United States Patent

Machida et al.

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[54] LIQUID DEVELOPER FOR USE IN ELECTROPHOTOGRAPHY

[72] Inventors: **Hazime Machida; Zenjiro Okuno,** both of Tokyo, Japan

[73] Assignee: **Kabushiki Kaisha Ricoh,** Tokyo, Japan

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.**..... **252/62.1,** 106/308, 260/41

[51] **Int. Cl.**.....**G03g 9/04**

[58] **Field of Search**.....252/62.1; 106/308; 260/41

[56] **References Cited**

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Primary Examiner—George F. Lesmes
Assistant Examiner—J. P. Brammer
Attorney—Woodhams, Blanchard and Flynn

[57] **ABSTRACT**

A liquid developer for use in electrophotography, comprising a copolymerically grafted pigment toner dispersed in a carrier liquid consisting of a paraffinic or an isoparaffinic hydrocarbon having a high-electric resistance and a low-dielectric constant, said toner being prepared by subjecting the particles of at least two kinds of pigments each having a benzenoid ring to graft copolymerization with at least three kinds of unsaturated compounds each being capable of contributing to the stable regulation of the polarity of said particles of pigments, their uniform dispersion in the carrier liquid and the satisfactory adhesion of the particles onto the surface of electrophotographic copying papers thereby chemically uniting said compounds directly to said particles of pigments.

5 Claims, No Drawings

LIQUID DEVELOPER FOR USE IN ELECTROPHOTOGRAPHY

This application is a continuation-in-part of our copending application, Ser. No. 682,512, filed Nov. 13, 1967.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is concerned with a liquid developer which is used in the wet development of electrophotographs.

2. Description of the Prior Art

A liquid developer for use in electrophotography, in general, is prepared by first kneading a mixture of particles of a pigment, a resin, a fat, a surface active agent, a stabilizer or like materials which, individually, are capable of either regulating the polarity of the particles of the pigment, dispersing the particles uniformly in a solvent or imparting to the particles the property of adhering to the electrophotographic copying papers, and then dispersing the kneaded mixture in an organic solvent. The liquid developer is operative in such a way, in practice, that the polarity of the particles of the pigment contained in the developer is kept under a regulated state, by being impressed with either a positive or a negative charge. Therefore, when a copying paper carrying an electrostatic latent image on one surface thereof is brought into contact with these particles of pigment contained in the developer, the pigment particles are electrostatically absorbed onto the oppositely charged areas of the copying paper, and thus there is formed a visible copied image on the surface of the copying paper.

Such a liquid developer for use in electrophotography as described above is required to possess the following properties:

1. the particles of pigment must be satisfactorily dispersed in the carrier liquid,

2. these particles are impressed distinctly with either a positive or a negative charge,

3. the particles must have an interfacial potential which is sufficient for generating electrophoresis, and

4. these properties do not deteriorate during repeated use of the developer for an extended period of time.

Many of the conventional liquid developers have employed naturally occurring rosin, asphalt or synthetic alkyd resins as the agent for dispersing the particles of pigment in the carrier solution and also for regulating the polarity of these particles. These conventional liquid developers further used paraffinic hydrocarbons as the carrier liquid (media for dispersing the pigment particles). However, when naturally occurring rosin or asphalt was used as a constituent of a developer, it was impossible to manufacture a liquid developer having uniform developing ability and uniform quality. Also, conventional liquid developers were of a simple composition, namely, a kneaded mixture consisting of particles of pigment, a polarity regulating agent, a particle dispersing agent and the like dispersed in a carrier liquid. Such a liquid developer of the prior art showed, for some time after it was manufactured, a satisfactory dispersion of pigment particles and also a distinct polarity of the particles, because, during this initial period, the polarity regulating agent as well as other agents were maintained in their state of being relatively firmly absorbed onto the surfaces of the pigment particles. With the passage of time, however, these agents which had been absorbed onto the surfaces of the pigment particles gradually became released therefrom, causing deterioration of the dispersability of the particles and the property of effecting a satisfactory polarity regulation of these particles. For this reason, it was extremely difficult to preserve, for an extended period of time, as excellent developability of the liquid developer which it possessed at the time the developer was manufactured.

