrylic acid resins and polystyrenes. Also, mixtures of these resins can be used.

Inorganic and/or organic pigments and/or dyestuffs may be mixed with these resins, as well as fluorescent agents.

The following are, for example, suitable: carbon black, zinc oxide, titanium dioxide, barium sulfate, red lead, Helio-red, Helio-blue, Sudan dyestuffs, Cellitone dyestuffs, spirit-soluble Nigrosine, Pigment Black, Alizarin Blue-Black B, Diamond Black F, Fanal Violet LB and also mixtures of such dyestuffs and/or pigments.

It is, further, often advantageous for waxes and/or low melting point organic compounds and substitution products thereof to be added to the positive toners so that the melting point and the adhesive power of the toner mixture may be favorably affected.

Suitable waxes for this purpose include natural waxes such as carnauba wax, beeswax, Japan wax, montan wax, and ceresine, and synthetic waxes such as those known under the trade names A-Wachs, OP-Wachs, SPO-Wachs, V-Wachs, O-Wachs, E-Wachs, Hartwachs H, Hartwachs W, various of the waxes known as Ruhrwachse and, particularly, the products commercially available under the name of Gersthofener Wachse with the codings S, L, O and OP.

The low melting point organic compounds that are particularly of interest are substituted and unsubstituted aromatic compounds having a melting point of between about 40 and 150° C.

Such compounds include naphthols, e.g., 1-naphthol and 2-naphthol, and also aromatic compounds such as acenaphthene, acylamino compounds such as acetanilide, aromatic halogen compounds such as p-dibromobenzene, amino compounds such as 2,4-diaminotoluene, o-phenylenediamine, and phenols such as resorcinol and diphenylamine and its derivatives.

For the preparation of negatively charged toners, metal resinates and vinyl chloride interpolymers containing carboxyl groups are particularly suitable.

Metal resinates, also known as resin soaps, are to be understood to cover metal salts of resin acids, the metals being those of groups 1 to 8 of the Periodic Table.

In the present case, the compounds of particular interest are metal resinates, and mixtures thereof, involving metals such as aluminum, barium, lead, calcium, cerium, iron, cobalt, copper, magnesium, manganese and zinc.

In addition to these resinates, up to 50% of resins such as are used in the preparation of the positive toners may be added to the negative toners. Also, quantities of the waxes and low melting point organic compounds, with a melting point between about 40 and 150° C., may be added to the metal resinates. Further, as dyestuffs and pigments, those described for the positive toners may be used. However, in general, the content of pigments and dyestuffs should not exceed 10% by weight of the metal resinates if the negative charging characteristics are to be adequately maintained.

If, however, dyestuffs containing metals are used, quantities of up to about 50% by weight but preferably not more than 35%, can be used.

As dyestuffs with metal content, those may be mentioned which, for example, contain metals such as copper, zinc, magnesium, iron, sodium or potassium incorporated in complex form in the molecule. They include complexes such as chlorophyll or copper, zinc or magnesium phthalocyanines or Naphthol Green B.

Further, double salts of dyestuff molecules, e.g., zinc chloride double salts of Toluidine Blue O, Methylene Green B or Acridine Orange 2G may be considered, as also complexes of heteropoly acids such as phosphomolybdotungstenic acid with dyestuffs, e.g., the substances known as Fanal dyestuffs such as Fanal Red 6 B, Fanal Violet LB and Fanal Blue B. Also, metal salts of sulfonic and carboxylic acids of dyestuffs may be considered, e.g., Alizarin Blue Black B, and Diamond Black F. The metal resinate toners are advantageously prepared as follows: the pulverized starting materials are ground together very finely; the mixture is heated until melted, stirred until a high degree of homogeneity is achieved and then the melt is cooled. It is also possible for the fusible starting materials to be liquefied by heating and the remaining components added with stirring; the mixture is then cooled. The toner mass thus obtained is finely ground and then screened. Fractions of an average particle size of about 5 to 100μ, preferably about 5 to 30μ, are used for the toner.

For the preparation of the negative toners containing vinyl chloride interpolymers with carboxyl groups, compounds obtained by the polymerization of vinyl chloride with esters of fatty acids such as acetic acid, propionic acid and butyric acid and also containing small quantities of unsaturated monocarboxylic acids, such as crotonic acid and cinnamic acid, or unsaturated dicarboxylic acids, such as maleic acid, fumaric acid or itaconic acid, are exemplary of those used. Such products are commercially available.

The interpolymers may also be colored. For this purpose, dispersion dyestuffs (Colour Index, vol. 1, pages 1655–1742), which are used for the coloring of polyvinyl chloride, may be employed, e.g. Cellitone, Cibacete and Setacyl dyestuffs.

Furthermore, organic pigments having properties that are physically related to those of the dispersion dyestuffs, may also be used for coloring the interpolymers, e.g., fat dyestuffs such as Sudan dyestuffs or development dyestuffs of the Naphthol AS series.

Also fluorescent agents may be added in small amounts to one of the above toners, either alone or in combination with dyestuffs or pigments. As fluorescent agents there may be used organic aromatic or heterocyclic multinuclear uncolored or colored compounds, which are known per se.

The coloring of these interpolymers is performed in the well known manner used in the case of polyvinyl chloride. For example, 5–20 percent of the dyestuffs mentioned, in relation to the quantity by weight of the interpolymer that is to be colored, are suspended in water together with the powdered interpolymer at a temperature within the range of 40–70° C. and the suspension is stirred for 2–3 hours.

About 2–15 percent of a carrier, e.g., phenylethylurethane, p-chlorotoluene or 2,6-dibromo-toluene, may be added to facilitate the coloring process. This carrier is used in quantities of from 1 to 6 percent, preferably 4–6 percent, with respect to the quantity by weight of the interpolymer used. When coloring is completed, the powder is separated by suction filtration, washed either with water alone or water to which natural or synthetic washing agents have been added, and is then dried. In certain cases fine grinding in a ball mill is then performed.

The material is then sieved and a fraction with an average particle size of about 1 to 100μ, preferably 5–30μ, is used as toner.

For the preparation of the developer, one of the carriers mentioned is mixed with at least one of the negative and one of the positive toners. The proportion of carrier to toner should be in the range of about 100:10 to about 100:0.1, preferably from about 100:2 to about 100:1.

The toners can be used in very varied proportions but preferably in proportions of about 1:1 to about 1:0.1. Advantageously, the proportions will be selected so that they approximate the proportions of electrostatically charged areas to discharged areas of the photoconductor coating being developed. Thus, in the case of a photoconductor coating the greater part of which consists of positively charged image parts, a high proportion of negative toner will be selected for the developer.

The developer falling within the scope of the invention has the advantage of enabling an electrostatic image to be developed in two colors or be otherwise distinguished in the image and non-image parts. Also, it is possible, if a black toner and a white toner are used, for a black and white copy to be produced, even if the photoconductor material is colored.

The invention will be further illustrated by reference to the following specific examples:

Example 1

(a) 1 part by weight of a red dispersion dyestuff (Cellitonechtrot GG) is suspended in 150 parts by volume of water at 55° C. and 1 part by weight of phenylethylurethane, as carrier, is stirred in. This carrier suspension is allowed to cool to 40° C. and then, with stirring, 5 parts by weight of an interpolymer consisting of 85 percent of vinyl chloride, 14 percent of vinyl acetate and 1 percent of maleic acid are added, fractionally. After all the interpolymer has been added, stirring is continued for half an hour at 40° C. The temperature is then raised, over the course of 1.5 hours, to 65° C. and stirring is continued for one hour at this temperature. After cooling, the interpolymer is separated by suction filtration; it is washed with water and dried.

The red-colored material is finely ground in a ball mill and then sieved. A fraction with a grain size of 20–30μ is used as toner.

(b) 3 parts by weight of a polystyrene ("Polystyrol LG") and 3 parts by weight of a maleinate resin with a melting point of 69–70° C., an acid number of 32 and a color number of 9–10 ("Hobimal P 59") are mixed with 0.3 part by weight of spirit-soluble Nigrosine and a 0.1 part by weight of Pigment Black. The mixture is then melted.

After cooling, the solidified melt is ground in a ball mill and then sieved. A fraction containing particle sizes of from 20–30μ is used for the toner.

2 parts by weight of the red toner (a) and 2 parts by weight of the black toner (b) are mixed with 200 parts by weight of glass balls of a diameter of about 300μ. During this mixing process, the red toner takes on a negative charge and the block toner a positive charge. For the preparation of black and red copies, an electro-

photographic material, e.g., a paper having zinc oxide incorporated in a resin as a photoconductor coating, or an aluminum plate coated with zinc oxide incorporated in a resin, is negatively charged by means of a corona discharge of 6000–7000 volts. The photoconductor coating is exposed to light behind a master and then the developer described is scattered over the surface. The red toner adheres to the portions struck by light and the black toner adheres to the negatively charged image parts. A copy in black and red becomes visible and is fixed by heating.

Example 2

A paper having a zinc-oxide photoconductor coating and sensitized with Rhodamine B extra is provided with a negative electrostatic charge by means of a corona discharge in the manner described in Example 1 and is then exposed to light under a master. After development, fixing by heating is performed. The developer used is prepared as follows:

(a) 3 parts by weight of an interpolymer consisting of 85 percent of vinyl chloride and about 15 percent of vinyl acetate and in which a small proportion of dicarboxylic acid is also polymerized (Vinnol G 15/45 M) are introduced with stirring, at 40° C., into 60 parts by volume of water in which 0.12 part by weight of a black dispersion dyestuff ("Cellitonechtschwarz BTN") and 0.12 part by weight of p-chlorotoluene are suspended. The mixture is then heated to 65° C. and stirred for 3 hours at this temperature. After cooling, the colored interpolymer is separated by suction filtration, ground in a ball mill and sieved. Fractions having a particle size of about 20–30μ are used.

(b) 2 parts by weight of a maleinate resin with a melting point of 95–105° C., an acid number of 20–25, and a color number of 35 ("Beckacite" K 105), 1 part by weight of colophony and 3 parts by weight of polystyrene (Polystyrol LE) and 4 parts by weight of a fine silicon dioxide powder with a mean particle size of about 5–40 mμ (Aerosil), and 1 part by weight of titanium dioxide are mixed together and then melted. After cooling, the solidified melt is ground and sieved and a fraction with a particle size of about 20–50μ is used as toner.

1 part by weight of toner (a) and 5 parts by weight of toner (b) are mixed with 100 parts by weight of iron powder and passed by means of a bar magnet over the electrostatic image. The negatively charged, black toner adheres to the portions struck by light, while the white, positively charged toner is attracted by the negative charge of the photoconductor coating. In this way, a reversed image of the master is obtained. The electrophotographic material, which has been colored red by the sensitizer, is substantially covered by the white toner.

Example 3

10 parts by weight of a zinc resinate with a melting temperature ("Kofler-Heizbank") 150/140–125° C. and an acid number of 0 ("Erkazitharz RF") are finely ground, mixed with 1 part by weight of copper phthalocyanine and then melted. The cold melt is ground in a ball mill and then seived. A fraction of this toner with an average particle size of about 30–50μ is used, when used with a glass carrier it acquires a negative charge. 2 parts by weight of this toner are mixed with 2 parts by weight of the toner described under (a) in Example 1 in which, however, a yellow dispersion dyestuff ("Cellitonechtgelb RR") is used for the coloring of the toner instead of the red dispersion dyestuff. This mixture of negatively charged blue toner and negatively charged yellow toner is mixed with 3 parts by weight of a positively charged red toner and 300 parts by weight of glass balls. In this way, a developer is obtained which developes the electrostatic image on a photoconductor coating in green and red.

For the preparation of the red toner, 1 part by weight of a ketone resin with a melting point of 76–82° C., a color number of 1–2.5 and an acid number of 0 ("Kunstharz AP"), 3 parts by weight of polystyrene ("Polystyrol LG"), 0.5 part by weight of montan wax, 0.25 part by weight of acetanilide, and 1 part by weight of Helio-red are melted together. After being cooled, the melt is ground in a ball mill and then sieved. A fraction with a particle size of 30 to 50μ is used. The photoconductor material, treated in the manner described in Example 1 with the developer detailed above, consists of a paper which is coated with the organic semiconductor, 2,5 - bis - [4'-diethylaminophenyl-(1')]-1.3.4-oxadiazole, as described in Belgian Patent 558,078.

If the photoconductor coating is positively charged, a green image is obtained from the negatively charged mixture of yellow and blue toner particles. The uncharged portions appear in red.

Example 4

(a) 10 parts by weight of a low melting point polystyrene and 10 parts by weight of a maleic resin having a melting point range from 69–77° C., an acid number of 32, and a dye number of 9–10, one part by weight of spirit-soluble Nigrosine, and 0.3 part by weight of Pigment Black are mixed and then melted together. After cooling the solidified melt is ground in a ball mill and then sieved. The fraction having an average particle size of about 5–13μ is selected for use as a toner. When used with a glass bead carrier it acquires a positive charge.

(b) 30 parts by weight of an interpolymer of vinyl chloride (85%), vinyl acetate (14%), and maleic acid (1%), are fused with 2.4 parts by weight of a black dispersion dyestuff ("Cellitonechtschwarz BTN") and subsequently cooled, ground and screened. The fraction having an average particle size of about 5–13μ is again selected for use as a toner. When used with a glass bead carrier it acquires a negative charge. 5 parts by weight of each of the foregoing toners are mixed together with 200 parts of glass balls having a diameter of about 300μ. In this way a developer is obtained which develops an electrostatic image on a photoconductive coating partly with a glossy appearance and partly with a mat appearance. By charging an electroconductive layer with a negative corona discharge, images having a glossy appearance on a mat backround are obtained.

By changing the polarity of the charge applied to the electroconductive layer images can be obtained having a mat appearance on a glossy background. After development the toner particles are fixed to the support by heating.

Example 5

(a) 30 parts by weight of a low melting point polystyrene, 30 parts by weight of maleic resin having a melting point range from 69–77° C., an acid number of 32 and a dye number of 9–10 and 10 parts by weight of 2,5 - bis-[4'-diethylaminophenyl-(1')]-oxadiazole-(1.3.5) are converted into a homogenous toner by fusion, grinding and sieving. The fraction having an average particle size of about 5–13μ is selected for use as a toner. When used with a glass bead carrier it acquires a positive charge.

(b) An uncoloured interpolymer of vinyl chloride (85%), vinyl acetate (14%) and maleic acid (1%) is converted into a toner by grinding and sieving. The fraction having an average particle size of about 5–13μ is again selected for use as a toner. When used with a glass bead carrier it acquires a negative charge.

5 parts by weight of each of the foregoing toners are mixed together with 200 parts of glass balls having a diameter of about 200μ. An electroconductive material containing zinc oxide is charged by means of a negative corona discharge and exposed to light under a positive film original. After development with the toner described above images are obtained, the image free parts of

which exhibit a strong fluorescence under U.V. illuminations.

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 developer for use in electrophotographic processes comprising a carrier and a toner, one portion of the toner having, with respect to the carrier, a positive charge and one portion having a negative charge, the latter portion being selected from the group consisting of metal resinates and vinyl chloride interpolymers containing carboxyl groups.

2. A developer according to claim **1** in which the positively charged portion of the toner is selected from the group consisting of natural and synthetic resins.

3. A developer according to claim **2** in which the resin is in admixture with a compound selected from the group consisting of pigments, dyestuffs, fluorescent agents, waxes, and low melting point organic compounds.

4. A developer according to claim **1** in which the negatively charged portion of the toner is a metal resinate in admixture with a compound selected from the group consisting of resin, waxes, low melting point organic compounds, dyestuffs, fluorescent agents, and pigments.

5. A developer according to claim **1** in which the negatively charged portion of the toner is a vinyl chloride interpolymer containing carboxyl groups in admixture with a compound selected from the group consisting of dyestuffs, fluorescent agents, and pigments.

6. A developer according to claim **1** in which one portion of the toner comprises a colored interpolymer of vinyl chloride, vinyl acetate, and maleic acid, and one portion comprises a mixture of polystyrene and a maleinate resin.

7. A developer according to claim **1** in which one portion of the toner comprises a colored interpolymer of vinyl chloride, vinyl acetate and a dicarboxylic acid, and one portion comprises a colored mixture of a maleinate resin, colophony, polystyrene, and finely divided silicon dioxide.

8. A developer according to claim **1** in which one portion of the toner comprises a colored zinc resinate and one portion comprises a colored mixture of a ketone resin, polystyrene, montan wax and acetanilide.

9. A process for developing an electrostatic image which comprises contacting the image with a developer comprising a carrier and a toner, one portion of the toner having, with respect to the carrier, a positive charge and one portion having a negative charge, the latter portion being selected from the group consisting of metal resinates and vinyl chloride interpolymers containing carboxyl groups.

10. A process according to claim **9** in which the positive charge portion of the toner is selected from the group consisting of natural and synthetic resins.

11. A process according to claim **10** in which the resin is in admixture with a compound selected from the group consisting of pigments, dyestuffs, waxes and low melting point organic compounds.

12. A process according to claim **9** in which the negatively charged portion of the toner is a metal resinate in admixture with a compound selected from the group consisting of resins, waxes, low melting point organic compounds, dyestuffs, and pigments.

13. A process according to claim **9** in which the negatively charged portion of the toner is a vinyl chloride interpolymer containing carboxyl groups in admixture with a compound selected from the group consisting of dyestuffs, and pigments.

14. A process according to claim **9** in which one portion of the toner comprises a colored interpolymer of vinyl chloride, vinyl acetate and maleic acid, and one portion comprises a colored mixture of polystyrene and a maleniate resin.

15. A process according to claim **9** in which one portion of the toner comprises a colored interpolymer of vinyl chloride, vinyl acetate and a dicarboxylic acid, and one portion comprises a colored mixture of a maleinate resin, colophony, polystyrene and finely divided silicon dioxide.

16. A process according to claim **9** in which one portion of the toner comprises a colored zinc resinate and one portion comprises a colored mixture of a ketone resin, polystyrene, montan wax, and acetanilide.

17. A developer according to claim **1** in which one portion of the toner comprises a colored interpolymer of vinyl chloride, vinyl acetate, and maleic acid of mat appearance, and one portion comprises a colored mixture of polystylrene and maleic resin of glossy appearance.

18. A developer according to claim **1** in which one portion of the toner comprises an interpolymer of vinyl chloride, vinyl acetate, and maleic acid, and one portion comprises a fluorescent mixture of polystyrene, maleic acid, and 2,5 - bis - [4'-diethylaminophenyl-(1')]-oxadiazole-(1.3.5).

19. A process according to claim **9** in which one portion of the toner comprises a colored interpolymer of vinyl chloride, vinyl acetate, and maleic acid of mat appearance, and one portion comprises a colored mixture of polystyrene and maleic acid of glossy appearance.

20. A process according to claim **9** in which one portion of the toner comprises an uncolored interpolymer of vinyl chloride, vinyl acetate, and maleic acid, and one portion comprises a fluorescent mixture of polystyrene, maleic acid, and 2,5 - bis - [4'-diethylaminophenyl-(1')-]-oxadiazole-(1.3.5).

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NORMAN G. TORCHIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 26 and 27, after "carrier" insert -- and a toner. In the case of the carrier --; column 4, line 74, for "block" read -- black --; column 5, line 62, for "seived" read -- sieved --; line 63, for "used," read -- used; --.

Signed and sealed this 17th day of January 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents