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3,770,637

LIQUID DEVELOPER FOR DEVELOPING ELECTROSTATIC LATENT IMAGE

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Ser. No. 181,216

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43/38,516

Int. Cl. G03g 9/04

U.S. Cl. 252—62.1

3 Claims

ABSTRACT OF THE DISCLOSURE

A liquid developer for use in developing an electrostatic latent image formed on an electrostatic recording material or an electrophotographic copying material which is prepared by dispersing, in a suitable carrier liquid, a toner consisting essentially of pigment particles whose surfaces are coated with a coating agent, said coating agent consisting of a first resin having a high solubility in said carrier liquid and a second resin having a low solubility in said carrier liquid.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our co-pending application Ser. No. 828,784, filed May 28, 1969, now Pat. No. 3,640,863, issued Feb. 8, 1972.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a liquid developer for use in developing the electrostatic latent image formed on an electrostatic charge-carrier, such as an electrophotographic copying material or an electrostatic recording material.

Description of the prior art

An electrostatic latent image is generally formed by the electrostatic recording method wherein said image is directly formed through impression of an electrostatic charge on an electrostatic recording paper, such as a synthetic resin film, and the electrophotographic method wherein said image is indirectly formed by imparting an electrostatic charge, by means of corona discharge, on the surface of a photoconductive layer of an electrophotographic copying paper and exposure subsequent thereto.

The methods of developing the above-described electrostatic latent images are classified into two categories, namely, the dry-developing method which employs a powder developer and the wet-developing method which employs a liquid developer. In the dry-developing method, development is effected by thermal fixing of a powder developer on an electrostatic charge-carrier provided with an electrostatic latent image, while, in the wet-developing method, development is effected by dipping said electrostatic charge-carrier in a liquid developer.

With regard to the liquid developer, the one which has hitherto been popular is a developer prepared by the steps of coating pigment particles with a single resin having both (1) a property of providing the pigment particles with a controllable polarity, i.e., a distinct electric charge, and (2) a property of providing the developer liquid with stability, i.e., the maintenance of a stable dispersion of the pigment particles in the carrier liquid. The thus-treated pigment particles are then dispersed in a

carrier liquid comprising petroleum hydrocarbon having a comparatively high electric resistance (more than 10^{10} Ω -cm.) and a low dielectric constant (less than 3). Other well-known developers include a developer prepared by dispersing, in a carrier liquid, pigment particles coated with two kinds of resins simultaneously, both of which are easily soluble in the carrier liquid, wherein one resin is capable of controlling the polarity of the pigment particles and the other is effective for providing dispersion stability though somewhat inferior in polarity control. In a further developer, which is a modification of the preceding one, a field activator is added to said resin of superior dispersibility to thereby control the pigment polarity. However, with these conventional developers, it has been extremely difficult to maintain for a long time the initial developing efficiency thereof as displayed in the period immediately following their preparation because the resin coated on the pigment particles has the drawback that it separates gradually from the pigment particles during storage and use of the developer, to thereby cause a deterioration of the developing efficiency thereof. This deficiency has hitherto been considered unavoidable inasmuch as it is mainly attributable to the fact that the resin (or resins) used in coating the pigment particles is easily soluble in the carrier liquid. In addition to the foregoing developers, a liquid developer on the market, whose composition is characterized by the fact that the pigment particles are coated with microlith resin (maleic resin of denatured rosin) and the coated pigment particles are dispersed in a carrier liquid together with an oil having a dispersing effect, such as tung oil, has also been popular. However, this liquid developer, when put to practical use, has also been deficient in controlling or preventing polarity deterioration of the toner as well as being deficient in the fixability thereof on the surface of an electrostatic charge-carrier.

