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[54] **PROCESS OF MAKING LIQUID ELECTROSTATIC DEVELOPERS CONTAINING GELATIN**

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[58] **Field of Search** 252/62.1; 106/125, 106/135; 260/8, 118; 96/94, 96, 97, 98, 1, 14.7

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[57] **ABSTRACT**

A liquid developer containing a gelatin toner for developing electrostatic latent images is made by cooling an aqueous solution of gelatin to produce a gelatin gel, adding the gelatin gel to a solvent which is miscible with water but is incapable of dissolving the gelatin and mechanically pulverizing to form a dispersion of gelatin. The finely divided gel powder is collected and added to an insulating carrier liquid.

4 Claims, No Drawings

PROCESS OF MAKING LIQUID ELECTROSTATIC DEVELOPERS CONTAINING GELATIN

BACKGROUND OF THE INVENTION

This invention relates to imaging materials and more particularly to liquid developers for developing electrostatic latent images such as are obtained in electrophotography and electrostatic recording process. More specifically, this invention relates to improvements in the methods of making liquid developers having incorporated therein a gelatin toner which developer is to be used in a reproduction process which converts an electrostatic latent image into a gelatin image which may subsequently absorb a colored dye and transfer the dye from the gelatin matrix to a receiver sheet.

The most popular process for obtaining multicolor prints of good quality, is the technique which combines the chromophoric developing method with a silver salt emulsion. The tanning developing method which similarly used silver salt emulsion and the so-called dye transfer method or dye imbibition method and which is based on the formation of a gelatin relief image has also been popularized such as in technicolor process.

Comparison of the two methods reveals that the former method is suitable for volume processing in a wide range of applications but is unsatisfactory in that the image has insufficient durability against light irradication and therefore has poor storability. In contrast thereto, the dye transfer method can provide images with outstanding light resistance and storability. This dye transfer method is similar to printing techniques and possesses improved economy when many duplicates are obtained from the original. When the number of duplicates to be obtained is small, however, this method is rather expensive since great time, effort and skill are consumed in the preparation of the gelatin matrix which serves as the plate.

Recently, a simplified method of rapidly, easily and inexpensively producing a master for use in the dye transfer process has been invented. United States copending application Ser. No. 780,495 filed Dec. 2, 1968, discloses this novel color reproduction process, the disclosure of which is hereby incorporated by reference. Therein disclosed is a technique of producing multicolored prints of excellent quality in color and which are light fast and which comprises the following steps:

1. An electrostatic latent image is formed on the photoconductive insulating layer of an electrophotographic recording member or on the insulating coating of an electrostatic recording member.

2. The electrostatic latent image is converted into a visible toner image by using the finely divided powder of a suitable substance such as gelatin toner, for example, which readily absorbs an aqueous solution of a water-soluble dye.

3. The toner image is fixed by a suitable method.

4. An aqueous solution of a water-soluble dye is brought into contact with the toner image to allow the dye to be absorbed by the image.

5. A separately prepared material having a surface capable of absorbing the dye solution is so positioned that the dye receiving layer will come into contact with the toner image having the absorbed dye. The dye transfers itself to the dye receiving layer producing a final image on the dye receiving layer.

In this process, the electrostatic latent image may be developed with a liquid developer containing a powdered toner image. Particularly desirable results are obtained with a liquid developer containing a gelatin toner. The quality of the toner image and the color prints produced therefrom is dependent to a large extent upon the quality of the gelatin used and the manner of making the gelatin. Difficulties have been encountered with the use of gelatin obtained from known processes.

One process produces gelatin powder by the dry pulverization of gelatin grains. However, since grains and flakes of gelatin are solid, hard and tenacious, it is very difficult to reduce them to a uniform fine size. A second method includes the use of an aqueous solution of gelatin which is added to and dispersed in a solvent in which gelatin is insoluble. Fine particles of gelatin are produced and collected from the resultant dispersion. This method, however, suffers from a shortcoming that in the steps up to the collection of the aqueous solution of gelatin, gelatin tends to coagulate. Still another available method by which the gelatin particles may be obtained is by spraying the aqueous solution of gelatin into dried air. With this method, however, it is not possible to produce gelatin particles fine enough to serve as the toner 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 a developing system which overcomes the above noted deficiencies.

It is another object of the invention to provide a liquid developer which overcomes the above noted deficiencies.

It is another object of the invention to provide an improved manufacturing process for a liquid developer containing a gelatin toner.

It is another object of the invention to provide a liquid developer useful in the preparation of a gelatin matrix to produce high quality color prints by the dye transfer method.

It is another object of the invention to provide a novel method of producing uniformly finely divided gelatin powder.

The above aforementioned objects and others are accomplished generally speaking by providing a novel process for manufacturing a liquid developer containing a gelatin toner. More specifically, in manufacturing a liquid developer to be used for developing electrostatic latent images according to this invention, the following steps are followed:

1. An aqueous solution of gelatin is cooled and solidified to produce a gelatin gel;

2. The gelatin gel is added to an organic solvent, which is miscible with water and which is incapable of dissolving the gelatin, and the mixture is mechanicially pulverized to form a dispersion of gelatin, and the finely divided gelatin powder is collected from the gelatin dispersion; and

3. The finely divided gelatin powder obtained is dispersed in a carrier liquid having an electric resistance greater than about 10^{10} ohm-cm.

Better imaging results are obtained when the additional step of washing the resultant finely divided gelatin powder with an organic solvent, which is miscible with water and which is incapable of dissolving gelatin,

is accomplished between steps (2) and (3). The washing step serves to eliminate the moisture contained in the finely divided gelatin powder.

Any suitable gelatin may be used in the present invention. Typically, the gelatin may be selected from either skin gelatin or bone gelatin. It is however preferred that the gelatin not have a very wide range of solidifying temperatures. Ordinary refined gelatin of photographic grade is therefore suitable for the objects of this invention.

Any suitable amount of gelatin may be dissolved in water to form the aqueous solution. When the aqueous solution of gelatin is prepared by using gelatin of the above described nature, the gelatin concentration is in the range of from about 1 to about 30 percent by weight of the solution. A gelatin concentration which is too low is disadvantageous because the solidifying point is excessively lowered and at the same time an excessively large volume of water is allowed to remain in the finely divided gelatin powder obtained at the end of step (2). In addition, even if the above described washing step is employed to eliminate the moisture contained in the finely divided gelatin powder, the efficiency of such a washing step is low. On the other hand, if the gelatin concentration is too high, the gelatin gel becomes more solid so that it may become difficult to obtain sufficiently fine gelatin powder by mechanical pulverization. The present invention is characterized by utilizing the fact that a gelatin gel of low concentration has an extremely low degree of mechanical strength.

The aqueous solution of geletain turns into a gelatin gel when it is cooled to the neighborhood of about 0°C. Cooling the solution to a temperature below about −5°C. for a long time should be avoided since at such temperatures the moisture present in the gelatin gel is frozen, and as a consequence, the homogeneous gelatin gel is spoiled.

The gelatin gel thus obtained may be cut to pieces of any suitable size. The gelatin gel may, for example, be cut into cubes each having 1-cm sides, and preserved in a refrigerator, if required. As needed, the gelatin gel may be added to an organic solvent, which is miscible with water but is incapable of dissolving the gelatin.

Any suitable organic solvent may be employed. Particularly satisfactory results are obtained with alcohols such as methanol and ethanol, and ketones such as acetone and methylethyl ketone. The organic solvents are added in amounts of one to 100 parts by volume per one part of gelatin gel. If an insufficient volume of organic solvent is employed, it is not possible to obtain sufficiently fine gelatin particles. If an excessive volume of organic solvent is used, the operational efficiency is degraded and it becomes difficult to collect gelatin in step 2 mentioned above.

When the gelatin gel is pulverized within the above described organic solvent, the gel is finely cut and at the same time the moisture transfers itself from within the gel particles into the organic solvent. As a consequence of this pulverization, the gelatin gel is finely divided and dispersed in the organic solvent. Any suitable means for pulverizing the gelatin gel may be employed. Typical pulverizing means which may be employed include: a ball mill, a vibrating mill, a homogenizer, an attriter such as that manufactured by Mitsui Miike Machinery Company, Ltd., and the like.

The pasty dispersion which is obtained through such pulverization is composed of gelatin and the organic solvent contains a considerable volume of the moisture which was contained in the gelatin gel. In the pasty dispersion, this moisture is mixed partly in the organic solvent and partly in the gelatin particles. Since the presence of moisture in the liquid developer for electrophotography is not desired, it therefore is necessary to remove the moisture from within the finely divided gelatin powder. For this purpose, the fine particles of gelatin present in the paste obtained by the mechanical pulverization of the step (2) are additionally washed with any suitable organic solvent which is miscible with water but incapable of dissolving the gelatin. Typically, the organic solvent is also selected from the group of organic solvents described above. To be more specific, the gelatin particles in the paste are separated from the paste by any suitable means such as filtration, centrifugal separation, and flocculation and subsequently redispersed in the freshly supplied organic solvent. As a result of this treatment, which may be repeated as required, the quantity of moisture contained in the gelatin particles is substantially decreased. Simultaneously, the gelatin particles shrink so that it may be more difficult to collect the particles.

The gelatin particles which have been sufficiently dehydrated by washing are recollected by any suitable means such as by filtration, centrifugal separation, flocculation and the like and then are dispersed in the developer carrier liquid. Alternatively, the gelatin particles may be dried to a powdery state and then added to the developer carrier liquid. It has been found, however, that a more stable dispersion of gelatin can be obtained by adding the gelatin particles while still wet with the organic solvent to the developer carrier liquid. To this end, the paste of gelatin particles in the carrier liquid may be added to the developer carrier liquid.

Any suitable carrier liquid may be employed in the practice of this invention. Typically, the carrier liquid is substantially the same as that which is used in conventional liquid developers in electrophotography and is a nonpolar organic solvent having high electric resistance. Preferably, the electric resistance is greater than about 10^{10} ohm-cm since with a low electric resistance, destruction of the electrostatic latent image formed on the imaging surface may occur. Examples of typical solvents which may be used as the carrier liquid are cyclohexane, kerosene, gasoline, isooctane, heptane, hexane, and chlorofluorinated hydrocarbons.

The carrier liquid may also contain various soluble components, such as nonionic surface active agents, dispersing agents, and fixing agents. Any suitable amount of gelatin may be added to the carrier liquid to form the liquid developer. The toner concentration of gelatin in the carrier liquid is preferably within the range of from about 0.001 to about 5 percent by weight based on the weight of the carrier liquid. When the quantity of gelatin 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 gelatin toner concentration is too high, fogging tends to occur and the dispersion stability required for the liquid developer may deteriorate.

By using the liquid developer containing the gelatin according to this invention, a gelatin 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 a liquid developer containing the gelatin toner.

3. The gelatin toner image thus obtained is fixed by any suitable method to form the gelatin matrix of the printing master.

To form 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 gelatin toner image and the image is allowed to absorb the dye. If desired, excess dye may be removed.

5. A separately prepared material having a surface layer capable of readily absorbing the dye solution is positioned so that the dye receiving layer thereof may be brought into contact with the dye absorbing gelatin toner image. At this point, the dye transfers to the dye receiving layer to form a final image on the dye receiving layer.

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

Any suitable imaging surface may be employed. Typically, the imaging surface comprises an insulating recording layer capable of retaining an electric charge. It may, for example, be selected from the well known group of dielectric materials and an electrophotographic sensitive layer containing a photoconductive substance and an insulating resin on a waterproof base. In ordinary electrophotographic sensitive materials, a low electric resistant layer is provided between the sensitive layer and the base. The well known photoconductive materials may typically be employed.

When an electrophotographic sensitive layer using zinc oxide is employed as the imaging surface, the electrostatic latent image is generally of negative polarity. Since the gelatin toner according to the present invention assumes a positive polarity, a positive image is obtained with the gelatin particles being attracted to the charged areas of the imaging surface. Where a selenium deposited layer is used as the imaging surface, the electrostatic latent image generally assumes a positive polarity. When the liquid developer agent of this invention is used on this layer, therefore, a negative image may be obtained with the gelatin particles being repelled from the charged areas of the imaging surface.

After the toner image is formed, it is fixed to the imaging surface in any suitable manner. Typical satisfactory methods for fixing the toner image to the imaging surface include thermo fixation wherein the gelatin image is softened by the application of heat; solvent fixation wherein a certain solvent softens the toner image; and, steam fixation wherein the application of steam softens or melts and fixes the toner. The toner image may also be fixed by either embedding the image in the surface of the recording layer or by overcoating the image with a suitable resinous material which permits the dye solution to diffuse through a thin film into the toner material.

DESCRIPTION OF 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

Five grams of photographic grade gelatin (bone gelatin) are added to 95 milliliters of distilled water. After standing for 30 minutes, the gelatin swelled. The gelatin is dissolved by heating the mixture to 60°C. while under agitation. The aqueous solution containing 5 percent by weight of gelatin so obtained is placed in a refrigerator kept at 5°C. and the gelatin is permitted to solidify. Ten (10) grams of solidified gelatin and 100 milliliters of acetone are placed in a ball mill and pulverized for ten hours. An acetone dispersion of gelatin having a milky white color is obtained. The gelatin particles are collected by subjecting the acetone dispersion to centrifugal separation. The collected gelatin particles are combined with 100 milliliters of fresh acetone and pulverized in a ball mill for one hour. The resultant gelatin dispersion is again subjected to centrifugal separation to collect the gelatin particles. The geletin particles are washed an additional time with acetone. Finally, 5 milliliters of acetone paste containing gelatin particles are obtained.

This paste is combined with 5 milliliters of soybean oil and agitated sufficiently. The mixture is dispersed in a carrier liquid having the following composition, while under the application of ultrasonic waves.

Cyclohexane	400 ml
Kerosene	80 ml
Soybean Oil	18 ml
Rosin-modified phenolformaldehyde	2 g

A liquid developer having a milky white color is obtained. The soybean oil in the carrier liquid serves as the dispersant. The rosin-modified phenolformaldehyde functions as the fixing agent. In other words, the rosin-modified phenolformaldehyde resin remains dissolved in the carrier liquid, but, when placed in a washing bath for example of Isopar E, an isoparaffin bath for cleaning, available from Humble Oil and Refining Company, it is insolubilized. The insolubilization enables the gelatin toner to be fixed.

The kerosene is added for the purpose of suitably controlling the speed at which the liquid developer is evaporated. In this liquid developer, the gelatin toner assumes positive electric charge.

Separately, 100 parts by weight of photoconductive zinc oxide and 20 parts by weight of the epoxy ester of dehydrated castor oil fatty acid are mixed with a suitable quantity of toluene and mixed into a uniform coating solution. In a small quantity of ethylene glycol monomethly ether, 1000 parts of fluorescein 20 and 100 parts of tetrobromophenyl blue 20 are dissolved, and the resultant solution is added to the coating solution to extend the photosensitivity of the zinc oxide to the entire visible zone. The mixture, with a suitable quantity of toluene combined therewith, is spread on a polyethylene-terephthalate film having a thickness of about 90 microns and having deposited therein a dry aluminum coating of about 8 microns. When sufficiently dried in a dark place, the product functions satisfactorily as an electrophotographic sensitive material.

This electrophotographic sensitive material is exposed to a negative corona discharge in a dark place to have its surface uniformly electrically charged. A color

slide chosen as original is loaded on an enlarger, with a red filter laid 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 above described liquid developer 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 close to the vat bottom. After being submersed in the developer for about 90 seconds, the sensitive material is removed, washed with isoparaffin, and then dried. After development, the sheet is soaked in 1 percent methanol solution of formalin. The sheet is then left to stand overnight at room temperature to allow the gelatin image to form into a hard membrane.

After the hardening treatment, the sensitive material now carrying the gelatin toner image is soaked in an aqueous solution containing 40 percent by weight of acetic acid for 2 minutes. This treatment caused substantially all of the zinc oxide present in the sensitive layer to be removed from the layer.

The procedure to this point produces a matrix to be used for cyan printing.

By following the same procedure, another sheet is exposed to light projected through the combination of the same original with a green filter. With the same development technique with the liquid developer containing a gelatin toner a matrix for magenta printing is obtained. By combining the original with a blue filter in the similar manner, a matrix for yellow printing is obtained.

The three matrixes are soaked for two minutes in the aqueous solutions of Color Index Acid Blue 54, Acid Violet 7, and Acid Yellow 23 respectively, removed from the baths, and then washed in a bath of acetic acid.

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

EXAMPLE II

Methylethyl ketone is used in the place of acetone as the solvent when the gelatin gel is pulverized in the procedure of Example I. The other operating conditions are the same as in Example I. A liquid developer having a milky white color is obtained. The gelatin toner in this liquid developer assumes a positive electric charge. By the same procedure as in Example I gelatin matrixes are obtained.

EXAMPLE III

Ethanol is used in the place of acetone as the solvent while the gelatin gel is pulverized in the procedure of Example I. The other operating conditions are the same as in Example I. A liquid developer containing the gelatin toner and having positive electric charge is obtained. Through the same procedure as in Example I, gelatin matrixes are produced.

EXAMPLE IV

Methylethyl ketone is used as the solvent for washing the gelatin particles in the procedure of Example I. Gelatin matrixes are obtained by following the same procedure as in Example I.

EXAMPLE V

A liquid developer is prepared by following the procedure of Example I, while using methylethyl ketone as the solvent during the time of pulverizing the gelatin gel. A 1:1 methylisobutyl ketone-acetone mixture as the solvent for washing the gelatin particles is employed. Gelatin matrixes prepared by following the same procedure as in Example I are obtained.

EXAMPLE VI

In the procedure of Example I, methylethyl ketone is used as the solvent during the time of pulverizing the gelatin gel. Methanol is used for washing gelatin particles, and finally acetone is used to prepare the paste of gelatin. The paste is dispersed in the same carrier liquid as in Example I and the procedure of Example I is followed with the resultant liquid developer to produce gelatin matrixes.

EXAMPLE VII

On an aluminum plate, selenium is vacuum deposited to a thickness of about 60 microns to produce a xerographic plate. The plate is exposed to positive corona discharge in a dark plate to uniformly charge the surface to +350V. A colored negative film is selected as an original and loaded on an enlarger, with a red filter laid on the slide. The positively charged sensitive plate is then exposed to light projected through the original.

The exposed xerographic plate is then wetted with kerosene and soaked in the liquid developer described in Example I. At this time, a separately prepared metal plate is positioned close to the surface of the xerographic plate so as to serve as the developing electrode. The space between the xerographic plate and the developing electrode is about 0.2mm. In order to effect the so-called solid area development, a bias voltage of −180V was applied to the xerographic plate. After about 90 seconds of submersion, the plate is removed and washed with Isopar E (isoparaffin solvent available from Humble Oil and Refining Company) and dried.

Subsequently, the developed xerographic plate is soaked in a methanol solution containing 1 percent by weight of formalin and thereafter left to stand at room temperature for 5 hours.

A matrix for cyan printing is produced. In entirely the same manner, another xerographic plate is exposed to light projected through the same original combined with a green filter. The same treatment is given thereafter to obtain a matrix for magenta printing. A matrix for yellow pringing is obtained by combining the same original with a blue filter.

The three matrixes are dyed respectively in the same manner as in Example I.

A sheet having a gelatin layer deposited on the surface thereof is mordanted. Thereafter, the three matrixes were registered with and pressed against the sheet, one after another. This treatment causes the dyes absorbed on the toner images to be transferred to the gelatin layer. Consequently, a colored positive image having excellent quality was obtained. Forty duplicates

are made using these matrixes with no appreciable change in print quality.

The xerographic plate which had been used is washed sufficiently with warm water followed by washing with an acetone-toluene mixture and finally washed with toluene and dried. After this treatment, the xerographic plate may be reused.

Although specific materials and operational techniques are set forth in the above exemplary embodiments using the developing materials and techniques of this invention, these are merely intended as illustrations of the present invention. There are other materials and techniques than those listed above which may be substituted with similar results. 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 method of making a liquid developer containing gelatin toner comprising the steps of:

a. forming an aqueous solution consisting essentially of from about 1 to about 30 percent by weight of gelatin based on the weight of the solution;

b. cooling the aqueous gelatin solution to solidify the gelatin to form a gelatin gel;

c. adding the gelatin gel to an organic solvent which is miscible with water and is incapable of dissolving gelatin;

d. mechanically pulverizing the gelatin gel in said solvent to form a fine dispersion of gelatin in said solvent;

e. collecting finely divided gelatin powder from the gelatin dispersion and washing said gelatin powder with an organic solvent which is miscible with water and is incapable of dissolving gelatin, so as to at least substantially reduce the water content of said gelatin powder; and,

f. dispersing the finely divided gelatin powder in a carrier liquid having an electrical resistivity greater than about 10^{10} ohm-cm to form a liquid developer.

2. The method of Claim **1** wherein the aqueous solution of gelatin is cooled to a temperature between about 0°C. and about −5°C.

3. The method of claim **1** wherein the gelatin powder is of substantially uniform size and is substantially free of water.

4. The method of claim **1** wherein the finely divided gelatin powder is added to the carrier liquid in an amount of form about 0.001 to about 5 percent by weight of the carrier liquid.

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