SUMMARY OF THE INVENTION

It is, therefore, the object of the present invention to provide a liquid developer for use in electrophotography, which is free of all of the aforesaid various drawbacks of the liquid developers of the prior art.

We have already worked out and proposed a liquid developer for use in electrophotography, as disclosed in out U.S. Pat. application, Ser. No. 682,512, which provides an improvement in the liquid developers of the prior art. This liquid developer was prepared by dispersing, in an organic carrier liquid, a toner obtained from a graft copolymerization of two kinds of unsaturated compounds performed on the pigment particles. More particularly, this liquid developer is prepared by dispersing, in an organic solvent either directly or together with a surface active agent, a toner which is made by subjecting the particles of one kind of pigment to a graft copolymerization with two kinds of unsaturated compounds.

The present invention has been discovered as a result of further research we conducted on the aforesaid improved liquid developer.

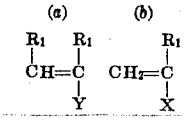
According to the present invention, there is provided a novel liquid developer for use in electrophotography, which has, in particular, an ability to keep a stable polarity for an extended period of time and also an ability to cause a splendid adhesion of the pigment particles onto the surface of the copying paper when the latter is developed, and which further permits the user to freely perform the regulation of the polarity of the pigment particles contained in the carrier liquid and to freely control the color tone of the copied image which is developed. The liquid developer is prepared by dispersing in

1. a dispersing medium consisting of either a paraffinic or an isoparaffinic hydrocarbon having a relatively high electric resistance and a relatively low dielectric constant,

2. a toner consisting of the particles of a multiple-copolymer which is obtained from a graft copolymerization of at least three kinds of unsaturated polymeric compounds which are expressed by the general formula (a) and also by the general formula (b) as mentioned below and the particles of at least two kinds of pigments.

GENERAL FORMULAS

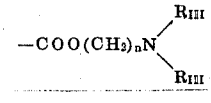
(a) (b)



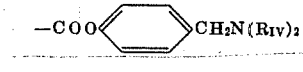
wherein: R_I is selected from the group consisting of radicals of the formula $-C_nH_{2n+1}$ (an alkyl radical wherein n=1 −3), phenyl radicals, tosyl radicals and hydrogen;

Y is selected from the group consisting of $-COOR_{II}$ [wherein R_{II} is selected from the group consisting of radicals expressed by formula $-C_nH_{2n+1}$ (wherein $4 \leqq n \leqq 20$)], $-OCOC_nH_{2n+1}$ (wherein $1 \leqq n \leqq 20$), and $-C_nH_{2n+1}$ (an alkyl radical wherein $1 \leqq n \leqq 20$);

X is selected from the group consisting of



(wherein n=2–4, and R_{III} is selected from the group consisting of hydrogen, alkyl radicals having one to four carbon atoms, phenyl radicals and tosyl radicals), —OH, —CN, $-NH_2$, $-CON(R_V)_2$ [wherein R_V is selected from the group consisting of hydrogen and $-C_nH_{2n+1}$ (an alkyl radical, wherein $1 \leqq n \leqq 3$)] and



[wherein R_{IV} is selected from the group consisting of hydrogen and C_nH_{2n+1} (an alkyl radical, wherein $1 \leqq n \leqq 3$)].

In the present invention, there is used a toner consisting of a so-called graft copolymer which is obtained from the graft copolymerization of the following materials,

1. at least three kinds of unsaturated compounds which are expressed by the aforesaid general formulas (a) and (b) and

2. the particles of at least two kinds of pigments each having a benzenoid ring and being selected from the group including Carbon Black (C.I. No. 77266), Aniline Black (C.I. No. 50440), Blue (C.I. No. 42563), Spirit Black (C.I. No. 50415), Phthalocyanine Dyes (C.I. No. 74250), Violet R (C.I. No. 42535), Red R (C.I. No. 12085), Green B (C.I. No. 42000), Suviane Resin Black, Transfast Yellow (C.I. No. 77492) and Permanent Red (C.I. No. 12370). By the combined use of two or more kinds of, for example, black and blackish pigments, it is possible to produce a toner which is capable of developing a copied image having a desired color tone ranging from dark black to light black.

The polar radical represented by X in the aforesaid general formulas (*a*) and (*b*) by which the unsaturated compounds used in the present invention are expressed works very effectively on the particles of the toner in the liquid developer to regulate the polarity of the particles. The polar radical represented by Y, on the other hand, is selected from those having an increased affinity toward the particle-dispersing medium consisting of a paraffinic or an isoparaffinic hydrocarbon. Therefore, the object of obtaining uniform dispersion of the toner in the dispersing medium is attained. These polar radicals which are represented by X and Y serve to enhance the adhesion of the toner onto the copying papers used.

According to the present invention, it is mandatory that the toner contain both types of the compounds which are expressed by the aforesaid general formulas (a) and (b) and that at least three kinds of these compounds be copolymerically grafted onto the particles of the pigments. However, a toner which is prepared by graft copolymerization of these two types of compounds in which the proportion of the amount of the compound type (a) to the amount of the compound type (b) is such that 3 moles of the total compounds expressed by the general formula (a) is used with not more than 1 mole of the total compounds expressed by the general formula (b), exhibits a superior particle dispersion in the dispersing medium, a superior polarity-holding and a good adhesion of the particles onto the copying papers used. Also, the desirable range of proportions of the amount of the unsaturated compounds to the amount of the pigments to which the compounds are to be united is from 0.5 to 5 parts by weight of the compounds to 1 part by weight of the pigments. By altering the combination pattern of the particles of the pigments and the unsaturated compounds, it is possible to obtain toners having polarities which are regulated to be either positive or negative as desired.

As has been described, according to the present invention, there is provided a liquid developer in which

1. a toner, which is prepared by having the particles of at least two kinds of pigments — which have been so arranged to produce a desired color tone of the copied image — graft-copolymerized directly, by a chemical procedure, with unsaturated compounds which are capable of contributing to the stable regulation of the polarity of the particles of the pigments, the uniform dispersion of the particles and the good adhesion of the particles onto the copying papers, is dispersed in

2. a carrier liquid consisting of a paraffinic or an isoparaffinic hydrocarbon. Therefore, even after repeated use of this liquid developer for an extended period of time, there occurs no detachment, from the surfaces of the particles of the pigments, of the copolymer contributing to the stable polarity regulation and the uniform dispersion of the particles of the pigments. As a result, the liquid developer of the present invention preserves a good and satisfactory developing ability for a long time. Besides, when a development is performed by the use of the liquid developer of the present invention, not only is there obtained a very clear copied image, but also there is provided an advantage that the fading of the color of the copied image is negligibly small — in other words, there is obtained a copied image which undergoes no changes due to the passage of time — owing to the fact that the toner has a satisfactory adherency and also that the toner is of a structure such that the particles of the pigments are individually wrapped by the aforesaid polymer. It is to be noted also that, since the liquid developer of the present invention uses no naturally occurring rosin or asphalt at all, it has a stable uniform quality and developing ability.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE 1

Eighteen moles of lauryl methacrylate, 2 moles of hydroxyethyl methacrylate, 3 moles of methacrylic acid and 0.005 mole of azobisisobutylonitrile (a polymerization initiator) were dissolved in 6 moles of toluene. Into this mixture were added Carbon Black (a product sold under the trade name of Mitsubishi No. 44, manufactured by Mitsubishi Chemical Industries Ltd.) in an amount of one-third of the total amount by weight of the aforesaid unsaturated compounds and also Spirit Black in an amount of one-tenth of the total amount by weight of said unsaturated compounds. The resulting mixture was allowed to react at 80° C. for 10 hours, and as a result a graft-copolymerized toner was obtained. The toner thus obtained was added to an isoparaffinic hydrocarbon (ISOPAR-H, a product of ESSO Standard Oil, Inc.) and the mixture was kneaded in a ball mill for 3 hours. Then, 1 gram of the kneaded mixture was dispersed in 500 cc. of ISOPAR-H, and as a result, a liquid developer for use in electrophotography having a toner with a polarity regulated to be positive was obtained.

Separately, an electrophotographic copying paper which had been impressed with a negative charge by corona discharge was exposed to light through a positive original laid thereon to form an electrostatic latent image (meaning that the areas of the photoconductive layer of the copying paper corresponding to the original image were impressed with a negative charge). This copying paper carrying a latent image was immersed in the liquid developer of the present invention obtained according to the procedure described above, with the result that a very clear positive copy of the image was obtained. Also, the same liquid developer was used repeatedly over an extended period of time, but no deterioration of the developing ability was noted.

TABLE 1

Developer	Pigment used	Compounds used in graft copolymerization	Initial density of copied image*	Density of copied image at the end of 1 month*
Present invention	Carbon black, spirit black.	Lauryl methacrylate, hydroxyethyl methacrylate, acrylic acid.	1.63	1.60
Control:				
(1)	Carbon black	Lauryl methacrylate, hydroxyethyl methacrylate.	1.10	0.90
(2)	do	Lauryl methacrylate, acrylic acid.	0.94	0.78
(3)	do	Lauryl methacrylate, lauric acid.	1.10	0.80

Note.—The columns marked * represent the density of the copied image obtained from the comparison with the Wedge and the standard samples.

In order to make a comparison of the changes of the copied images due to the passage of time, three kinds of control liquid developers were prepared by dispersing, in ISOPAR-H, a toner obtained from the graft copolymerization of Carbon Black with two kinds of unsaturated compounds selected from those expressed by the general formulas (a) and (b), and the development of exposed copying papers was performed by the use of these control liquid developers. The fading of color of the copied images which were thus formed on the copying papers was studied, with the following results as given in table 1.

As will be understood clearly from table 1, the copied image obtained by the use of the liquid developer of the present invention has a markedly increased initial density of the image and the image showed a negligible fading of the color at the end of storage for a long time.

EXAMPLE 2

Eighteen moles of octyl methacrylate, 1 mole of dimethylaminoethyl methacrylate, 3 moles of hydroxyethyl methacrylate and 0.005 mole of azobisisobutylonitrile were dissolved in 6.5 moles of toluene. Into this mixture were added Carbon Black (Condatex SC, a product of Columbia Carbon Black Company of U.S.A.) in an amount of one-third of the total amount by weight of the aforesaid unsaturated compounds and also Aniline Black in an amount of one-fifth of the total amount by weight of the unsaturated compounds. The resulting mixture was subjected to a reaction at 90° C. for 12 hours, and thus a toner resulting from the graft copolymerization was obtained. The toner thus prepared was then added to an equal amount of ISOPAR-H and the mixture was kneaded in a ball mill for 3 hours. Thereafter, 1 gram of the kneaded mixture was dispersed in 500 cc. of ISOPAR-H. As a result, a liquid developer for use in electrophotography containing the toner with its polarity being regulated to be positive was obtained. An exposed copying paper was developed by the use of this liquid developer in a manner similar to that described in example 1. It was found that this liquid developer had a developing ability which was as much superior as that of the example 1.

EXAMPLE 3

Eighteen moles of lauryl methacrylate, 2 moles of dimethylaminoethyl methacrylate, 1 mole of acrylonitrile and 0.004 mole of azobisisobutylonitrile were dissolved in 6.0 moles of toluene. Into this mixture were added Carbon Black (Mogul A, a product of Cabot, Company of U.S.A.) in an amount of one-third of the total amount by weight of the aforesaid unsaturated compounds and also Dry Alkali Blue in an amount of one-tenth of the total amount by weight of said unsaturated compounds. The resulting mixture was allowed to react at 80° C. for 12 hours, and thus a copolymerically grafted toner was obtained. The toner thus prepared was added to an equal amount of ISOPAR-H, and the mixture was kneaded in a ball mill for 3 hours. then, 1 gram of this kneaded mixture was dispersed in 500 cc. of ISOPAR-H, and thus a liquid developer containing a toner with its polarity having been regulated to be negative was obtained.

Separately, an electrophotographic copying paper impressed with a negative charge by corona discharge was exposed to light through a negative original which was laid thereon. This exposed copying paper was immersed in the liquid developer obtained according to the manner described above, with the result that a very clear negative black copied image bearing slight bluish color was obtained. After repeated use of this liquid developer over a extended period of time, there was noted no appreciable change in the developing ability of this developer. Furthermore, a color fading test, as has been described in connection with the product of the present invention in example 1, was conducted on the copied images obtained by the use of the liquid developer of this instant example, and the result was that the changes in the density of the image were negligible.

What we claim is:

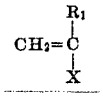
1. A liquid developer for electrophotography, comprising a toner made by graft-polymerizing a reaction mixture comprising

1. two pigment materials, each pigment material selected from the group consisting of Carbon Black (C.I. No. 77266), Aniline Black (C.I. No. 50440), Alkaline Blue (C.I. No. 42563), Spirit Black (C.I. No. 50415), Phthalocyanine Dyes (C.I. No. 74250), Violet R (C.I. No. 42535), Red R (C.I. No. 12085), Green B (C.I. No. 42000), Transfast Yellow (C.I. No. 77492) and Permanent Red (C.I. No. 12370) and
2. three unsaturated compounds of the following two formulas (a) and (b), including at least one of each type of compound,

(a)

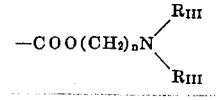
wherein: R_1 is selected from the group consisting of radicals of the formula $-C_nH_{2n+1}$ (an alkyl radical wherein $n=1-3$), phenyl radicals, tosyl radicals and hydrogen; Y is selected from the group consisting of $-COOC_nH_{2n+1}$ (wherein $4 \leqq n \leqq 20$), $-OCOC_nH_{2n+1}$ (wherein $1 \leqq n \leqq 20$), $-C_nH_{2n+1}$ (wherein $1 \leqq n \leqq 20$);

and a compound containing a polar radical X, said compound being of the formula:

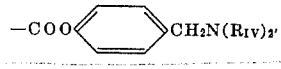


(b)

wherein: X is selected from the group consisting of



(wherein $n=2-4$, and R_{III} is selected from the group consisting of hydrogen, alkyl radicals having one to four carbon atoms, phenyl radicals and tosyl radicals), —OH, —CN, $-NH_2$, $-CON(R_V)_2$, where R_V is selected from the group consisting of hydrogen and $-C_nH_{2n+1}$ (an alkyl radical, wherein $1 \leqq n \leqq 3$), and



wherein R_{IV} is selected from the group consisting of hydrogen and C_nH_{2n+1} (an alkyl radical, wherein $1 \leqq n \leqq 3$), said toner being dispersed in carrier liquid having a high electric resistance and a low dielectric constant, said carrier liquid being selected from the group consisting of paraffinic hydrocarbons and isoparaffinic hydrocarbons.

2. The liquid developer of claim 1 wherein the ratio of (b) to (a) is such that the total weight in moles of (b) is not in excess of 1 relative to a total of 3 moles of (a).

3. The liquid developer of claim 1 in which the ratio of total unsaturated compound to total pigment is 0.5–5 to 1.

4. A liquid developer according to claim 1, wherein said toner is a graft copolymer obtained from a graft copolymerization of said unsaturated compounds expressed by the general formulas (a) and (b) with said pigments, in which the ratio of the total weight in moles of the unsaturated compounds expressed by the general formula (b) is not in excess of 1 relative to a total of 3 moles of the unsaturated compounds expressed by the general formula (a).

5. A liquid developer according to claim 1, wherein said toner is a graft copolymer which is prepared by a graft copolymerization of a total of from 0.5 to 5.0 parts by weight of said unsaturated compounds expressed by the general formulas (a) and (b) performed with a total of 1 part by weight of said pigments.

* * * * *