The wet-developing method has a remarkable advantage in that the fixing operation is quite simple, as compared with the thermal fixing used in the dry-developing method, because fixing of the developed image by the wet-developing method is effected by dipping an electrostatic charge-carrier, bearing the electrostatic latent image, in a liquid developer containing dispersed therein a toner having a positive or a negative charge, then removing the charge carrier from the liquid developer, and then evaporating the carrier liquid contained in the developer adhering to the charged carrier to thereby fix the toner on the surface of said electrostatic charge-carrier. But, on the other hand, the liquid developing method using prior liquid developers has the drawback that the fixability of the toner, which functions to form the visible image, is comparatively poor. For example, an image fixed on a copy by the prior liquid developers is easily erased by rubbing with a finger, so that if the developed copy is intended to be preserved for a long time or if it will be frequently handled, the image not only may become blurred but also it may be entirely destroyed. For this reason, copies prepared by prior liquid developers cannot be used for important papers, such as official documents. The foregoing drawback is considered to be attributable to the small amount of resin adsorbed onto the pigment particles in the toner, said amount usually having been in the range of less than 1 part by weight of resin per 1 part by weight of pigment particles. In order to overcome this drawback, it has been attempted to employ a toner prepared by coating pigment particles with a resin which is comparatively insoluble in a carrier liquid, but this has also proved to be unsatisfactory because such a toner is apt to undergo agglomeration or clumping of particles so that the particles have an inferior dispersibility in the carrier liquid.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a liquid developer for use in developing electrostatic latent images, which contains a toner dispersed in a carrier liquid, said toner being capable of maintaining a distinct polarity during protracted storage or repeated use and also having a superb fixability to the latent image area of an electrostatic charge-carrier.

The liquid developer according to the present invention is a liquid developer obtained by dispersing, in a carrier liquid comprising petroleum hydrocarbon having an electric resistance of more than $10^{10}\Omega\cdot\text{cm.}$ and a dielectric constant of less than 3, a toner prepared by coating pigment particles with (A) a first resin, which has a low solubility in said carrier liquid, so that it is insoluble or hard to dissolve in the carrier liquid and also has a polarity-controlling effect on said pigment together with (B) a second resin, which has a high solubility in said carrier liquid, so that it is soluble or easily soluble in the carrier liquid and also contributes to the dispersibility of said pigment in the carrier liquid.

The resin (A) which is insoluble or hard to dissolve in the carrier liquid according to the present invention, refers to a resin which is soluble in an organic solvent having an aniline point below 50°C. , but which is insoluble in an organic solvent having an aniline point above 70°C. Accordingly, the carrier liquid employed for the present invention is a hydrocarbon having an aniline point above 70°C. coupled with a resistance value and a dielectric constant as stated above. Further, the second resin (B) which is soluble or easily soluble in the carrier liquid refers to the property of the resin relative to the foregoing hydrocarbon carrier liquid.

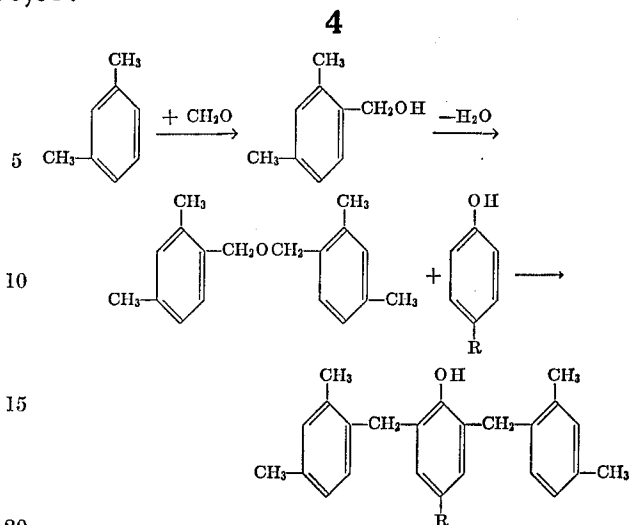
The carrier liquid having a high resistance and a low dielectric constant used in the liquid developer of the present invention can be any of the known carrier liquids which have hitherto been used in electrophotographic liquid developers for example, paraffinic hydrocarbons, isoparaffinic hydrocarbons, naphtha hydrocarbons, halogenated hydrocarbons, etc. There can be used commercially available carrier liquids, such petroleum hydrocarbons manufactured by Esso Standard Sekiyu Ltd. and sold under the trademarks "Isopar-H" and "Isopar-G," a product of Shell Oil Co., Ltd. sold under the trademark "Shellsol" and a product of Mobil Sekiyu Co., Ltd. sold under the trademark "Pegasol."

The coating agent for the pigment particles consists essentially of resin (A) and resin (B), as follows:

Resin (A), i.e., a resin of low solubility or insoluble in the carrier liquid:

(1) A phenolic resin resulting from the reaction of phenols with aldehydes and which is soluble in an organic solvent having an aniline point below 50°C. , but which is insoluble in an organic solvent having an aniline point above 70°C. The phenols used may be phenol itself, or resorcinol, or substituted phenols such as cresols, xylenols, p-tert-butylphenol, p-tert-amylphenol, p-tert-octylphenol, p-phenylphenol and diphenylolpropane (bisphenol A). The aldehydes used are formaldehyde, paraformaldehyde, acetaldehyde, butyraldehyde and furfural (furfuraldehyde). The phenolic resins can be reacted with (1) natural resins, such as rosin, followed by esterification with glycerol or other polyhydric alcohols, and with (2) ester gums (glyceryl ester of rosin) to make modified phenolic resins.

(2) A phenol-modified xylene resin resulting from the reaction of xylene, usually m-xylene, with an aldehyde, such as formaldehyde, p-formaldehyde, acetaldehyde, butyraldehyde or furfural, followed by reaction with a phenol such as phenol itself, resorcinol, cresol, xylene, p-tert-butylphenol, p-tert-amylphenol, p-tert-octylphenol, p-phenylphenol or diphenylolpropane. The reaction scheme is as follows:



Commercially available coating agents whose principal component is phenol modified xylene resin, such as products of Japan Gas-Chemical Co., Inc. sold under the name "Nikanol HP-100" and "Nikanol HP-120," are most suitable for the present invention.

Resin (B) i.e., a resin of high solubility in the carrier liquid:

The suitable resins in this category include (1) laurylmethacrylate-dimethylaminoethylmethacrylate copolymer, (2) laurylmethacrylate - n - butylmethacrylate copolymer (containing more than 20% laurylmethacrylate in terms of mol ratio) and (3) laurylmethacrylate-isobutylmethacrylate copolymer and the like. With reference to the mol ratio range of each monomer constituting the above-described three kinds of copolymers, it is desirable that in the case (1) copolymer the content of laurylmethacrylate therein should be 70 to 95 mol percent, and that in the cases of (2) and (3) copolymers the content of laurylmethacrylate therein should be 20 to 90 mol percent, respectively.

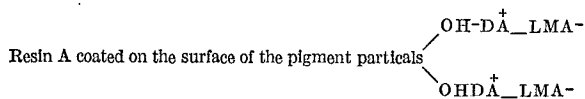
Commercially available resins whose principal component is acrylate copolymer, such as products of Rohm & Haas Co., U.S.A., sold under the trademarks "Plexol #966" and "Plexol #917," are most suitable for the present invention.

According to the present invention, at least one of the resins (A) and at least one of the resins (B) are combined to form a coating agent for the pigment particles to form a toner which can be dispersed in the carrier liquid to form the liquid developer of the invention.

The aforesaid toner is prepared by dissolving the resin A in a small amount of an organic solvent, such as toluene, having an aniline point below 50°C. , then kneading or milling this solution with pigment particles, thereafter adding to the kneaded mixture the resin (B) dissolved in a small amount of the same organic solvent, then carrying out further kneading or milling of the mixture, and then dispersing the thus kneaded mixture (i.e. a concentrated toner) in the carrier liquid. The toner contained in the liquid developer thus prepared, according to the present invention, is capable of coating the pigment particles with an amount of insoluble resin (A) several times as large as the maximum possible in conventional toners (in which resin/pigment=1/1, by weight), but satisfactory results are obtained when as little as 0.3 part by weight of resin A is coated on 1 part by weight of pigment particles. As a result, when a visible image is developed by the use of an ample quantity of said resin A, there is effected a quite stable fixation of the toner onto the latent image areas of an electrostatic charge-carrier. Moreover, because the toner according to the present invention is composed of pigment particles coated with resin (B) and resin (A) adsorbed with each other or combined chemically, it has advantages, as compared with conventional toners, such that not only is the

stability of the toner dispersion in the carrier liquid remarkably high, but also there occurs no phenomenon such as desorption of the resin, i.e., coating agent, from the pigment particles, thereby resulting in a long-lived, superb, developing efficiency. In other words, the toner contained in a liquid developer according to the present invention is of such a composition that the pigment particles are coated with a resin (resin A) either insoluble or of low solubility in the carrier liquid all over their surfaces and the exterior of the thus coated pigment surfaces is further coated with a resin (resin B) which is easily soluble in the carrier liquid, resin B having been firmly combined with or adsorbed to the foregoing insoluble or hard-to-dissolve resin A. As for the mode of combination of said pigment with the resin A and the resin B, it is considered that the hydroxyl radical, for instance, of the molecules of resin A is firmly combined with, for instance, laurylmethacrylatedimethylaminoethylmethacrylate copolymer (resin B) in the way expressed by the following schematic formula.

Formula expressing the mode of combination of resins (A) and (B)



(Note: DA in the above formula denotes dimethylaminoethylmethacrylate, and LMA denotes laurylmethacrylate.)

According to the present invention, therefore, the employment of resin (A) and resin (B) for coating pigment particles in the order as stated above will be most effective. And in the present invention, it is desirable for satisfactory display of aforesaid efficiency of toner that 1 part by weight of pigment particles should be coated with 0.3 to 5 parts by weight of resin A and that 1 to 5 parts of resin (B) per 1 part by weight of said pigment particles should be applied to thus obtained coated particles.

As the pigment particles to be employed for the present invention, any of those known heretofore are applicable. They include, for instance, inorganic or organic pigments such as carbon black (C.I. No. 77266), aniline black (C.I. No. 50440), spirit black (C.I. No. 50415), phthalocyanine blue (C.I. No. 74160), benzidine yellow (C.I. No. 21090), carmine 6B (C.I. No. 15850), zinc oxide powder and lake red (C.I. No. 15585).

A liquid developer according to the present invention contains a toner which displays a much more distinct polarity than conventional developers and maintains a uniform stable dispersion in the carrier liquid by virtue of the polarity-controlling action as well as dispersion-stabilizing action of the coating agent as stated above, and said toner has a strong fixability to an electrostatic latent image consisting of a small electric charge. A visible image once fixed onto an electrostatic charge-carrier cannot be erased readily with an india-rubber eraser or the like, so that it serves to form an image of superb preservability and durability. The thus formed image, when once fixed, does not become swollen even if it is dipped in a carrier liquid and it retains resistance to solvents. Such being the case, said liquid developer according to the present invention is quite suitable for use in repeated development, such as is employed in developing multi-color electrophotographs.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the preparation and use of the liquid developers according to the invention.

Example 1

A mixture, comprising:

		G.
Carbon black (manufactured by Mitsubishi Kasei Kogyo Co., Ltd. and sold under the name "Carbon Black #100")	5	5
50%-toluene solution of Nikanol HP-100	30	30
was subjected to kneading in a ball-mill for one hour, and then		
		G.
Plexol #966	10	10
Toluene	55	55

were added to the thus kneaded mixture and the same was further kneaded for 16 hours. Subsequently, 5 g. of the resultant kneaded mixture was dispersed in 1 liter of Isopar-H (as a carrier liquid), whereby there was obtained a liquid developer for use in developing electrostatic latent images.

Preparation of control liquid developer.—For the purposes of comparing the efficiencies of developers, a toner comprising carbon black coated with alkyd resin was prepared by almost the same procedure as the above-mentioned toner of the present invention. Then, about 2 g. of the thus prepared comparative toner was dispersed in 1 liter of Isopar-H to thereby obtain a liquid developer for use in comparison.

Subsequently, by a conventional electrophotographic method, electrostatic latent images were imparted onto commercially available electrophotographic copying papers, and then said copying papers were respectively dipped in the above stated developers in order to compare their image fixabilities. Also, the degrees of deterioration of the developing efficiency due to prolonged preservation of the respective developers was observed. The results of said observations are summarized in the following Table 1.

TABLE 1

Test	Developer according to the present invention	Comparative developer
Image fixability ¹	Satisfactory	A little inferior.
Preservability-condition when stored for 90 days.	No precipitation occurred.	Precipitation occurred (agglomeration observed at the bottom of the storage receptacle.).
Ratio of transmittancy when stored for 90 days (percent). ²	94	23
Image formed by a developer stored for 90 days, distinctness.	Satisfactory	Unsatisfactory.
Image density ratio ³	94	10.

¹ An image which could not be erased by rubbing several times with an india-rubber eraser was rated "satisfactory".

² The ratio of transmittancy is expressed in percent and is calculated by the formula $\frac{T_0}{T_90} \times 100$,

wherein T_0 denotes the transmittancy of the liquid at the time of preparing the developer (liquid depth being 1 cm.) and T_90 denotes the transmittancy when said developer was stored for 90 days subsequent to preparation thereof.

³ The image density was measured with a densitometer manufactured by Photovolt Co., U.S.A. The image density ratio is expressed in percent and is calculated by the formula $\frac{R_0}{R_90} \times 100$,

wherein R_0 denotes the density of an image formed with the developer just after the preparation thereof, and R_90 denotes the density of an image formed with a developer after storage for 90 days.

Example 2

(a) Solution, comprising:		G.
Carbon black (manufactured by Asaki Carbon Mfg. Co. Ltd. and sold under the name "XC-550")	5	5
50%-toluene solution of Nikanol HP-120	30	30
(b) Solution, comprising:		
Plexol 966	10	10
Toluene	55	55

The above solutions (a) and (b) were respectively treated in the same way as Example 1, whereby there was obtained a liquid developer for use in developing electrostatic latent images.

The thus prepared developer, when put to practical use for copy development and observed as regards efficiency, proved to have a fixability as well as a preservability equivalent to the developer of Example 1 according to the present invention.

Example 3

- (a) Solution, comprising:
Carbon black (manufactured by Cabot Co., U.S.A. and sold under the name "Mogul-A") ----- 5
50%-toluene solution of Nikanol HP-100 ----- 30
- (b) Solution, comprising:
Plexol #966 ----- 10
Toluene ----- 55

The above solutions (a) and (b) were respectively treated in the same way as Example 1, whereby there was obtained a liquid developer for use in developing electrostatic latent images. The thus prepared developer proved to have an efficiency equivalent to the foregoing developer according to the present invention.

Example 4

This example describes the preparation and use of six liquid developers (A)-(F), according to the invention, and compares them with three control developers (1)-(3).

Liquid developer (A).—A mixture, comprising:

- Carbon black (the same as Example 1) ----- 5
50%-toluene solution of o-phenyl-phenolic resin ---- 20

was subjected to kneading for one hour in a ball-mill, and then

- laurylmethacrylatedimethylaminoethylmethacrylate copolymer (mol ratio of laurylmethacrylate/dimethylaminoethylmethacrylate is 9/1) ----- 10
Toluene ----- 55

were added to the thus kneaded mixture and the resultant mixture was kneaded for a further period of 16 hours. Subsequently, 5 g. of the resultant mixture was dispersed in 1 liter of Isopar-H, whereby there was obtained a liquid developer for use in developing electrostatic latent images.

Liquid developer (B).—The liquid developer (B) was prepared exactly in accordance with the procedure as described for developer (A), except that the same amount by weight of laurylmethacrylate-n-butylmethacrylate copolymer (mol ratio of laurylmethacrylate/n-butylmethacrylate is 3/7) was used in place of laurylmethacrylatedimethylaminoethylmethacrylate copolymer.

Liquid developer (C).—The liquid developer (C) was prepared exactly in accordance with the same procedure as described for developer (A), except that the same amount by weight of each of o-methyl phenolic resin (50%-toluene solution) and laurylmethacrylate-n-butylmethacrylate copolymer (mol ratio of laurylmethacrylate/n-butylmethacrylate is 3/7) were used in place of o-phenyl phenolic resin (50%-toluene solution) and laurylmethacrylatedimethylaminoethylmethacrylate copolymer.

Liquid developer (D).—The liquid developer (D) was prepared exactly in accordance with the same procedure as described for developer (A), except that the same amount by weight of each of o-methyl phenolic resin (50%-toluene solution) and laurylmethacrylate-isobutylmethacrylate copolymer (mol ratio of laurylmethacrylate/isobutylmethacrylate is 4/6) were used in place of o-phenyl phenolic resin (50%-toluene solution) and laurylmethacrylatedimethylaminoethylmethacrylate copolymer.

Liquid developer (E).—The liquid developer (E) was prepared exactly in accordance with the same procedure as described for developer (A), except that the same amount

by weight of p-tert-butyl phenolic resin (50%-toluene solution) was used in place of o-phenyl phenolic resin (50%-toluene solution).

Liquid developer (F).—The liquid developer (F) was prepared exactly in accordance with the same procedure as described for developer (A), except that the same amount by weight of each of p-tert-butyl phenolic resin (50%-toluene solution) and laurylmethacrylate-n-butylmethacrylate copolymer (mol ratio of laurylmethacrylate/n-butylmethacrylate is 3/7) were used in place of o-phenyl phenolic resin (50%-toluene solution) and laurylmethacrylatedimethylaminoethylmethacrylate copolymer.

Preparation of control liquid developers:

- Control (1):
Carbon black ----- 5
Laurylmethacrylatedimethylaminoethylmethacrylate copolymer (mol ratio of laurylmethacrylate/dimethylaminoethylmethacrylate is 9/1) -- 20
Toluene ----- 65

were kneaded in a ball-mill for 16 hours. Subsequently, 5 g. of the resultant mixture was dispersed in 1 liter of Isopar-H.

- Control (2):
Carbon black ----- 5
Laurylmethacrylate - n - butylmethacrylate copolymer (mol ratio of laurylmethacrylate/n-butylmethacrylate is 3/7) ----- 20
Toluene ----- 65

were kneaded in a ball-mill for 16 hours. Subsequently, 5 g. of the resultant mixture was dispersed in 1 liter of Isopar-H.

- Control (3):
Carbon black ----- 5
Laurylmethacrylateisobutylmethacrylate copolymer (mol ratio of laurylmethacrylate/isobutylmethacrylate is 4/6) ----- 20
Toluene ----- 65

were kneaded in a ball-mill for 16 hours. Subsequently, 5 g. of the resultant mixture was dispersed in 1 liter of Isopar-H.

- Control (4):
Carbon black ----- 5
50%-toluene solution of Nikanol HP-100 ----- 30
Toluene ----- 65

were kneaded in a ball-mill for 16 hours. Subsequently, 5 g. of the resultant mixture was dispersed in 1 liter of Isopar-H.

- Control (5):
Carbon black ----- 5
50%-toluene solution of o-phenyl-phenolic resin - 40

were kneaded in a ball-mill for 16 hours. Subsequently, 5 g. of the resultant mixture was dispersed in 1 liter of Isopar-H.

Test method

With regard to the liquid developers (A)-(F) and controls (1)-(5), there was made, by the under-mentioned method, a comparison with respect to the concentration of visible images formed by the respective developers.

According to a conventional electrophotographic method, electrostatic latent images were imparted onto commercially available electrophotographic copying papers, and said copying papers were dipped in each of the above brand-new developers. Thereafter, the concentration of each of the resultant images was measured with a densitometer manufactured by Photovolt Co., Ltd., U.S.A.

Then, by the same method as described above, the same developers were tested after having been allowed to stand in an atmosphere of 25° C. and 60% RH for 90 days after preparation thereof.

9

Results

The results of the image concentration measurement tests were as shown below.

	Image concentration	
	Developed by the brand-new developer	Developed by the developer allowed to stand for 90 days
Developers:		
(A)-----	1.28	1.21
(B)-----	1.34	1.30
(C)-----	1.30	1.25
(D)-----	1.37	1.34
(E)-----	1.26	1.25
(F)-----	1.31	1.28
Control:		
(1)-----	1.15	0.54
(2)-----	1.07	0.59
(3)-----	1.04	0.42
(4)-----	0.19	0.10
(5)-----	0.18	0.10

Description of resins identified by trademarks in the preceding description

Plexol 917 is a methacrylate copolymer in solvent refined (150 SUS/100° F.) neutral oil. It has a specific gravity (60° F./60° F.) of 0.904, a density (pounds/gallon at 60° F.) of 7.53, color (ASTM D-1500) of 3 and a neutralization number (ASTM D-974) of 0.2.

Plexol 966 is a methacrylate copolymer in solvent refined (100 SUS/100° F.) neutral oil. It has a specific gravity (60° F./60° F.) of 0.899, a density (pounds/gallon at 60° F.) of 7.49, color (ASTM D-1500) of 3 and a neutralization number (ASTM D-974) of 0.2.

Nikanol HP 100 is an alkyl phenol modified xylene resin which is a light yellow solid, having a color value of less than 8 and a viscosity (cp.) of 200-400.

Nikanol HP 120 is an alkyl phenol modified xylene resin which is a light yellow solid, having a color value of less than 10 and a viscosity (cp.) of 200-400.

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

1. In a liquid developer for developing electrostatic images on electrostatic charge carriers, said liquid developer consisting essentially of a toner dispersed in a carrier liquid, said carrier liquid being selected from the group consisting of paraffinic hydrocarbons, isoparaffinic hydrocarbons, naphtha hydrocarbons and halogenated hydrocarbons having an electric resistance of not less than 10^{10} Ω -cm. and a dielectric constant of not greater than 3 and an aniline point above 70° C., said toner consisting

10

essentially of pigment particles coated with a coating agent, said pigment particles being selected from the group consisting of carbon black (C.I. No. 77266), aniline black (C.I. No. 50440), spirit black (C.I. No. 50415), phthalocyanine blue (C.I. No. 74160), benzidine yellow (C.I. No. 21090), carmine 6B (C.I. No. 15850), lake red (C.I. No. 15585) and zinc oxide;

the improvement in which said coating agent consists essentially of an inner coating layer consisting of at least one (A) resin which is soluble in organic solvents having an aniline point below 50° C. and is insoluble in organic solvents having an aniline point above 70° C., said (A) resin being selected from the group consisting of phenol-aldehyde resin and phenol modified xylene resin, and an outer coating layer consisting of at least one (B) resin selected from the group consisting of (1) laurylmethacrylate-dimethylaminoethyl methacrylate copolymer, (2) laurylmethacrylate-n-butylmethacrylate copolymer and (3) laurylmethacrylate-isobutylmethacrylate copolymer.

2. The liquid developer of claim 1 in which the amount of the (A) resin constituting said inner coating layer formed on the surface of said pigment is in the range of from 0.3 to 5 parts by weight per one part by weight of said pigment particles.

3. The liquid developer of claim 1 in which the amount of the (B) resin constituting said outer coating layer formed on the surface of said inner coating layer is in the range of from 1 to 5 parts by weight per one part by weight of said pigment.

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NORMAN G. TORCHIN, Primary Examiner

J. P. BRANNER, Assistant Examiner

U.S. Cl. X.R.

117-37 LE

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3 770 637

Dated November 6, 1973

Inventor(s) Zenjiro Okuno, Akinori Mizuno and Ikuyo Kondoh

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

Col. 1, line 11; add to the priority data the following:

---and application, Japan, September
25, 1968, 43/68,753---.

Signed and sealed this 16th day of April 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents