

United States Patent

Okuno et al.

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[54] LIQUID DEVELOPER ELECTROPHOTOGRAPHY

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Nov. 21, 1966 Japan.....41/76103

[52] U.S. Cl. 252/62.1, 260/41 C, 106/308 M,
260/33.6 UA

[51] Int. Cl. G03g 9/04

[58] Field of Search.....252/62.1; 117/37 LX; 106/308;
260/41

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[57] ABSTRACT

A liquid developer for electrophotography, which is prepared by dispersing, in a suitable carrier liquid, either independently or together with a surface active agent, a toner which is obtained by the so-called graft-copolymerization technique by a direct chemical bonding between a pigment and unsaturated compounds having a dispersing effect and a large electric charge polarity controlling ability, or more specifically, unsaturated compounds capable of chemically bonding to pigment, resulting in a large and distinct electric charge polarity of said toner in the carrier liquid and also capable of facilitating the dispersion of said particles in said carrier liquid which consists of a paraffinic hydrocarbon (including both isoparaffinic and paraffinic hydrocarbons) having a relatively high electric resistance and a low-dielectric constant.

5 Claims, No Drawings

LIQUID DEVELOPER ELECTROPHOTOGRAPHY

BACKGROUND OF THE INVENTION

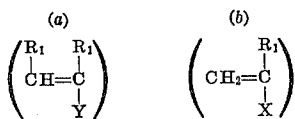
The present invention is concerned with a liquid developer for use in the wet-developing process of electrophotography.

Various liquid developers for electrophotography have been proposed. These conventional developing agents, however, consist of a pigment-dispersing agent, an electric charge polarity controlling agent such as rosin, alkyd resin and asphalt, and a carrier liquid consisting of a paraffinic hydrocarbon or the like which includes isoparaffinic hydrocarbons and paraffinic hydrocarbons or the like. Because these commonly used liquid developers employ, as the dispersing and electric charge polarity controlling agents, natural substances such as rosin and asphalt which are by nature not uniform in quality, it has been difficult to prepare developers which were uniform in their developing ability and quality. In addition, the conventional developers had the shortcomings that the dispersing ability of the particles of the developer deteriorated to a great extent during a short period of time, and that repeated use of the developer led to a marked attrition of the initial large electric charge, and a marked based distinct polarity controlling action which was exerted on the fine particles of pigment, resulting in a small electric charge, in distinct polarity of the fine particles of pigment. Furthermore, the deteriorated dispersing ability of the particles of the developer caused these particles to aggregate together and sediment, resulting in an extreme reduction in the developing ability of the developer. These many defects of the developers of the prior art may be explained as follows. Fine particles of pigment retain their excellent dispersing ability as well as their distinct polarity for some time after the developing agent is made, because, during such period, a dispersing agent and an electric charge controlling agent both remain sticking, with relative firmness, to the fine particles of pigment, but these agents which have for some time been adsorbed firmly to the fine particles of pigment will gradually begin to detach from the particles as time goes by.

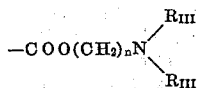
SUMMARY OF THE INVENTION

The present invention relates to a liquid developer for electrophotography, which is free from the aforesaid shortcomings of a liquid developer of the prior art. More specifically, the present invention contemplates the provision of a liquid developer for electrophotography which is excellent in both developing ability and stability, by first subjecting the two types of unsaturated compounds expressed by the below-mentioned general formulas (a) and (b) to graft-copolymerization with fine particles of pigment, and then dispersing the resulting reaction product, as particles, in a suitable carrier liquid for the liquid developer, either independently or together with a surface active agent.

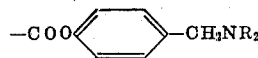
General formulas:



wherein R_1 is selected from the group consisting radicals of the formula $-\text{C}_n\text{H}_{2n+1}$ (an alkyl radical wherein $n=1-3$), phenyl radicals, tosyl radicals and hydrogen; Y is the radical $-\text{COOR}_n$ (wherein R_n is selected from the group consisting of radicals expressed by formulas $-\text{C}_n\text{H}_{2n+1}$ (wherein $4 \leq n \leq 20$), $-\text{OCOC}_n\text{H}_{2n+1}$ (wherein $1 \leq n \leq 20$) and $-\text{C}_n\text{H}_{2n+1}$ (an α -alkyl radical wherein $1 \leq n \leq 20$); 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), $-\text{COOH}$, $-\text{OH}$, $-\text{CN}$, $-\text{NH}_2$, $-\text{CONR}_2$ (wherein R is selected from the group consisting of hydrogen and $-\text{C}_n\text{H}_{2n+1}$ (wherein $1 \leq n \leq 3$)) and



(wherein B is selected from the group consisting of hydrogen and $\text{C}_n\text{H}_{2n+1}$ (wherein $1 \leq n \leq 3$))

The pigments which are used in the present invention preferably are substances such as carbon black and aniline black CC.I. No. 50440) which have a benzenoid ring in their chemical structures. The functional radicals which are represented by Y in the aforesaid general formula (a) of the unsaturated compounds are selected from among those which effectively improve the dispersing ability of the toner graft-copolymer in the hydrocarbon dispersion medium, and which have an intensive chemical affinity to said dispersion medium.

In the group of unsaturated compounds having the general formula (b), on the other hand, those functional radicals which are represented by X are selected from among those radicals that can effectively control the polarity of the electric charge borne by the particles of the liquid developer. The dispersing ability and the stability of the particles of the liquid developer can be improved further by the use of a product of reaction, namely, a product obtained from a graft-copolymerization between particles of pigment and a mixture of the two groups (a) and (b) of unsaturated compounds said mixture being such as to have an (a) to (b) mol ratio wherein the ratio of (b) is not in excess of 4 against 6 mols of (a). With respect to the compounds of group (b) however, the use of $-\text{COOR}_n$ as the functional radical which is represented by Y , will extremely improve the dispersing ability as well as the developing ability of the particles of the liquid developer.

In case the toner graft-copolymers consisting of fine particles of pigment and a mixture of the aforesaid unsaturated compounds of the (a) (a) and (b) are dispersed alone in dispersion media, said toners, in many cases, will be impressed with a negative electric charge. The present invention, however, further provides a liquid developer such that the electric charge to be impressed on the toner is controlled so as to be distinctly positive.

The surface active agents which are used in the present invention consist of higher aliphatic acids such as stearic acid, palmitic acid and naphthenic acid, and also metal soaps which are the salts of the aforesaid higher aliphatic acids and metals selected from the group consisting of aluminum, cadmium, cobalt, nickel, manganese, chromium and copper. These surface active substances have an ability, when placed in the developing liquid, to reverse the polarity of the large electric charge impressed on the particles of the developer to an extremely distinct positive charge and also to hold the electric charge polarity controlling function of the particles of the liquid developer stable for an extended period of time.

As has been described, the present invention provides liquid developers for electrophotography, which are uniform in quality and which are of a predetermined uniform ability and whose electric charge regulating agent and dispersing agent intended for the pigments both consist of synthetic substances instead of using any small amount of naturally occurring rosin or asphalt which have been commonly used in a liquid developer of the prior art. Because the fine particles of pigment are graft-copolymerized with the large electric charge polarity controlling agent and also with the dispersing agent, there is produced an extremely firm bonding between these components, so that there is noted no appreciable deterioration in the dispersing as well as the developing abilities of the developing agent even after a repeated use of the latter continuously for a prolonged period of time. In addition, the liquid developer of the present invention which incorporates a

surface active agent allows the particles of the liquid developer to be impressed with a very distinct electric charge polarity controlling due to the action of the surface active agent, and therefore, those copying materials which are developed by the use of such liquid developer provide prints which carry well-contrasted, clear images.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE 1

To 0.9 mol of laurylmethacrylate was added 0.1 mol of β -dimethylaminoethylmethacrylate. Then, 25 percent by weight of carbon black and 0.8 percent by weight of azobisisobutyronitrile (polymerization initiator), both percentages relative to the total weight of said mixture, and also toluene equal in amount to the total weight of the aforesaid monomers were added to said mixture. The resulting mixture was subjected to reaction at 100°–110° C. for 10 hours, with the result that a carbon black graft-copolymer was obtained. This graft-copolymer was then kneaded in a ball mill for 20 hours. One g. of this kneaded graft-copolymer was dispersed in 500 cc. of an isoparaffinic hydrocarbon (ISOPAR-H, a product of Esso Standard Oil, Inc.), and thus, a liquid developer for electrophotography was obtained.

A positive original was placed on the photoconductive layer of an electrophotographic copying material already impressed with a negative electric charge by the application of corona discharge, and after exposing to light, the copying material was developed by the use of the aforesaid liquid developer of the present invention. The result was that a very clear negative print of the image was obtained. After repeated use of this liquid developer for an extended period of time, there was noted no appreciable deterioration in the developing ability of said liquid developer.

EXAMPLE 2

To 0.9 mol of laurylmethacrylate was added 0.1 mol of acrylonitrile. Then, 25 percent by weight of carbon black and 0.6 percent by weight of azobisisobutyronitrile, both percentages relative to the total weight of said mixture, and also toluene in an amount equal to half of the total weight of the aforesaid monomers were added to said mixture. The resulting mixture was subjected to reaction at 110° C. for 15 hours, with the result that a carbon black graft-copolymer was obtained. A small amount of an isoparaffinic hydrocarbon (ISOPAR-H) was added to this copolymer, followed by kneading in a ball mill for 20 hours. One g. of the kneaded copolymer was dispersed in 500 cc. of an isoparaffinic hydrocarbon identical to the aforesaid one, and thus a liquid developer for electrophotography was obtained.

A positive original was placed on the photoconductive layer of an electrophotography copying material already impressed with a negative electric charge by the application of corona discharge, and after exposure to light, the copying material was developed by the use of the aforesaid liquid developer of the present invention. The result was that a clear positive print of the image was obtained. After repeated use of this liquid developer for an extended period of time, no appreciable deterioration of the developing ability was noted.

EXAMPLE 3

To 0.9 mol of laurylmethacrylate was added 0.05 mol of acrylic acid. Then, 33 percent by weight of aniline black and 0.8 percent by weight of azobisisobutyronitrile, both percentages relative to the total weight of said mixture, and also toluene in an amount equal to the total weight of the aforesaid monomers were added to said mixture. The resulting mixture was subjected to reaction at 120° C. for 10 hours, with the result that a graft-copolymer was obtained. This graft-copolymer was kneaded in a ball mill for 16 hours. One g. of this kneaded copolymer was dispersed in 500 cc. of an isoparaffinic hydrocarbon (ISOPAR-H), and thus, a liquid developer for electrophotography was obtained.

After exposing to light electrophotography copying materials already impressed with a negative electric charge by the application of corona discharge, in a manner similar to that described in examples 1 and 2, the copying materials were developed by the use of the aforesaid liquid developer of the present invention. The result was that very clear positive prints of the image were obtained. After repeated use of this liquid developer for an extended period of time, no appreciable deterioration of the developing ability was noted.

EXAMPLE 4

To 0.95 mol of laurylmethacrylate was added 0.05 mol. of acrylic acid. Then, 25 percent by weight of carbon black and 0.7–0.8 percent by weight of azobisisobutyronitrile (polymerization initiator), both percentages relative to the total weight of said mixture, and toluene equal in an amount to the total weight of the aforesaid monomers were added to said mixture. The resulting mixture was subjected to reaction at 70° C. for 8 hours, with the result that a carbon black graft-copolymer was obtained. One g. of this copolymer was dispersed in 500 cc. of an isoparaffinic hydrocarbon (ISOPAR-H), and furthermore, 2 cc. of 0.5 percent manganese naphthenate solution was added thereto, and thus a liquid developer for electrophotography was obtained.

A positive original was placed on the photoconductive layer already impressed with a negative electric charge, and after exposure to actinic light, development was performed by the use of the aforesaid liquid developer of the present invention. The result was that a very clear positive print of the image was obtained. After repeated use of the liquid developer for a prolonged period, no reduction in the dispersing ability of the particles of the liquid developer, nor any deterioration of the developing ability of the liquid developer was noted.

EXAMPLE 5

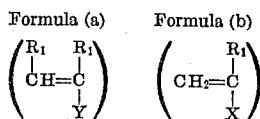
To 0.9 mol of laurylmethacrylate was added 0.1 mol of hydroxymethacrylate. Then, 33 percent by weight of carbon black and 0.7–0.8 percent by weight of azobisisobutyronitrile, both percentages relative to the total weight of said mixture, and also toluene in an amount equal to the total weight of the aforesaid monomers were added to the mixture. Thereafter, in a manner similar to that described in example 4, a carbon black graft-copolymer was obtained. One g. of this copolymer was dispersed in 500 cc. of an isoparaffinic hydrocarbon (ISOPAR-H), and furthermore, 0.5 cc. of 0.5 percent cobalt naphthenate solution was added thereto, and thus, a liquid developer for electrophotography was obtained. After developing a copying material similar to that used in example 4 by the use of the aforesaid liquid developer, a very clear positive print of the image was obtained. After repeated use of this liquid developer for a prolonged period, no reduction in the dispersing ability of the particles of the developer nor any deterioration of the developing ability was noted.

EXAMPLE 6

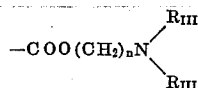
0.03 mol of β -dimethylaminoethylmethacrylate was admixed with 0.97 mol of isooctylmethacrylate. Then, 50 percent by weight of carbon black and 0.8 percent by weight of azobisisobutyronitrile, both percentages relative to the total weight of said mixture, and toluene in an amount equal to the total weight of the aforesaid monomers were added to the mixture. Thereafter, in a manner similar to that described in connection with example 4, a carbon black graft-copolymer was obtained. One g. of this copolymer was dispersed in 500 cc. of an isoparaffinic hydrocarbon (ISOPAR-H), and furthermore, 3 cc. of 1 percent aluminum stearate solution was added thereto, and thus, a liquid developer for electrophotography was obtained. By developing a copying material similar to that in example 4 with the aforesaid liquid developer, a very clear positive print of the image was obtained. After repeated use of this liquid developer for an extended period of time, no reduction in the dispersing ability of the particles of the liquid developer nor any deterioration of the developing ability of the liquid developer was noted.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

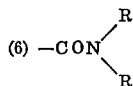
1. A liquid developer for electrophotography, comprising a toner of a single pigment having a n -ring in its chemical structure selected from the group consisting of carbon black and aniline black and a graft-polymer bonded to said benzenoid ring of said pigment by a reaction of graft-copolymerization between one each of an unsaturated compound expressed by formula (a), another unsaturated compound expressed by formula (b) and said pigment:



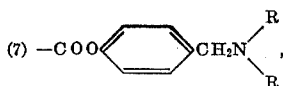
wherein R_1 is selected from the group consisting of $-C_nH_{2n+1}$ wherein $n=1$ to 3, a phenyl radical, a tosyl radical, and H; Y is selected from the group consisting of (1) $-COOC_nH_{2n+1}$ wherein $4 \leq n \leq 20$, (2) $-OCOC_nH_{2n+1}$ wherein $1 \leq n \leq 20$, and (3) $-C_nH_{2n+1}$, wherein $1 \leq n \leq 20$ (each expression C_nH_{2n+1} denoting an alkyl radical); X is selected from the group consisting of



wherein $n=2$ to 4 and R_{III} are selected from the group consisting of H, alkyl radicals having one to four carbon atoms, a phenyl radical and a tosyl radical, (2) $-COOH$, (3) $-OH$, (4) $-CN$, (5) $-NH_2$,



wherein R is selected from the group consisting of H and an alkyl radical of one to three carbon atoms,



wherein R is selected from the group consisting of H and an alkyl radical of one to three carbon atoms; and a carrier liquid consisting of a paraffinic hydrocarbon, said toner being dispersed in said carrier liquid.

2. A liquid developer for electrophotography according to claim 1, wherein said toner is dispersed in said carrier liquid together with only a small amount of at least one surface active agent selected from the group consisting of stearic acid, palmitic acid, naphthenic acid and aluminum, cadmium, cobalt, nickel, manganese, chromium and copper salts of an acid selected from the group consisting of stearic acid, palmitic acid and naphthenic acid.

3. A liquid developer for electrophotography according to claim 1, wherein said toner consists of a product of a graft-copolymerization reaction between said pigment and a mixture consisting of said unsaturated compound expressed by said formula (a) and said another unsaturated compound expressed by said formula (b), said mixture being of an (a) to (b) mol ratio wherein the ratio of (b) is not in excess of 4 to 6 mols of (a).

4. A liquid developer for electrophotography according to claim 1, wherein said toner consists of a product of a reaction obtained from a mixture consisting of said unsaturated compound expressed by said general formula (a) and said another unsaturated compound expressed by said general formula (b), said mixture being added with said pigment in an amount ranging from 25 to 50 percent by weight of the total weight of said mixture.

5. The method of forming a liquid developer for electrophotography according to claim 1, comprising forming a mixture of a member of the group consisting of laurylmethacrylate and isooctylmethacrylate, and a member of the group consisting of β -dimethylaminoethylmethacrylate, acrylonitrile, acrylic acid and hydroxymethacrylate in the molal ratio of 6 mols of the former to not more than 4 mols of the latter, adding a pigment from the group consisting of aniline black and carbon black to the mixture in the amount of 25 to 50 percent by weight of the total weight of the mixture, a catalytic amount of polymerization initiator, and a hydrocarbon solvent, heating the mixture in the range of about 100° to 120° C. for a sufficient time to obtain a pigment graft-copolymer, milling said copolymer and dispersing the milled copolymer in a hydrocarbon solvent.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3 639 243

Dated February 1, 1972

Inventor(s) Zenjiro Okuno and Hazime Machida

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 4; change "n=ring" to ---benzenoid ring---.
Column 5, line 26; before the formula insert "(1)".

Signed and sealed this 11th day of July 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents