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3,679,586

LIQUID ELECTROPHOTOGRAPHIC DEVELOPERS CONTAINING A DYE MODIFIED POLYPEPTIDE

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6 Claims

ABSTRACT OF THE DISCLOSURE

An electrophotographic liquid developer comprising a highly insulating non-polar carrier liquid and a toner dispersed therein, characterized by that said toner comprises a polypeptide compound which is chemically united with a reactive dye containing both of an electron affinitive functional group capable of reacting with NH_2 , or OH group in a hydrophilic polypeptide compound and of a chromogenic group exhibiting an optical absorption in the visible region of the spectrum and the method for making the developer.

This invention relates to a new electrophotographic liquid developer which is especially suited for reproduction of multicolored images. Further, it relates to a developer which exhibits complete color mixing when used in over-print multicolor development and which has improved spectral absorption characteristics.

Electrophotographic process is widely used to produce visible image informations, referred to as electrophotography or xerography, in which the most prevailing system in photocopy use comprises the following operations. A photoconductive layer coated on a more or less electrically conductive support is imparted a uniform surface charge in subdued light, and then subjected to image exposure by means of suitable radiation energy source modulated imagewise, whereby the surface charge is discharged in proportion to radiation intensity. Thus, an electrostatic surface pattern results on the photoconductive layer having a charge density distribution inversely proportional to the amount of exposure. That is, the strongly irradiated area of the photoconductive layer holds a low residual charge density, while weakly irradiated area retains a relatively high charge density.

The electrostatic charge pattern which is sometimes referred to as electrostatic latent image is converted visible by developing technique well known in the field of xerography. A most common operation of development comprises applying a finely-divided developing powder or toner onto the exposed layer. The toner deposits in accordance with the charge density distribution on the latent image thus forming a visible image.

A variety of development techniques are carried out according to requirement to final images. A toner which is made to assume a charge of an opposite polarity to the latent image to be developed accomplishes positive to positive reproduction by virtue of coulomb attraction. Alternatively, a toner having the same polarity of charge may be employed whereby the toner deposits on discharged area in the latent image thus realizing negative to positive reproduction. The latter process is sometimes referred to as repulsion or reversal development and forms a visible image optically inverted to the one obtained by attraction development.

Many types of developing agent are known among which a liquid developer described in, for example, U.S. patent specification 2,907,674 can provide a high-resolution image.

The developers disclosed in the above patent are remarkably improved by utilizing charge-control agents in place of dispersing sole pigment particles in carrier liquids. The purpose or function of charge-control agent is to provide dispersed particles with desired polarity as well as suitable amount of charge. In other words, electrophoretic properties of pigment particles dispersed by themselves are quite unstable, and such instability can be controlled or overcome by covering the particles with resinous charge-control agents. Accordingly, the toner of the developers based on such an idea are associated with resinous surface coating or adsorption layer.

There has been developed an electrophotographic color print process in which two or more differently colored toner images are over-printed on a single electrophotographic sheet by repeating charging, exposure and development sequentially. This method, usually not including toner transfer operation, is called over-print technique.

When the multicolored toner image is formed by over-print technique with the use of liquid developers such as described above, unsatisfactory mixing of color takes place due to incomplete transparency of pigment particles. This defect can be improved to some extent by minimizing toner particle size. Besides, spectral absorption characteristics of ordinary pigments considerably deviate from ideal ones; therefore, in order to realize a faithful reproduction of color one needs to resort to the technique of color masking which makes the process quite complicated.

The inventors have developed a new type of developer overcoming the above mentioned deficiencies as a result of investigation on the possibility of producing developers with materials quite different from those of conventional developers.

Accordingly, the object of the present invention is to provide a new type of liquid developer having new composition and improved properties. Another object is to provide liquid developers capable of accurate reproduction of color in over-printing electrophotographic process. Still another object is to disclose a new method of preparing a new type of liquid developer.

Liquid developers of the present invention are characterized by that they comprise a highly electrically insulating carrier liquid and finely-divided toner dispersed therein comprising originally water soluble polypeptide, the hydroxyl and/or amino radicals of which are reacted with reactive dyestuffs.

It is to be noticed that the present invention is based on the development of new technique which has made it possible to disperse with high stability polypeptide particles such as gelatin, glue, casein, albumine, etc. in non-polar insulating liquids. This invention has its primary importance in utilization of reactive dyes in conjunction with this new technique.

The toner in the developer prepared in accordance with the present invention is dye-connected polypeptide, and the dye molecules are dispersed in the polymer in molecular order thus providing the toner with perfect clarity far better than that of pigment based toners. Thus, when such developers are used for over-print electrophotography to produce multicolored images, images of noticeably improved quality result by virtue of perfect mixing of primary colors.

Toners including a relatively small quantity of reactive dye may also be used to prepare dye-transfer master image in accordance with procedures disclosed in another patent application of the same inventors (German Pat. 1,811,872) whereby developed toner images are easily observed so as to examine the quality.

Now there will be explained the method of preparing developers according to the invention.

REACTION OF POLYPEPTIDES WITH
REACTIVE DYES

Any types of polypeptide may be used for the present purpose provided that they contain hydroxyl and/or amino radicals which can enter into chemical reaction with reactive dyes and that they are soluble in water or strongly hydrophilic. Typical examples include gelatin, glue, casein, albumen, etc. and their derivatives such as phthalated gelatin. One or more of these is dissolved in a solvent system mainly comprising water; to the resulting solution or colloidal dispersion is added one or more of reactive dyes well known in the field of textile or dyestuff industry. The polypeptide and the dye are then allowed to react under a suitable condition.

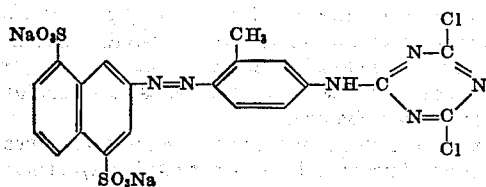
Various types and properties of chemically reactive dyes are described in detail in the following literatures: "Shin Senryo Kagaku" (Revised Dyestuff Chemistry) by Yutaka Hosoda from pp. 290-295; "Atarashii Gosei Kagaku Vol. 7" (Advance of Synthetic Chemistry—New Types of Dyes and Pigments—pp. 9-34; Journal of Industrial Chemistry Japan vol. 1, No. 1 (1964), pp. 17-25; and from pp. 485-522 of Color Index, 2nd edition, published by The Society of Dyers and Colorists, the American Association of Textile Chemists and Colorists.

Our experiments have proved that chemically reactive dyes which consist of a chromophore and one or more chemically active groups capable of entering into coupling reaction with OH radical in cellulose fiber or NH₂ radical in polyamide resin can also react with polypeptides such as gelatin, casein, albumin, etc., to form colored products.

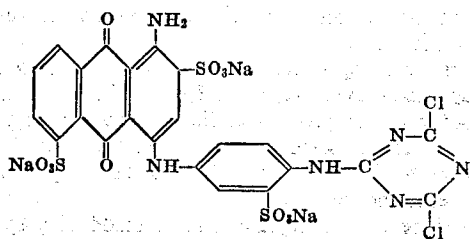
Reactive dyes generally consist of a chromophore exhibiting absorption in the visible region of the spectrum, suitable solubilizing groups and reactive groups; typical ones have as reactive group dichlorotriazine or monochlorotriazine radicals. They are designed so as to react with OH or NH₂ groups in textile fibers under alkaline conditions. Reaction with polypeptide also proceeds under mildly alkaline condition. Formation of chemical bond between polypeptide and reactive dyes can clearly be confirmed by the following testing method; to a processed gelatin solution is added a hardening agent to convert the polypeptide insoluble in water, then the hardened gelatin is immersed in cold fresh water; when a bond formation has taken place between the gelatin and the dye, no dissolution of the dye from the hardened mass is observed.

Structural formulas of several typical reactive dyes are shown below.

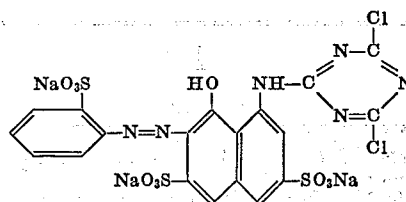
Procion Yellow RS (ICI)



Procion Blue 3GS (ICI)



Procion Brilliant Red 2BS (ICI)



One can effect a reaction between a polypeptide such as gelatin and these dyes by dissolving the two components together with a weakly alkaline material such as sodium carbonate in water and keeping the resulting solution at 60 to 100° C. for about ten to several ten minutes.

Normally 0.1 to 20 parts by weight of a reactive dye may be chemically united with 100 parts by weight of gelatin. To obtain a pale color toner a dye less than 2 parts is sufficient, while for a deeply colored toner 2 to 10 parts of dye is preferred. A black or grey toner can be prepared by utilizing two or more differently colored dyes, or by mixing two or more kinds of toner each of which includes a differently colored dye.

For a rapid completion of reaction it is desirable for a polypeptide to be water soluble, but after the reaction the resulting material should preferably be water-insoluble. Accordingly, the dye connected polypeptide is advantageously hardened by a suitable hardening agent. The solvent system for reaction may comprise solely of water or contain water-miscible organic solvents such as alcohols, ketones, Cellosolves, etc., among which acetone is preferred as regards the feasibility of liquid developer preparation. The content of organic solvents ordinarily falls in the range from 10 to 20%.

The solution after the completion of reaction is cooled to undergo gelling and the gel is suitably dehydrated and rinsed for subsequent processing.

PREPARATION OF A FINELY DIVIDED
POLYPEPTIDE

A gel or sol of a polypeptide united with a reactive dye, which will be referred to as dyed polypeptide for simplicity, is adequately diluted with water or a mixture of water and an organic solvent. The amount of the organic solvent is limited so as not to cause the precipitation of the dyes polypeptide. Then the diluted sol is thrown into an excessive amount of water-miscible organic solvent under vigorous stirring for example by means of ultrasonic vibration to form fine particles of the dyed polypeptide.

A practical example of formulation of a dyed polypeptide solution containing an organic solvent is given by the following:

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Dyed gelatin	5
Water	95
Methanol	100

This mixture forms a clear solution when heated at 25° C.

It is possible to obtain a fine powder of a dyed polypeptide by adding directly an aqueous solution of the polypeptide into an organic solvent which is a nonsolvent for said polypeptide, but such a process is prone to bring about coagulation of the polypeptide. Coagulation can be prevented by simultaneously adding a nonpolar organic solvent solution of a resinous material which also becomes insoluble in the resulting mixture. The nonpolar solvent to be used must be compatible with the polar solvent employed to insolubilize the polypeptide. This requirement can be met for almost any non-polar solvent in case of acetone as the polar solvent, while methanol is immiscible with solvents of extremely low solubility parameter such as kerosene or isoparaffinic solvents. Generally speaking, suitable nonpolar solvents include cyclohexane, Decalin, benzene, toluene, xylene, esters, in which there may be dissolved one or more of the following resins which are

insoluble in polar solvents such as acetone or methanol; polyisobutylene, polybutene, polystyrene, styrenebutadiene copolymer, rosin modified phenol-formaldehyde resin, etc.

When a nonpolar solution of such formulation is added with vigorous stirring into a large excess of a polar solution such as acetone, methanol, and ethanol, simultaneously with the addition of a dyed-polypeptide solution, insolubilization of the polypeptide and of the resin in the nonpolar solution proceed whereby the latter encapsulates the former preventing coagulation of the former.

A prominent feature of this coprecipitation method lies in that it enables formation of an extremely fine toner as well as perfect removal of residual water content in the polypeptide. The supernatant liquid may be removed by either decantation or centrifugal separation. The precipitate usually includes a polypeptide powder of less than 1 micron, and the size of the powder does not tend to grow during a prolonged storage.

PREPARATION OF A LIQUID DEVELOPER

The precipitate including a finely divided dyed polypeptide is repeatedly purified by washing to remove inorganic ingredients and residual water. Then it is added to a nonpolar organic solvent which plays a roll of carrier liquid for the liquid developer whereby the resin in the precipitate dissolves in the solvent, releasing the dyed polypeptide in the solvent in the form of fine particles. In the resulting dispersion, part of the resin seems to be adsorbed on the surface of the polypeptide particles to stabilize colloidal dispersion. Therefore no intense stirring operation is necessary at this process.

The dispersion thus prepared experimentally proved quite stable for a prolonged storage.

Cyclohexane, Tetralin, Decalin, and kerosene are among suitable carrier liquid; isoparaffinic and fluorinated hydrocarbons which have a far weak solving power are less suited since they cannot dissolve many of above-mentioned resins.

Organic liquids which have solubility parameters greater than 7.0 and about 8.8 at room temperature or Kauribitanol values of from 26 to 85 are suited for carrier liquid. A minor amount of more powerful solvents such as aromatic hydrocarbons or ketones may be added to those solvents, the upper limit of addition being about 5 parts in 100 parts of the total carrier liquid. Mixed solvent systems may also be used provided that the solubility parameters for the systems fall in the above mentioned range.

The carrier liquid phase of a developer prepared in the described manner therefore comprises a non-polar organic liquid and a resinous component dissolved in said liquid, and the liquid phase should desirably have an electrical resistance not lower than 10^{10} ohms-cm. not to cause destruction of an electrostatic latent image.

Other ingredients permitted include viscosity controlling agents and surface active agents. Polypeptide structure is known favorable to assume an electrostatic charge of positive polarity in many non-polar organic liquids which characteristic still holds in most cases after reactive dyestuffs are united.

To strengthen or improve electrophoretic properties of developers of the present invention, one may resort to a technique in which particles having a strong tendency of acquiring a charge of desired polarity are added to the developer. According to this technique developers of either polarity, positive or negative, are possible depending on the amount and the nature of the particles to be added. Materials used to prepare positively charged particles include ethyl cellulose, hydroxyethyl cellulose, polymethacrylates, etc., while resinous materials which acquire negative charges in insulating liquids are copolymers containing vinyl chloride, nitrocellulose, polyvinylidene fluoride, etc.

Liquid developers of the present invention offers another advantage that the resulting toner images would not accept a high electrical potential because of the extremely hydrophilic nature of the principal ingredients. This means that in the over-printing electrophotographic process, whereby charging of the developed image at the subsequent charging is not desirable, the present developers are especially suited, not permitting undesirable deposition of toner on the already developed area.

In such uses as require less hydrophilic toners, one may resort to hardening of polypeptides during the manufacturing procedures to convert the toner water-insoluble, or may harden the image after development.

EXAMPLE I

5 g. of gelatin was dissolved in 20 ml. of water by heating after being allowed to swell. A reactive dye solution was prepared by dissolving 200 mg. of Remazol Brilliant Violet (Hoechst) in 2 ml. of water.

These two solutions were mixed together and 5 g. of 5% sodium carbonate solution was further added. The resulting solution was heated over a boiling water bath for 15 minutes. Then the solution was left to cool; the resulting gel assumed magenta color. A part of the gel was thrown in a cold water kept at 0° C., but no dissolving of the dye was observed to show the formation of chemical bonding between the dye and the gelatin.

Three g. of this gel was dissolved upon heating into a mixture of water and methanol in the ratio of 7:8.

On the other hand, a solution was prepared comprising 80 g. of toluol, 10 g. of linseed oil, and 15 g. of resin modified phenolformaldehyde resin, which is soluble in toluol or cyclohexane and not in acetone. This solution and the gelatin solution prepared above were simultaneously added into 320 g. of acetone whereby a precipitate resulted. The precipitate was separated by means of centrifuge and further washed with acetone. The obtained pasty precipitate was dispersed in 400 ml. of cyclohexane.

The dyed gelatin particles in the dispersion proved to be positively charged and thus to undergo an attractive deposition on an electrostatic latent image of negative polarity. The appearance of a developed image was deep magenta.

EXAMPLE II

A dyed gelatin gel was prepared in the same procedure as was described in the foregoing example except that Remazol Brilliant Violet purchased from ICI was replaced by Procion Brilliant Red H-3BS.

Five of the resulting gel was dissolved in 8 g. hot water, and to the solution was added 15 g. of methanol.

Separately 90 g. of 20% toluol solution of rosin modified phenol-formaldehyde resin was prepared. These two solutions were simultaneously added in 320 g. of acetone with vigorous stirring. Immediately a bulky precipitate was formed, which was processed just as in Example I. The dispersion also contained a positively charged toner which gave a reddish magenta image.

EXAMPLE III

The same operations were repeated with the use of polybutene resin in place of rosin modified phenol-formaldehyde resin. A similarly good liquid developer was obtained.

EXAMPLE IV

1 g. of soya bean casein was dissolved in 5 g. of water together with a slight amount of sodium carbonate then 20 mg. of Reactone Navy Blue GRL was dissolved. This mixture was heated at 100° C. for 15 minutes. After cooling, 5 ml. of methanol was added.

Separately, a second solution was prepared by dissolving 10 g. of linseed oil and 15 g. of rosin modified phenol-formaldehyde resin in 80 g. of toluol. To 300 g. of acetone were added dropwise these two solutions to obtain a colored precipitate. The precipitate was taken

out by a centrifuge, and the supernatant liquid was replaced by acetone. After washing, the paste was dispersed in 400 ml. of cyclohexane. A satisfactory liquid developer for electrophotography resulted.

EXAMPLE V

A liquid developer containing a toner of negative polarity was prepared by adding to 40 parts of the developer prepared in Example II 60 parts of a dispersion comprising a finely-divided (particle size 0.3 micron) vinyl chloride/vinyl acetate copolymer dispersed in cyclohexane.

EXAMPLE VI

A black toner containing developer was obtained by following the procedure of Example I with the use of Cibacron Black RP of Ciba Ltd. in place of Remazol.

What is claimed is:

1. An electrophotographic liquid developer comprising a highly insulating non-polar carrier liquid and a toner dispersed therein, said toner comprising finely divided particles of the reaction product of about 100 parts by weight of a hydrophilic polypeptide and about 0.1 to 20 parts by weight of a reactive dye containing both an electron affinitive functional group capable of reacting with the NH_2 or OH groups of said polypeptide and a chromogenic group exhibiting an optical absorption in the visible region of the spectrum.

2. Method of forming a liquid developer comprising a highly insulating, non-polar carrier liquid and a toner dispersed therein, said toner comprising a reactive dye-modified polypeptide compound group consisting of gelatin, casein, albumen and glue, said polypeptide being chemically united with a reactive dye containing both an electron affinitive functional group capable of reacting with NH_2 or OH group in a hydrophilic polypeptide compound and a chromogenic group exhibiting an optical absorption in the visible region of the spectrum, which comprises the steps of

(1) dispersing in an organic solvent which is miscible with water but is a non-solvent for the reactive dye modified polypeptide, an aqueous solution of said modified polypeptide or a solution of said polypeptide in a mixed solvent of water and an alcohol prepared by incorporating in the aqueous solution of said polypeptide an alcohol in an amount which causes no precipitation of said polypeptide to provide a dispersion of said polypeptide grains;

(2) adding to the resultant dispersion of said polypeptide a solution of a resin which is insoluble in the

organic solvent for said polypeptide dispersion but soluble in a carrier liquid having an electric resistance of higher than 10^{10} ohm-cm. to coprecipitate the said polypeptide grains and the resin; and

(3) adding the precipitates of said polypeptide grains and the resin to the carrier liquid mentioned above.

3. The method as claimed in claim 2, wherein said resin used in step (2) is polyisobutylene resin, polybutene resin, styrene resin, styrene-butadiene copolymer or resin-modified phenol-formaldehyde resin.

4. An electrophotographic liquid developer as in claim 1 where said polypeptide compounds is selected from the group consisting of gelatin, casein, albumen, and glue.

5. An electrophotographic liquid developer as in claim 1 where said polypeptide compound is gelatin and where 0.1 to 20 parts by weight of said reactive dye are chemically united with 100 parts by weight of said gelatin.

6. An electrophotographic liquid developer as in claim 2 where said polypeptide compound is gelatin and where 0.1 to 20 parts by weight of said reactive dye are chemically united with 100 parts by weight of said gelatin.

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GEORGE F. LESMES, Primary Examiner

J. P. BRAMMER, Assistant Examiner

U.S. Cl. X.R.

106—135; 260—8, 117, 119, 121