

- [54] **LIQUID ELECTROSTATIC HAVING
PIGMENT PARTICLES COATED WITH
A CYCLIZED RUBBER**
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- [57] **ABSTRACT**
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 substantially of pigment particles whose surfaces are coated with a coating agent selected from the group consisting of cyclized rubber, a resin containing cyclized rubber, and a resin combining a resin having a high solubility for said carrier liquid and a resin having a low solubility for said carrier liquid.

5 Claims, No Drawings

A LIQUID ELECTROSTATIC HAVING PIGMENT PARTICLES COATED WITH A CYCLIZED RUBBER

BACKGROUND OF THE INVENTION

1. 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 and an electrostatic recording material.

2. 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 through the step of imparting an electrostatic charge with corona discharge on the surface of a photoconductive layer of an electrophotographic copying paper and exposure subsequent thereto.

As for the method of developing the electrostatic latent images formed as above, they 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. According to the dry-developing method, the development is effected by thermal fixing of a powder developer on an electrostatic charge carrier provided with an electrostatic latent image, while, according to the wet-developing method, the development is effected by merely dipping said electrostatic charge carrier in a liquid developer.

As for the liquid developer for use in developing an electrostatic latent image, the one which has hitherto been popular is a developer prepared by the steps of coating a single resin combining a property of providing pigment particles with polarity controllability, to wit, a distinct electric charge and a property of providing a carrier liquid with stability, to wit, a property of satisfactorily dispersing pigment particles in a carrier liquid on said pigment and then dispersing thus treated pigment 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 a carrier liquid providing that one is capable of controlling the polarity of the pigment and the other is superior in dispersibility though somewhat inferior in polarity controllability, and a developer which is a modification of the preceding one, wherein a field activator is further added to said resin of superior dispersibility to thereby control its polarity. However, with these conventional developers, it has been extremely difficult to maintain the initial efficiency thereof as displayed in the early period subsequent to their manufacture since the resin coated on the pigment particles, to wit, a toner contained in any of said developers, has such a drawback that it breaks away gradually from the pigment of the toner while the developer is used or stored, to thereby cause a deterioration of developing efficiency thereof. This phenomenon has hitherto been considered inevitable inasmuch as it is mainly attributable to the fact that a resin for use in coating on the pigment 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 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 from the viewpoint of control or prevention of said polarity deterioration phenomenon of the toner as well as the fixability thereof on the surface of an electrostatic charge carrier. In other words, the wet-developing method has a remarkable advantage that the fixing operation is quite simple as compared with the thermal fixing in case of the dry-developing method in so far as the fixing under the

former method is effected through the steps of dipping an electrostatic charge carrier having the electrostatic latent image in a liquid developer wherein a toner charged with a positive or negative charge has been dispersed and pulling it out subsequent thereto, and then evaporating the carrier liquid contained in said developer to thereby fix the toner on the surface of said electrostatic charge carrier, but, on the other hand, it has the drawback that the fixability of the toner which functions to form an image is comparatively poor. For instance, an image fixed on a copy is so easily erased by mere rubbing with a finger that in case of protracted preservation of such a copy or frequent taking in and out thereof during the preservation may cause the image not only to get blurred but also to be entirely eliminated. For this reason, such a copy could hardly be put to practical use for important papers such as official documents. The foregoing drawback is considered attributable to the small amount of resin adsorbed onto the pigment particles in the toner. (Said amount has been usually in the range of less than 1 part by weight of resin against 1 part by weight of pigment particles.) With a view of preventing said drawback, there has been an attempt to employ a toner prepared by coating pigment particles with such a resin which is comparatively insoluble in a carrier liquid, but it has also proved unsatisfactory because said toner is apt to cause agglomeration and have an inferior dispersibility in a 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 having such a polarity that it will never become indistinct during protracted preservation or repeated use thereof and also having a superb fixability with respect to the latent image area of an electrostatic charge carrier.

One of the liquid developers 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} Ω -cm. and a dielectric constant of less than 3, a toner prepared by coating pigment particles with such a resin, which has a low solubility for said carrier liquid, so that it is insoluble or hard to dissolve in a carrier liquid and also having a polarity controlling effect on said pigment together with a second resin, which has a high solubility for said carrier liquid, so that it is soluble or easily soluble in a carrier liquid and also contributes to the dispersibility of said pigment in a carrier liquid.

Another liquid developer according to the present invention is such a developer obtained by dispersing, in a carrier liquid having a high resistance and a low dielectric constant as stated in the foregoing, a toner prepared by coating pigment particles with a cyclized rubber or a resin containing a cyclized rubber.

The resin which is insoluble or hard to dissolve in a carrier liquid according to the present invention, means 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, it goes without saying that the second resin which is soluble or easily soluble in a carrier liquid refers the property of the resin relative to the foregoing carrier liquid comprising a hydrocarbon.

As for the carrier liquid having a high resistance and a low dielectric constant to be employed for the present invention, any of those known carrier liquids which have hitherto been employed for electrophotographic liquid developers—for instance, paraffinic hydrocarbon, isoparaffinic hydrocarbon, naphtha hydrocarbon, halogenated hydrocarbon, etc.—is applicable. And, as for commercially available carrier liquids, such petroleum hydrocarbons as are manufactured by ESSO Standard Sekiyu Ltd. and sold under the name of "ISOPAR-H" and "ISOPAR-G," a product of Shell Oil Co., Ltd. sold

under the name "SHELLSOL" and a product of Mobil SEKIYU Co., Ltd. sold under the name "PEGASOL" are most suitable.

In connection with said carrier liquid, the coating agent for the pigment particles which constitute the toner to be dispersed in the carrier liquid is elucidated in the following.

A. Re: resins hard to dissolve or insoluble in a carrier liquid

For the coating agent in the present invention, a phenol resin obtained from the group of phenols (such as phenol, cresol, xylenol and resorcinol) and the group of aldehydes (such as formaldehyde, acetaldehyde and furfural) and modified resins thereof are employed. Concrete and typical examples are as follows:

phenol resin, having 100 percent or less oil dissolving property

phenol modified xylene resin

And, as for commercially available coating agents, those resins 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.

B. Re: resins easily soluble in a carrier liquid

Vinyl polymer resins

The suitable resins in this category include laurylmethacrylate-dimethylaminoethylmethacrylate copolymer, laurylmethacrylate-n-butylmethacrylate copolymer (containing more than 20 percent laurylmethacrylate in terms of mol ratio) and the like.

Further, such copolymers as laurylmethacrylate-isobutylmethacrylate and the like are also applicable.

And, as for commercially available resins, those resins whose principal component is acryl copolymer, the products of ROHM & HASS Co., U.S.A. sold under the name "Plexol No. 966" and "Plexol No. 917," are most suitable.

Cyclized rubbers

The cyclized rubbers suitable for the present invention can be obtained through the following processes by employing a natural resin having a molecular weight in the range of 50,000-2,000,000.

1. Said rubber and any one of sulfuric acids or sulfonic acids are caused to interact.
2. A halogenide rubber is reduced to a dehalogenated hydrogen.
3. A solid rubber or a rubber solution is heated up to more than 250° C. in the presence of a catalyzer.
4. The rubber and a nonmetal halogenide or a hydroxy-halogenide are caused to interact.
5. The rubber and an amphoteric metal chloride are caused to interact, and the metal chloride is subjected to decomposition by alcohol.
6. The rubber is exposed to ultraviolet rays.
7. A cyclizing agent such as sulfuric acid is caused to act on an acid latex.

And, as for cyclized rubbers as stated above, products of SEIKO CHEMICAL Co., Ltd. sold under the names "Thermolite P," "Thermolite S," "Thermolite O" and "Thermolite N" are available. Further, a manufacture of Goodyear Co., U.S.A. sold under the name "Pliolite NR" is also suitable.

C. Re: resins to be employed in combination with cyclized rubbers

This kind of resin includes:

1. alkyd resins
2. varieties of synthetic resin varnishes, to wit, varnishes obtained from synthetic resins and drying oils (e.g., polymerized linseed oil)
3. styrene-containing resin, such as styrene-butadiene rubber, and polystyrene.

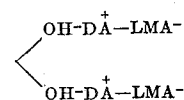
According to the present invention, the various coating agents as stated above are combined as follows for use in coating pigment particles therewith.

- I. Resins (A) hard to dissolve + at least one member of easily soluble resins (B) + pigment particles
- II. Cyclized rubbers + pigment particles
- III. Cyclized rubbers + resins (C) + pigment particles

In this context, it is noted that the cyclized rubber proves effective in coating pigment particles whichever combination among (I) through (III) above it may be employed in, as will be elucidated later on.

To begin with, when a toner of said combination (I) is prepared by coating pigment particles with a coating agent combining the foregoing resins (A) and (B) and employing such materials as set forth above, the intended liquid developer is obtained through the steps of dissolving a resin insoluble in a carrier liquid (i.e., resin (A)) by means of a small amount of an organic solvent such as toluene having an aniline point below 50° C., kneading the resultant mixture together with the granular or powdery pigment, adding thereafter an easily soluble resin (i.e., resin (B)) dissolved in a small amount of the same organic solvent as above for further kneading, and dispersing the thus kneaded compound (i.e., a concentrated toner) in a carrier liquid. A toner contained in a liquid developer thus prepared according to the present invention is capable of increasing the amount of insoluble resin coated on pigment particles several times as large as that of conventional toners, which could provide a coating of about 1 part by weight of the resin employed per 1 part by weight of pigment at the utmost, but is used to provide a coating of only 0.3 part by weight thereof. As a result, when an image is actually formed by way of the use of an ample quantity of said coating, there is effected quite a stable fixing of the toner onto an electrostatic charge carrier. Moreover, since the toner under the present invention is composed of pigment particles coated with the resin which comprises an easily soluble resin (B) and an insoluble resin (A) adsorbed with each other or combined chemically in a body, it has such advantages, as compared with conventional toners composed by way of merely adsorbing a resin onto the active center for adsorption of the pigment employed therefore, that not only the stability of the toner dispersion in a carrier liquid is remarkable, but also there occurs no such phenomenon as desorption of the resin, i.e., coating agent from pigment particles, resulting in the durability of its superb developing efficiency. In other words, such a toner contained in a liquid developer according to the present invention is of such a composition that the pigment particles within the developing liquid are covered with a resin insoluble or hard to dissolve in the carrier liquid all over their surfaces and the exterior of the thus-covered surfaces is further coated with a resin easily soluble in a carrier liquid which has been firmly combined with or adsorbed to the foregoing insoluble or hard-to-dissolve type resin. And, as for the mode of combination of said pigment with a resin hard to dissolve and a resin easily soluble, it is considered that the hydroxyl radical, for instance, of molecules consisting a resin hard to dissolve is firmly combined with, for instance, laurylmethacrylate-dimethylaminoethylmethacrylate copolymer in such a mode of combination as is expressed by the following summary formula.

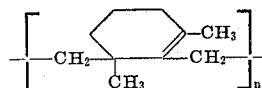
Formula expressing the mode of combination of resins (A) and (B)



Hard-to-dissolve type resin coated on the surface of pigment (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.

Meanwhile, a cyclized rubber is considered to have the following structural formula:



Since it is considered to be a compound composed of molecules of such structure as having a molecular weight with a relatively large numerical value of n in said formula and molecules of such structure as having a molecular weight with a relatively small numerical value of n in the formula arising out of the cutting of the principal chain of rubber, the molecular weight distribution of cyclized rubber extends over a wide range.

A cyclized rubber of said composition can be coated on the surfaces of pigment particles as much as desired regardless of the varieties of the carrier liquids, to wit, with no such restriction of the amount of coating according to the kind of carrier liquid employed. Moreover, when it is combined with resin (A), it displays properties and actions equivalent to those of resin (B).

In this context, it is considered that molecules with a structure of low molecular weight within a cyclized rubber coated on the surfaces of pigment particles accelerate the dispersibility of pigment particles or the dispersibility of pigment particles containing an adsorbed resin in a carrier liquid and act as a dispersion stabilizer, while molecules with a high molecular weight structure are adsorbed on said pigment particles and are in a swollen state in the carrier liquid so that in case of development they are absorbed in an electrostatic latent image area in that condition and are fixed firmly on said latent image area by evaporation of said carrier liquid. With respect to said properties, it is presumed that a molecule with a high molecular weight contained in a cyclized rubber has a property corresponding to that of resin (A) as stated above while a molecule with a low molecular weight has a property corresponding to that of resin (B) as stated above. And, a cyclized rubber having such a property is equally adaptable even to a carrier liquid prepared by blending different kinds of carrier liquids and it retains said property without being influenced by changes of temperature of the carrier liquid. Such property or action as stated above cannot be expected of any ordinary rubber such as natural rubber or isoprene rubber or any synthetic rubber such as butadiene rubber and the like. Further, a cyclized rubber has a peculiar field-activating effect in addition to the extensive molecular weight distribution as stated above.

Moreover, a cyclized rubber is capable of controlling the polarity of pigment particles per se to thereby provide a distinct polarity. For instance, in case of a substrate obtained by dispersing carbon black alone in an appropriate carrier liquid, there is not displayed any distinct polarity as required for development. However, in case of a liquid developer according to the present invention which is prepared by dispersing a kneaded mixture of carbon black and a cyclized rubber in a carrier liquid, that is, a developer prepared by employing a toner according to the aforesaid combination (II), the polarity becomes quite distinct. Further, even in case of a developer containing such a toner as has hitherto been of no practical use for the reason that is apt to cause aggregation within a carrier liquid, it is possible to improve said developer so as to make it suitable for practical use by employing a cyclized rubber, combination.

To take an illustration, when a vinyl polymer such as styrene-butadiene copolymer, polymer acrylate or styrene-acrylic copolymer is employed as a polarity-controlling resin for pigment particles, a satisfactory dispersion may be expected if said vinyl polymer has a superior affinity towards the carrier liquid employed, but the amount of such a resin adsorbed onto pigment particles is so small—in this case it is 30 percent or thereabout at the utmost—that the fixability of the toner on an electrostatic charge carrier is unsatisfactory. However, if a resin which is apt to somewhat swell in a carrier liquid is jointly used, the dispersibility will be deteriorated and aggregation will easily take place. On such an occasion, employment of a cyclized rubber together with such a defective resin as above is effective in preventing the occurrence of said phenomenon. Therefore, even in case of applying the aforesaid combination (III) in coating the surfaces of pigment

particles, not only a distinct polarity in a carrier liquid can be expected, but also a toner of superior dispersibility can be obtained.

When preparing a toner of the foregoing combination mode (II) according to the present invention, a cyclized rubber and a small amount of a carrier liquid are kneaded together with pigment particles. A toner of the combination mode (III) may be prepared either by employing the same components as the combination mode (II) plus the resin (C) and kneading them together, or by employing the resin (C) and a small amount of an organic solvent added thereto, kneading them together with pigment particles, and then adding a cyclized rubber and an organic solvent for further kneading subsequent thereto. And, the most suitable toner for the present invention is the latter one of the foregoing toners provided with a coating of the combination mode (III).

As for pigment particles to be employed for the present invention, any of those known heretofore is 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 contributes to displaying a much more distinct polarity than any conventional developer and maintains a uniform dispersibility 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 large fixability with respect to an electrostatic latent image consisting of a delicate electric charge and an image once fixed onto an electrostatic charge carrier cannot be erased so 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 retains a solvent resistance. And, especially when a toner employing a cyclized rubber is used, the rubber itself possesses superb electric properties, so that it is possible to adsorb an additional toner onto the image formed as above. Such being the case, said liquid developer according to the present invention is quite suitable for use in such repeated development as in case of developing color films of electrophotography.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Among the following Examples, 1 through 8 show the embodiments wherein the coating agents cyclized rubber and (C) are employed respectively, Examples 9 through 12 show the embodiments wherein the coating agents (A) and (B) are employed respectively and Example 13 is an embodiment of the use of cyclized rubber and coating agents (A).

EXAMPLE 1

A mixture, comprising:		
Carbon black (manufactured by Asahi Carbon Mfg. Co., Ltd. and sold under the name "XC-550")	4.5g.	spirit
black (manufactured by Orient Chemicals Co., Ltd. and sold under the name "Spirit Black-SB")	0.5 g.	
5%-toluene solution of styrene-butadiene copolymer (manufactured by Good Year Co., Ltd. and sold under the name "CPR")	62.5 g.	
toluene	400.0 g.	

was put in a ball mill for 16 hours kneading, and then taken out and subjected to spray drying. Subsequently, a mixture comprising 5 g. of a dry powder thus obtained, 36 g. of 25-percent toluene solution of a cyclized rubber (i.e., Thermolite-P) and 59 percent of naphtha hydrocarbon (i.e., a manufacture of ESSO Standard Oil Co., Ltd. Sold under the name "

Naphtha-No. 6") was also kneaded with a ball mill for 16 hours to thereby prepare a concentrated toner. Then, 10 g. of said toner was dispersed in 500 cc. of isoparaffin hydrocarbon (i.e., a manufacture of Standard Oil Co., Ltd. sold under the name "ISOPAR-H"), whereby there was obtained a liquid developer for use in developing an electrostatic image.

In this connection, it is noted that said spirit black was employed for the purpose of modifying the shade of the toner into pure black.

EXAMPLE 2

A mixture, comprising:
carbon black (manufactured by Mitsubishi Kasei Kogyo Co., Ltd. and sold under the name "Mitsubishi No. 44") 4.5 g.
spirit black 0.5 g.
5%-toluene solution of styrene-butadiene copolymer (manufactured by Good Year Co., Ltd. and sold under the name "Pliolite S-5 SD") 12.5 g.
toluene 400 g.

was treated in the same way as Example 1 for preparing a dry powder. Subsequently, a mixture comprising 5 g. of the dry powder thus prepared, 36 g. of 25-percent toluene solution of a cyclized rubber (i.e., Thermolite-S) and 59 g. of naphtha hydrocarbon was treated in the same way as Example 1 for preparing a concentrated toner. Then, 10 g. of said toner was dispersed in 500 c.c. of isoparaffin hydrocarbon, whereby there was obtained a liquid developer for use in developing electrostatic images.

EXAMPLE 3

By applying the same mixture and same treatment as Example 1, except that said cyclized rubber was replaced by Pliolite-NR, a liquid developer for use in developing electrostatic images was prepared.

EXAMPLE 4

By applying the same mixture and same treatment as Example 1, except that said cyclized rubber was replaced by Thermolite-O, a liquid developer for use in developing electrostatic images was prepared.

EXAMPLE 5

By applying the same mixture and same treatment as Example 1, except that said cyclized rubber was replaced by Thermolite-N, a liquid developer for use in developing electrostatic images was prepared.

EXAMPLE 6

A mixture, comprising:
Carbon black (XC-550) 4.5 g.
spirit black 0.5 g.
styrene-butadiene copolymer (aforesaid CPR) 6 g.
toluene 40 g.
cyclized rubber (Thermolite-P) 72 g.
naphtha hydrocarbon 77 g.

was subjected to 16 hours kneading within a ball mill to thereby prepare a concentrated toner. Then, 10 g. of said toner was dispersed in isoparaffin hydrocarbon, whereby there was obtained a liquid developer (of positive-to-positive type) for use in developing electrostatic images.

EXAMPLE 7

A mixture, comprising:
carbon black (MOGAL-A, manufactured by Cabbot Co., Ltd.) 5.0 g.
cyclized rubber 36 g.
Naphtha hydrocarbon 51 g.

was subjected to 16 hours kneading within a ball mill to thereby prepare a concentrated toner. Then, 5 g. of said toner was dispersed in 500 cc. of isoparaffin hydrocarbon, whereby was obtained a liquid developer (of negative- to -positive type) for use in developing electrostatic images.

Those developers which were prepared as in Example 1 through 6 above, when employed for dipping and developing an electrophotographic copying paper having positive electrostatic latent images impressed by a commercially available copying machine (i.e., a manufacture Kabushiki Kaisha Ricoh sold under the name "BS-1"); proved capable of forming copied images of superb distinction and stability. Besides, when an acetate film employed as an electrostatic recording paper was impressed with a latent image by applying a voltage of -10 kv. for 0.5 second and subjected to developing by those developers of Example 1 through 6, the fixing of copied images, was quite satisfactory, and further when the foregoing film was impressed with images by applying a voltage of +10 kv. for 0.5 second and subjected to developing with a developer of Example 7, the resultant images also displayed superb fixability.

EXAMPLE 8

By applying the mixture and same treatment as Example 1, except that said carbon black was replaced by copper phthalocyanine, carmine 6B and benzine dispersed respectively, an indigo-blue liquid developer, a red liquid developer and a yellow liquid developer for use in developing electrostatic images were respectively prepared. All of those developers proved superb in dispersibility as well as fixability, and also displayed a superb efficiency in the multilayer development (color development) by way of the three-color separation chart employing a conventional electrophotographic copying paper.

EXAMPLE 9

A mixture, comprising:
carbon black (manufactured by Mitsubishi Kasei Kogyo Co., Ltd., and sold under the name "Carbon Black No. 100") 5 g.
40%-toluene solution of NIKANOL HP-100) 30 g.

was subjected to 1 hour's kneading within a ball-mill, and then

Plexol No. 966 10 g.
toluene 55 g.

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

On the other hand, for the purpose of comparing the efficiencies of developers, a toner comprising carbon black coated with alkyd resin was prepared by almost the same treatment as a 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 way of a conventional electrophotographic method, electrostatic latent images were imparted onto commercially available electrophotographic copying papers, and then said copying papers were dipped in each of the above-stated developers in order to compare their fixability with respect to said images as well as to observe the degrees of deterioration of the developing efficiency due to prolonged preservation of respective developers. The results of said observations are summarized in the following Table 1.

TABLE 1

Developer, compared efficiency	Developer under the present invention	Developer for comparison's sake
Image fixability*.....	Satisfactory.....	A little inferior.
Preservability: condition when left intact for 90 days.	No precipitation occurred.	Precipitation occurred (Aggregation was observed at the bottom of the receptacle for preservation).
Ratio of transmittancy when left intact for 90 days (percent)**	94.....	23.
Image formed by a developer left intact for 90 days: Distinction.	Satisfactory.....	Unsatisfactory.
Image density ratio.....	94.....	10.

* As for the fixability, such an image as would not be erased out by rubbing several times with an india rubber eraser was rated "satisfactory."

** The ratio of transmittancy was shown by way of percentage, to wit, $T_0/T_{90} \times 100$, wherein T_0 denotes the transmittancy of the liquid at the time of preparing a developer (liquid depth being 1 cm.) and T_{90} denotes the transmittancy when said developer was preserved for 90 days subsequent to preparation thereof.

*** The concentration of image was measured with a densitometer manufactured by Photovolt Co., U.S.A. and shown by way of percentage, to wit, $R_{90}/R_0 \times 100$, wherein R_0 denotes the reflexivity of an image formed with a developer just after the preparation thereof, and R_{90} denotes the reflexivity of an image formed with a developer left intact for 90 days.

EXAMPLE 10

a. solution, comprising
carbon black (the same as Example 1)
50%-toluene solution of NIKANOL HP-120

5 g.
30 g. HP-
120 b.
solution,
-
comprising
10 g.
55 g.

Plexol 966
toluene

The above solutions (a) and (b) were respectively treated in the same way as Example 9, whereby there were obtained liquid developers for use in developing electrostatic latent images.

The thus-prepared developers, when put to practical use for copy development and observed as regards their efficiency, proved to have a fixability as well as a preservability equivalent to the developer of Example 9 according to the present invention.

EXAMPLE 11

a. solution, comprising
carbon black (manufactured by Cabbot Co., Ltd., U.S.A.
and sold under the name "MOGAL-A")
50%-toluene solution of NIKANOL HP-100
b. solution, comprising
Plexol No. 966
toluene

5 g.
30 g.
10 g.
55 g.

The above solutions (a) and (b) were respectively treated in the same way as Example 9, whereby there were obtained liquid developers for use in developing electrostatic latent images. And, the thus prepared developers proved to have efficiency equivalent to the foregoing developers according to the present invention.

Example 12

By applying a toner preparing solution having the same composition as Examples 9, 10 and 11 above respectively, except that only the resin easily soluble in a carrier liquid, to wit, Plexol No. 966 alone was replaced by either Plexol No. 917 or laurylmethacrylate-dimethyl-aminoethylmethacrylate copolymer, liquid developers for use in developing electrostatic latent images were prepared respectively. These developers also proved to have efficiency equivalent to those developers of Example 9 through 11 according to the present invention.

EXAMPLE 13

A mixture, comprising:
Carbon black (the same as Example 1)
50%-toluene solution of NIKANOL HP-100
was subjected to 1 hours kneading within a ball-mill, and then:

25%-toluene solution of a
cyclized rubber
toluene

30 g.
35 g.

were added to the thus kneaded mixture and were followed by 16 hours kneading thereafter. The resultant kneaded mixture was then treated in the same way as in case of the developer of Example 9 according to the present invention, whereby there was obtained a liquid developer for use in developing electro-

static latent images. The thus-prepared developer, when examined as regards its developing efficiency, proved to have an efficiency equivalent to the developer of Example 9 according to the present invention.

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.

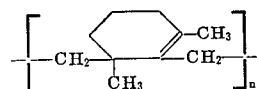
Nikanol HP 100 is an alkyl phenol modified xylene resin which is a light yellow solid, having a color value of less than 8 and a viscosity (cp.) of 200-400.

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-

What we claim is:

1. In a liquid developer for developing electrostatic images on electrostatic charge carriers, and 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 $10^{10} \Omega \cdot \text{cm.}$ and a dielectric constant of not greater than 3, said toner consisting 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 a member selected from the group consisting of (1) cyclized rubber, (2) said cyclized rubber and resin A, and (3) said cyclized rubber and resin C, said cyclized rubber having recurring structural units of the formula



and having a molecular weight in the range of from about 50,000 to two million;

said resin A is selected from the group consisting of phenolaldehyde resin and phenol modified xylene resin; and

said resin C is selected from the group consisting of alkyd resin, polymerized linseed oil, polystyrene resin and styrene-butadiene rubber.

2. A liquid developer according to claim 1, in which the coating agent consists of said cyclized rubber whose molecular weight distribution extends over a wide range.

3. A liquid developer according to claim 1, in which the coating agent consists of said cyclized rubber and said resin C and in which said resin C forms an inner coating layer on said pigment particles and said cyclized rubber is an outer coating layer covering said inner coating layer.

4. A liquid developer according to claim 1, in which said coating agent consists of a mixture of said cyclized rubber and said resin C forming a coating layer on said pigment particles.

5. A liquid developer according to claim 1, in which said coating agent consists of said cyclized rubber and resin A and in which said resin A forms an inner coating layer on said pigment particles and said cyclized rubber is an outer coating layer covering said inner coating layer.

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