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PROCESS FOR PRODUCING ELECTROPHOTOGRAPHIC LIQUID DEVELOPER

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ABSTRACT OF THE DISCLOSURE

A process for producing electrophotographic liquid developer containing finely divided powdered polypeptide polymeric particles which comprise preparing an intimate mixture of the said polypeptide material and a ferromagnetic powder material in an aqueous solution subjecting said mixture to a wet process crushing in a carrier liquid and, after said mixture is dried, removing said ferromagnetic powder from said mixture by means of a magnetic field.

BACKGROUND OF THE INVENTION

This invention relates to imaging materials and more particularly to a method of making liquid developers.

It is well known in a color reproduction process to use a liquid developer containing a gelatinous material. The quality of the image and the color prints produced therefrom is dependent to a large extent upon the quality of the gelatinous material used, the manner of making the same, and more specifically the ability to provide particles of fine and uniform size. Difficulties have been encountered using known processes in producing a gelatinous material of a uniformly fine particle size.

One process produces a gelatinous powder of dry pulverized gelatinous grains. However, since grains and flakes of this material are solid, hard and tenacious, it is difficult to reduce them to a uniformly fine size. A second method includes the use of an aqueous solution of a gelatinous material which is added to and dispersed in a solvent in which it is insoluble. Fine particles of the gelatinous material are produced and collected from the resultant dispersion. This method, however, suffers from a shortcoming in that prior to collecting the gelatinous material from the aqueous solution, it tends to coagulate. Still another available method by which the particles of a gelatinous material may be obtained is by spraying the aqueous solution of the same into dry air. With this method, however, it is not possible to produce gelatinous particles fine enough to serve as an imaging material in a liquid developer capable of producing fine images of high resolution.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide an improved process for producing liquid developers devoid of the above-noted deficiencies.

It is another object of this invention to provide a novel process for producing liquid developers containing polypeptide.

Still a further object of this invention is to provide a novel process for polypeptide liquid developers to be used in dye printing.

Yet another object is to provide a polypeptide, material useful in multi-color printing.

These and other objects of the present invention are accomplished generally speaking by blending a polypeptide material and ferromagnetic powder material in the presence of a liquid to obtain a uniform mixture, then subjecting said mixture to a wet process crushing after drying thereof, removing said ferromagnetic powder material

from said crushed mixture by means of a magnetic field and combining said mixture with an electrophotographic carrier.

More specifically, by adding and blending a ferromagnetic powder material, e.g., ferric oxide, with a solution of a polypeptide material, e.g., bone gelatin, dissolved in water or in water and methanol, it is possible to obtain an extremely stable dispersion because of the excellent protective colloidal effect of the oplymeric material. Blending may be realized by means for example, of ball mill, three-roll kneader, vibrating mixer and ultrasonic dispersion. The mixture is then dried to form a cake consisting of polypeptide material and ferromagnetic powder material.

Although particles or flakes consisting solely of a polypeptide material cannot be easily crushed as explained before, the cake consisting of a polypeptide material and ferromagnetic material obtained by the present process has proved to be easily crushable. The cake is then finely divided into a powder by a wet process crushing in an electrophotographic carrier liquid or in other liquids which are imiscible with such a carrier liquid. After being subjected to a wet process crushing, a mixture of ferromagentic powder and a polypeptide material is dispersed in an organic solvent and the ferromagnetic material is removed by a magnetic field.

By using the liquid developer containing the polypeptide material according to the process of this invention, a polypeptide matrix can be prepared according to the following steps:

(1) An electrostatic latent image is formed on a suitable imaging surface such as a photoconductive insulating layer of an electrophotographic recording member or an insulating coating of an electrostatic recording member.

(2) The electrostatic latent image is developed by using liquid developer containing the polypeptide polymeric material.

(3) The polypeptide polymeric material image thus obtained is fixed by any suitable method to form the polypeptide matrix of the printing master. To obtain a color print by the dye transfer method two additional steps are performed:

(4) An aqueous solution of a water soluble dye is brought into contact with the polypeptide polymeric material image and the image is allowed to absorb the dye. If desired, excess dye may be removed.

(5) A separately prepared dye receiving sheet provided with a surface layer capable of easily absorbing the dye solution onto a polypeptide polymeric material image is positioned so that the dye receiving layer thereof may be brought into contact with the dye absorbing polypeptide image causing a transfer of the dye from said polypeptide image to said surface layer to form a final image on said dye receiving sheet.

A multiplicity of prints each carrying the dye image can be obtained by repeating steps 4 and 5 with the same polypeptide matrix.

Any suitable polypeptide material may be used in the present invention. Typical polypeptide materials include gelatin, obtained from either hide or bone, casein glue, albumin and others. It is preferred to employ gelatin with relatively narrow setting point ranges. Ordinary refined photographic gelatin, is found to be adequate for the purposes of this invention.

Any suitable ferromagnetic powdered material may be employed in the process of this invention. Particularly, satisfactory results are obtained with ferromagnetic substance such as iron, nickel and cobalt; metallic oxides, such as iron and chromium; ferrites, such as iron cobalt oxides, iron magnesium oxides; or alloys such as iron-cobalt and iron-cobalt-nickel.

Any suitable method may be employed to fix the polypeptide imaging matrix. A preferred method is to incorporate a resinous fixing compound which is soluble in the carrier liquid.

Any suitable carrier liquid may be used in the process of this invention. Typically, the carrier liquid is a nonpolar highly insulative organic solvent substantially the same as that which is used in conventional liquid developers for electrophotography. Preferably, the electrical resistance of the carrier liquid is greater than 10^{10} ohms-cm. Typical solvents are kerosene, decaline, cyclohexane, heptane, isooctane, gasoline and chlorofluorinated hydrocarbons.

Any suitable amount of polypeptide material and ferromagnetic powder material may be employed in the process of this invention. The ferromagnetic powder material is preferably within the range of from about 0.1 to 10 parts by weight of said ferromagnetic powder material to about 1 part by weight of the polypeptide material. It is believed that the ferromagnetic powder material cannot exhibit sufficient effect when used in an amount less than about 0.1 part by weight while at the same time the yield of the polypeptide material is lowered when the amount exceeds about 10 parts by weight.

When the liquid developer is used for developing the electrostatic latent image, a deposition of both ferromagnetic powder material and a polypeptide material will be deposited onto the latent image. The effect of simultaneous dispersion decreases the amount of dye adsorbed on the polypeptide relief image resulting in lowering the density of the image in multicolor printing. The amount of polypeptide polymeric material deposited on a latent electrostatic image of a given electrostatic charge density becomes lower as the content of ferromagnetic powder material becomes larger. On the other hand, however, the crushing of the polypeptide cake is considerably easier when the content of the ferromagnetic powder material becomes larger. This dilemma can be prevented according to this invention by removing the ferromagnetic powder material by means of a magnetic field after the polypeptide cake is subjected to a wet-process crushing or after the product is diluted with a carrier liquid. Upon subjecting the system to a magnetic influence some polypeptide material is lost when the ferromagnetic powder material is removed, but a major portion of the polypeptide material remains in the dispersion. The amount of polypeptide material remaining in the system becomes larger as the crushing time of the cake becomes longer.

Any suitable amount of polypeptide material may be added to the carrier liquid to form the liquid developer. The concentration of polypeptide material in the carrier liquid is preferably within the range of from about 0.001 to 5% by weight based on the weight of the carrier liquid. When the quantity of the polypeptide material particles within the carrier liquid is extremely small, it is impossible to sufficiently develop the electrostatic latent image on the sensitive layer. On the other hand, if the concentration of the polypeptide material is too high, fogging tends to occur and the dispersion stability required for the liquid developer may deteriorate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following preferred examples further define, describe and compare preferred materials, methods and techniques of the present invention. In the examples, all parts and percentages are by weight unless otherwise specified.

Example I

1 part by weight of photographic bone gelatin and 2 parts by weight of gamma-ferric oxide are left to stand at room temperature with 30 parts by weight of water for 30 minutes, which causes the gelatin particles to swell due to water absorption. Successively, the mixture is warmed to 60° C. to dissolve the gelatin present in said mixture. The mixture is kept at 40° C. and blended by means of a high-speed mixer for one hour to obtain a brown colored dispersion.

The brown dispersion obtained is cooled to 3° C. to obtain a coagulated mass, which is successively cut into cubes of 1 cm. and dried, thereby obtaining brown cake consisting of gamma-ferric oxide and gelatin. The cake thus prepared is very fragile and can be easily crushed with the fingers. 4 parts by weight of the said cake is added to a mixture of the following composition and blended for 20 hours on a ball mill:

Safflower oil-modified alkyd resin 24 parts by weight
Kerosene (72 parts by weight)
100 parts by weight of brown paste thus obtained is diluted with 900 parts by weight of kerosene.

Gamma-ferric oxide present in the brown dispersion is removed by inserting a permanent magnet into the said dispersion thereby obtaining a milk-white liquid developer.

Example II

By following the same procedure as provided in Example I with the exception that gamma-ferric oxide is removed prior to the dilution of the brown paste with kerosene. The gelatinous particles present in the liquid developer are found to be electrostatically charged positive.

Example III

100 parts by weight of photoconductive zinc oxide and 20 parts of epoxy ester of dehydrated linseed oil fatty acids are blended with an adequate amount of toluene to obtain a homogeneous coating solution.

The coating solution is further added to 20/1000 parts by fluorescein and 20/1000 parts of tetrabromophenol blue dissolved in small amounts of ethylene glycol monomethylether in order to widen the photosensitive range of zinc oxide to cover the whole visible wavelength range. The coating solution is diluted appropriately with toluene and applied on a film (90 microns thick) of polyethylene terephthalate previously provided with a vacuum evaporated aluminum film, to obtain a coating of 8 microns after drying. After sufficient drying in a dark place, the coated composition shows a satisfactory performance as an electrophotographic sensitized material.

This electrophotographic sensitized material is exposed to a negative corona discharge in a dark place to have its surface uniformly electrically charged. A color slide of an original is loaded on an enlarger, with a red filter layed over the slide. The negatively charged sensitive material is exposed to light projected through the original.

The exposed sensitive material is first wetted with kerosene and then, with minimum loss of time, soaked in the liquid developer as described in Example I, contained in a stainless steel vat so that the vat may function as the developing electrode while the surface containing the electrostatic latent image is brought closer to the vat bottom. After being submersed is the developer for about 90 seconds, the sensitive material is removed, washed with isoparaffin, and then dried. After development, the sheet is soaked in a 1% methanol solution of formalin. The sheet is then left to stand overnight at room temperature to allow the gelatin image to form into a hardened member.

After the hardening treatment, the sensitive material now carrying the gelatinous image is soaked in an aqueous solution containing 40% by weight of acetic acid for 2 minutes. This treatment caused substantially all of the zinc oxide present in this sensitive layer to be removed from the layer. The procedure to this point produces a matrix to be used for cyan printing.

Example IV

By following the same procedure as provided in Example III, another sheet is exposed to light projected

through the combination of the same original with a green filter. With the same development technique as the liquid developer containing gelatin, a matrix for magneta printing is obtained.

Example V

By combining the original with a blue filter in a similar manner as described in Example III, a matrix for yellow printing is obtained.

Example VI

Each of the three matrices described in Examples III, IV and V are soaked for 2 minutes in an aqueous solution of Color Index Acid Blue 54, Acid Violet 7 and Acid Yellow 23 respectively, removed from the vats, and then washed in a bath of acetic acid.

A sheet having a gelatinous layer thereon is soaked in aluminum sulfate solution to be mordanted and thereafter registered correctly with and pressed against the three matrices, one after another. Through this treatment, the dyes absorbed in the toner image are transferred onto the gelatin layer. A duplicate of extremely high quality is obtained. 100 duplicates are made using these matrices with substantially no alteration in print quality.

Example VII

The process of Example I is followed except chromium dioxide is used instead of gamma ferric oxide to obtain similar liquid developer containing gelatin.

In this case, chromium dioxide is employed in 3 parts by weight with respect to 1 part by weight of gelatin, and the resulting liquid developer showed the performance and results comparable to those obtained in Example I.

Example VIII

The process of Example I is followed except that 4 parts by weight of cobalt ferrite with respect to 1 part by weight of gelatin is employed instead of gamma ferric oxide.

The liquid developer obtained in this example shows the performances and results comparable to those obtained in Example I.

Example IX

The process of Example I is followed except 0.3 part by weight of gamma ferric oxide instead of 2 parts by weight thereof is used in order to obtain results comparable to those obtained in Example I.

Although specific materials and operational techniques are set forth in the above embodiments using the developing materials and techniques of this invention, these are merely intended as illustrations of the present invention. These are other materials and techniques other than those listed above which may be substituted with similar results. For example, the wet process crushing can be preceding by a dry process crushing. Also, in the case of wet process crushing of a carrier liquid, dispersion can be facilitated by adding resinous charge controlling agent and dispersing agents into said carrier liquid, if desirable.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure which modifications are intended to be included within the scope of this invention.

What is claimed is:

1. A process for producing an electrophotographic liquid developer containing finely powdered polypeptide polymeric particles comprising the steps of:
   (a) forming an intimate mixture of one part by weight polypeptide polymeric particles and at least about 0.1 part by weight ferromagnetic powder in an aqueous solution;
   (b) drying the aqueous solution to form cakes;
   (c) forming a dispersion from said cakes by pulverizing said cakes into a finely divided powder by blending said cakes in a liquid dispersion comprising an organic carrier liquid and;
   (d) removing said ferromagnetic powdered material from said dispersion by means of a magnetic field.

2. The method of claim 1 wherein the carrier liquid has an electrical resistivity greater than 10^{10} ohms-cm.

3. The method of claim 1 wherein said pulverizing is performed by wet-crushing.

4. The method of claim 1 wherein said organic carrier liquid is a non-polar, highly insulating organic solvent.

5. The method of claim 1 wherein said polypeptide is selected from the group consisting of gelatin, casein glue, and albumin.

6. The method of claim 1 wherein said ferromagnetic powder is selected from the group consisting of iron, nickel, cobalt, iron oxide, chromium oxide, ferrites and alloys thereof.

7. The method of claim 1 wherein the ratio of ferromagnetic powder to polypeptide is from about 0.1 to 1 to about 10 to 1 parts by weight.

8. The method of claim 1 wherein said organic carrier liquid is selected from the group consisting of kerosene, decaline, cyclohexane, heptane, isooctane, gasoline, and chlorofluorinated hydrocarbons.

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