

[54] **METHOD OF PRODUCING
ELECTROPHOTOGRAPHIC LIQUID
DEVELOPERS HAVING VERY FINE
COLORING MATERIAL**

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[57] **ABSTRACT**

An electrophotographic liquid developer composed of a carrier liquid with a volume resistivity of over $10^9 \Omega \text{cm}$ and specific dielectric constant of below 3.5, colored material in fine powder form, a charge control agent selected from the group consisting of a vinyl chloride polymer and nitrocellulose which is insoluble in said carrier liquid, a material selected from the group consisting of resin, oil and mixtures thereof, having high compatability with said charge control agent and being soluble in said carrier liquid, a liquid which dissolves said charge control agent and is compatible with said carrier liquid, and a dispersion stabilizer accounting for less than 20 percent (by weight) and more than 0.5 percent (by weight) of the whole.

9 Claims, No Drawings

METHOD OF PRODUCING ELECTROPHOTOGRAPHIC LIQUID DEVELOPERS HAVING VERY FINE COLORING MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a liquid developer used for the development of an electrostatic latent image in electrophotography and, in particular, to a liquid developer containing negatively charged toners as well as the process of its preparation.

2. Description of the Prior Art

In the development of electrophotography, a process of applying toners charged with a polarity different in sign from that of the charge in an electrostatic latent image and causing the toners to adhere to a high potential region utilizing the mutual attraction of different electric charges (this method is referred to as attractive or ordinary development) and a process of employing the toners charged with a polarity of the same sign as the charge of electrostatic latent image and causing the toners to stick to a low potential region utilizing the repulsion between the electrostatic charges of the same polarity are available. The liquid developer according to the present invention, in which particles suspended in liquid are electrically charged negatively, makes it possible to accomplish reversal development in case the latent image is composed of negative charges and ordinary development in the case of a positive latent image.

Though liquid developer consists of fine colloidal particles suspended and dispersed in the electric insulating carrier liquid (for instance, chlorinated hydrocarbon, chlorinated-fluorinated hydrocarbon, aliphatic hydrocarbon, polymethyl siloxane, etc.) the polarity of the colloidal charge is determined by the carrier liquid, substances dissolved in the carrier liquid and the surface condition of the pigment or dye colloid particles to be suspended in the carrier liquid, etc. For instance, due to colloidal particles in some cases, colloidal particles are covered with suitable insulating resin so as to assure a charge of the desired polarity.

In respect to conventional pigments or dyestuffs to be suspended and dispersed in carrier liquid, for instance, phthalocyanine blue, crystal violet, ethyl eosine, mercury sulfide and zinc oxide, etc., they are liable to be charged positively, whereas cyanine green and powdered sulfur or selenium, etc., are liable to be charged negatively. In the meantime, for the purpose of charging the particles of pigment or dye to a desired polarity and lowering the conductivity of particles, the coating of the surface of suspended particles with insulating resin is being widely applied. For instance, ethyl cellulose, polyacryl ester resin, linseed oil modified alkyd resin and polyvinyl acetate resin, etc., are used as a charge control agent for positive charging and polyvinyl chloride resin, chlorinated polypropylene resin and polyvinylidene chloride, etc., for negative charging. For instance, in case where carbon black is incorporated as a toner material in a liquid developer to provide a black image, a dispersion of naked carbon black particles in petroleum, etc., brings about ordinary development in one case and reversal development in the other with respect to electrostatic latent images having the polarity of the same sign and, on the other hand, causes image blur and fog, etc., deemed to be originating from the conductivity of carbon black, for which reason carbon black cannot be applied by itself as a toner. Therefore, as the liquid developer containing toners with a positive charge, for instance, one prepared in the following procedure is applied:

Carbon Black	2 parts by weight
Polyvinyl Acetate Resin	6 parts by weight
Methyl Acetate	10 parts by weight

The above components are fully kneaded and mixed by means of a 3-roll kneading machine and 1 part of the obtained paste is dispersed in 100 parts of kerosene.

As for the developer containing toners with negative charge, for instance, one prepared in the following procedure is applied:

Carbon Black	3 parts by weight
Polyvinyl Chloride Resin	2 parts by weight
Tetrahydrofuran	5 parts by weight

The above components are kneaded and 1 part of thus obtained paste is dispersed in 100 parts of cyclohexane.

The present invention relates to a liquid developer containing toners with negative charges. Developers containing toners with negative charges are described in many patent specifications but are not so satisfactory. Time-instability of the negative toner in carrier liquid is reported, for instance, on Page 370 of "Electrophotography" written by R.M. Shaffert (published by Focal Press Co., 1965). In respect of a liquid developer to be employed in a developing equipment, it is necessary that its dispersed state stably remains uncharged over a long period and that the toner charge sign as well as the quantity of charge is stable in course of the lapse of time. For the purpose of ensuring a sharp line copy or reproduction of continuous gradation, it is necessary for the dispersed toner particles to be uniform in size and small in grain size. It has been extremely difficult to prepare a liquid developer containing toners with negative charge meeting these requirements.

SUMMARY OF THE INVENTION

As a result of research with due consideration of these disadvantages of the conventional negative toner liquid developers, the inventors have discovered a process of preparation of excellent liquid developer considerably overcoming these disadvantages. In summary, it has been found that a negative toner liquid developer possessing desirable characteristics can be obtained in such a way that resin or oil being soluble in a carrier liquid and possessing a high electric resistance and a polymer compatible with said high resistance resin, etc., and insoluble in said carrier liquid and possessing negative charges when brought into contact with said carrier liquid are mixed, to which are added a solvent in which said resin and said coloring matter such as pigment, etc., and these are fully kneaded to obtain paste, which paste is then strongly agitated and dispersed in the electric insulating carrier liquid in which a dispersion stabilizer (fixer) having high electric resistance is dissolved.

Accordingly, the object of the present invention consists of providing a process of preparation of a novel liquid developer containing toners with negative charges. Another object of the present invention is to provide a negative toner liquid developer possessing excellent time-stability. One of the other objects of the present invention is to provide a method of manufacturing liquid developer containing fine toners uniform in grain size, with excellent dispersion of toners therein being one of the prominent features of the present invention. Another important object is manufacturing of liquid developer suitable for achieving reproduction in continuous gradation and further in the provision of a preparation process of liquid developer suitable for color electrophotography. Providing a liquid developer possessing excellent preservability and especially suitable for use in automatic developing equipment is also one of the important objects of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The materials and operations applied under the present invention are described in detail in the following.

As for the photoconductive light sensitive layer, the one generally employed in the field of electrophotography may be employed. The liquid developer to be prepared according to the present invention includes toners with negative polarity, in the case of a sensitive layer such as selenium, which is used by positive charging, a positive image is obtained as the copy if

the original is a positive image (ordinary development). In the case of a sensitive layer comprising zinc oxide as photoconductive materials, for instance, Electrofax paper, etc., which is used by negative charging, a positive copy is obtained from a negative original (reversal development).

The liquid carrier employed under the present invention should preferably possess high insulating property and a low dielectric constant and concretely, the one with specific resistance of over $10^9 \Omega \text{ cm}$ and specific dielectric constant of less than 3.5, serves the purpose. Available as such substances are various aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, chlorinated-fluorinated hydrocarbon and fluorinated hydrocarbon, etc. Desirable in view of practical behavior are heptane, hexane, kerosene, cyclohexane, gasoline and light oil, etc.

In respect of coloring material, almost any finely divided particles may be applied. In the liquid developer of the present invention, the surface of the coloring material employed is covered with charge control agent and does not directly touch the carrier liquid, for which reason the polarity of charge on the dispersed particles is determined only by the nature of the control agent employed regardless of the surface property of the individual coloring material. Accordingly, various pigments can be applied as the coloring material, for instance, inorganic pigments such as carbon black, black iron oxide, nickel oxide, chrome oxide, cobalt ferrite, titanium oxide, zinc oxide, mercury iodide, mercury sulfide, lead oxide, cadmium sulfide, pulverized sulfur, various metallic powder and organic pigments such as phthalocyanine blue, alkali blue, hansa yellow, ponceaux 2R and naphthol yellow, etc. If dyestuff is employed as the coloring material, coloring matter can be obtained on another supporting medium by way of an appropriate mordanting process after development. As such examples, spirit blue for dye transfer using alcohol and acid violet 6, acid red 5, acid yellow 23 and acid blue 54, etc., for dye transfer by water, are available. Coloring materials can be applied without special restrictions under the present invention, provided that those materials are insoluble in the carrier liquid to be employed. Iodine, oil yellow and spirit black, etc., are eliminated for this reason.

Under the present invention, as for the polymer to control the charge of dispersed toner particles, those which carry negative charges on the surface when brought into contact with the carrier liquid are employed. Available as such polymers, are polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, chlorinated rubber, chlorinated polypropylene and nitrocellulose, etc., and various copolymers whose principal constituents are the monomers of these polymers, for instance, vinyl chloride-vinylidene chloride copolymer, vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinyl acetate-vinyl alcohol terpolymer, vinyl chloride-vinyl acetate-maleic acid terpolymer, vinyl chloride-acrylate copolymer, vinyl chloride-acrylonitrile copolymer and vinyl chloride-chlorotrifluoroethylene copolymer, etc. These are required to be selected in consideration of the relation to the resin soluble in the carrier liquid or solvent, etc. It is desirable that these polymers for charge control, as mentioned above, be insoluble in the carrier liquid. All of these substances enumerated here possess high electric resistance, satisfying the requirements of coating agents of liquid developer toner.

Now, the resin being soluble in carrier liquid and to be kneaded with coloring material and charge control polymer, will be described.

Various resins are applicable, but the ones having high electric resistance are preferable in that the resin exists eventually in the carrier liquid in a dissolved condition. It is also desirable for them to be well compatible with charge control polymer. Such characteristics help the minute dispersion of coloring material in the paste upon preparation of the paste by kneading and also serves the purpose of making very fine the grain size of toner particles consisting of charge control polymer and coloring material to be produced in the carrier liquid

upon dispersion and dissolution of the paste in the carrier liquid. In the case of poor or insufficient compatibility between the charge control polymer and the carrier liquid soluble resin, the paste can often be prepared successfully by addition of such solvent, etc., as will dissolve charge control polymer. As for the carrier liquid soluble resin to be employed according to the present invention, thermoplastic acrylic resin, drying oil type alkyd resin, nondrying oil type alkyd resin, epoxy ester, rosin modified alkyd resin, phenol-modified alkyd resin, styrenated alkyd resin, rosin modified phenol-formaldehyde resin, phenol-formaldehyde resin and epoxy ester of vegetable oil fatty acids, etc., are available. As these carrier liquid soluble resins are used in a dissolved state in carrier liquid, the tolerable limits of electric resistance or dielectric constant of these resins are determined according to the amount to be added to the liquid carrier. As the substance soluble in carrier liquid to be used jointly with charge control polymer, various types of high-insulating, various kinds of vegetable oils which comprise glycol ester of long chain fatty acids, are also applicable besides the above-mentioned various resins. For instance, linseed oil, tung oil, soybean oil, peanut oil, sesame oil and so on can be employed. In this case too, if their compatibility with the charge control polymer were insufficient, they may be utilized by adding a small quantity of solvent for the charge control polymer. It is also possible to use these oils in combination with the aforesaid carrier liquid soluble resins.

The dispersion stabilizer to be added to a carrier liquid under the present invention will be described in detail. In a number of patent specifications so far published concerning liquid developer, such dispersion stabilizer is described in detail as the so-called "fixer." The dispersion stabilizer in the present invention does not differ from the ones described in said published patents. That is to say, any types of resin, oil and wax, etc., which dissolve in carrier liquid can be used. In the present invention, many charge control polymers possess thermoplasticity and therefore these additives need not especially act as fixers and substantially the hitherto described additives as fixers may be said to act rather as dispersion stabilizers. In the meantime, drying of a developed sheet material becomes quite easy by dipping the wet sheet after development into a nonpolar liquid having a high evaporation speed, whereby much of the carrier liquid soluble resin is liable to be washed off by the nonpolar liquid of high volatility and accordingly, it cannot work as fixing agent. Accordingly, in case of carrying out such a process, they need not especially be the conventionally employed drying oil, etc., but liquid nondrying oil, etc., can also be employed. As these dispersion stabilizers are used in a dissolved condition in carrier liquid, it is desirable that they possess high electric resistance and low dielectric constant, but such property limitations are subject to considerable changes according to the volume of addition to carrier liquid.

Various materials required under the present invention have been described as above and it goes without saying that other additives, for instance, nonionic surface activator, curing accelerator and viscosity modifier, etc., can be added as long as the function of liquid developer is not impaired thereby.

Next, the combination of materials and their quantitative relationship in the present invention is described.

Under the present invention, in the case of preparation of paste composed of a coloring material, a charge control polymer and a carrier liquid soluble substance, it is an essential requirement that the charge control polymer, and the carrier liquid soluble substance are fully dissolved in each other and therefore, it is necessary to properly select them from among a number of substances described hereinbefore. Good results can be obtained by combined use, for instance, of alkyd resins and polymers including vinyl chloride being well soluble with the former. That is, the combinations of vinyl chloride-vinyl acetate-vinyl alcohol polymer with drying oil type alkyd resin, vinylchloride-vinyl chloride-vinyl

acetatemaleic acid copolymer with thermoplastic acrylic resin of low molecular weight and vinyl chloride-vinyl acetate-vinyl alcohol terpolymer with rosin modified alkyd resin, etc., are applicable. In the case of employing nitrocellulose as the charge control agent, those which are soluble in carrier liquid can be selected from among alkyd resins and maleic acid resins, etc. As for charge control agent and carrier liquid soluble substance, either one type of material or more than two types of material mixed may be employed respectively. Applying a small quantity of auxiliary solvent in paste preparation is an effective means in that compatibility is improved and kneading is made easy. However, the amount of such auxiliary solvent, especially when the solvent has a high polarity, should be minimized, since the solvent is introduced in the final liquid developer upon dissolution of the paste.

Explaining about the volume of each material in the preparation of paste, against 1 part by weight of a coloring material, generally the use of 0.1 to 20 parts by weight of a charge control polymer is preferable. An excessively small quantity of a charge control polymer in the prepared liquid developer makes it impossible to completely cover the surface of coloring material, producing toners of different signs and causing the dispersion to be unstable. On the other hand, an excessively large quantity of said polymer causes a lowering of image density on a sheet after development. In the case where it is necessary to impart a heat-fixing property to the resulting image, the minimum quantity required of said polymer with respect to the coloring material somewhat increases. For instance, in the case where a vinyl chloride polymer was employed as the charge control agent, as well as thermal fixer and carbon black as the coloring material, satisfactory fixability and image density could be obtained at the rate of 0.5 to 5 parts by weight of polymer as against 1 part by weight of carbon black. In the case where a dyestuff for dye-transfer is contained, in a tone too much charge control polymer is not desirable, with 0.5 to 5 parts by weight giving satisfactory results. As compared with a charge control polymer, the limitations as to the amount of a carrier liquid soluble substance (resin, oil, etc.) are not so severe. However, it is necessary that it is more than the amount of the charge control polymer employed therewith. The amount leading to a satisfactory result is some 3 to 50 parts by weight with respect to 1 part by weight of the coloring material. An example which led to a satisfactory result in the case of carbon black vinyl chloride copolymer nondrying oil type alkyd resin was 0.5 to 5 parts by weight of vinyl chloride copolymer and 10 to 50 parts by weight of alkyd resin as against 1 part by weight of carbon black. In this instance, vinyl chloride copolymer is the carrier-insoluble component serving as charge control agent, whereas nondrying oil type alkyd resin is the carrier-soluble component. Though the amount of solvent to be added in case of insufficient compatibility between carrier-soluble substance and polymer is determined by the relative amount and properties of these two substances, it was sufficient to add nearly equivalent to charge control polymer or 15 parts by weight. Though the amount of dispersion stabilizer (according to the conventional term, "fixer") to be added to the carrier liquid is dependent on the volume of paste to be dispersed and dissolved in the carrier liquid, it is desirable, from a viewpoint of handling, to add 0.5 to 20 parts by weight per 100 parts by weight of carrier liquid. In case the amount is too small, prepared liquid developer becomes unstable. In the case where the dispersion stabilizer has high resistance and low dielectric constant, such as linseed oil, applying a larger amount is quite acceptable. A developer containing such large volume of stabilizer has high viscosity and the dispersion of toners becomes excellent, but has a disadvantage the developing speed is reduced and accordingly it becomes necessary to employ a sensitive layer slow in dark decay of surface charge in the carrier liquid.

In dissolving and dispersing the paste prepared under the process of the present invention in the carrier liquid containing a dispersion stabilizer, 0.1 to 20 parts by weight per 100

parts by weight of carrier liquid could be applied. An excessively small amount is liable to lower the density of toners in the liquid developer. If prepared densely, edge effect in the case of development is reduced, making possible the reproduction of original in continuous gradation.

The operating procedures at the respective steps of the present invention are now described.

For the preparation of paste, porcelain ball mill, agitator, vertical ball mill, planetary type agate ball mill, colloid mill and attraiter, etc., are suitable. Use of chilled roll, etc., is also effective and suitable for the preparation of good paste. If, prior to the dispersion of prepared paste, a solvent was used for mixing polymer and resin, it is also desirable to volatilize it to some extent and then proceed to the next step.

The paste thus obtained is then dissolved and dispersed in the carrier liquid containing a stabilizer (fixer), for which purpose, generally speaking, it is desirable to employ a high performance agitator. For example, homogenizer and electric mixer are applicable and especially the use of ultrasonic disperser led to a satisfactory result. As regards the temperature at the time of dispersion, it has been found that not too high temperature generally leads to the developing liquid in stable dispersion condition. Though the liquid developer containing an insulating bonding medium such as wax in the developing liquid is described in the Japanese Pat. No. 40-9788, waxes are apt to be separated at low temperature according to the said description and affect the negative charge toners, for which reason the use thereof in the present invention is inappropriate.

As will be understood from the above explanation, in the liquid developer obtainable according to the present invention, the coloring material is covered with charge control polymer and surrounded by the adsorbed dispersion stabilizer. Though different in the process of preparation, similar compositions have hitherto been reported. For instance, according to the process published in the Japanese Pat. No. 38-22343, first the coloring material is covered with charge control agent and thereafter dispersed, for which reason it involved the disadvantage that fine grains of toner were hard to obtain and the dispersion was liable to be unstable. The cause is deemed to be attributable to the fact that kneading and crushing are carried out for many hours after the addition of charge control agent, for which reason impurities carrying opposite charges are liable to be introduced into the developing liquid and the surface of coloring material itself comes to touch the carrier liquid due to the peeling off or crushing of coat. According to the process as under the present invention, when the paste is added to the carrier liquid, carrier-soluble substance flows out of the paste into the carrier liquid, the paste is decomposed and charge control polymer insoluble in the carrier liquid and containing the coloring material, is separated as the toner and dispersed. Almost simultaneously therewith, the stabilizer in the carrier liquid and effluent carrier-soluble substance (resin, oil) are adsorbed to the fine toner particles just separated and prevent the adhesion of toner particles, extremely stable developing liquid being thus obtained. According to the present invention, the coloring materials are completely covered with charge control agents, becoming uniform in the size, and therefore, all the toner particles come to carry nearly equal charges.

In the mechanism of toner particle dispersion according to the present invention, there may be included partly the effect that the material covering the coloring material in the case of dispersion acts as a wetting agent, making easy the adsorption of stabilizer (fixer) in the carrier liquid. A process based on such concept is already described in the specification of British Pat. No. 1001570. However, the most important point of the present invention consists in that the paste is prepared by kneading the coloring matter and resin or oil soluble in carrier liquid together with charge control polymer being dissolved with said resin or oil and insoluble in the carrier liquid, for which reason when such paste is added to carrier liquid, carrier liquid soluble components contained in large quanti-

ties in the paste flow out and therefore toner particles comprising charge control agents covering the coloring material left behind become very fine in grain size. The advantage of vinyl chloride-vinyl acetate copolymer and nitro-cellulose as the charge control resins consists in that they are insoluble in most non-polar solvents and soluble with alkyd resin, etc. The present invention is further described with reference to some examples in the following.

EXAMPLE 1

The following components were kneaded for 15 hours using a porcelain ball mill:

Zinc Oxide	100 parts
Silicon resin varnish (solid content 60%)	50 parts
Toluene	20 parts

After providing these components on the surface of conductive paper, it was left in the atmosphere of 50° C., for 4 hours. The thickness of the sensitive layer after drying was 12 μ . On the other hand, as the raw material of liquid developer, the paste composed of the following was prepared:

Carbon Black (Nipeal No. 100 made by Nittetsu Chemical Industry Co. Ltd.)	1 g
Vinyl chloride-vinyl acetate-vinyl alcohol terpolymer (Denka Vinyl No. 1000G, made by Electric Chemical Industry Co. Ltd.)	3 g
Drying oil type alkyd resin (Solid Bekkosol 18, 70% oil, made by Nihon Reichhold Chemical Industry Co. Ltd.)	30 g.
Acetone	40 c.c.

These components were kneaded for 48 hours in a porcelain ball mill. 1 gram of this paste was dissolved and dispersed by means of ultrasonic disperser in the liquid having the following composition. In this case, vinyl chloride-vinyl acetate-vinyl alcohol copolymer is insoluble in the carrier liquid, whereas drying oil type alkyd resin is soluble in the carrier liquid.

Kerosene	50 c.c.
Cyclohexane	50 c.c.
Linseed Oil	2 c.c.
Non-ionic wetting agent	0.01 g.

Thus black liquid developer in good dispersed condition could be obtained.

The aforesaid zinc oxide light sensitive paper was charged by means of -7000 V corona and thereafter exposed for 2 seconds through a line image negative original by means of 5,500-lux light source (Printer for Quick Copy made by Fuji Photo Film Co. Ltd.). Next, this sensitive paper was dipped for 10 seconds in the above-mentioned liquid developer, taken out and dried. As a result, a sharp, somewhat mild and black positive image involving little fog could be obtained. This image was heat-fixed by means of infrared lamp.

EXAMPLE 2

The following components were kneaded for 5 hours using a planetary type agate ball mill. In this composition, drying oil type alkyd resin is the carrier liquid soluble component and vinyl chloride-vinyl acetate copolymer the carrier liquid insoluble component.

Carbon Black	2 g.
Phthalocyanine blue (finess blue, made by Tokyo Ink Co. Ltd.)	0.5 g.
Alkali blue	0.5 g.
Drying oil type alkyd resin	30 g.
Butyl acetate	20 c.c.
Vinyl chloride-vinyl acetate copolymer (Denka Lack made by Electric Chemical Industry Co. Ltd.)	5 g.

Acetone (0.5 c.c.) was added to 1 gram of paste thus obtained, which was then dispersed in the liquid similar to the one under Example 1 by means of ultrasonic disperser to prepare liquid developer, into which was dipped a sensitive paper exposed similarly as in the case of Example 1, and the sensitive paper was thereafter taken out and dried. A black positive image of cold tone involving little fog could be obtained.

EXAMPLE 3

The same sensitive layer as in the case of Example 1 was charged and then exposed through a negative original with continuous gradation and developed employing a gauze type developing electrode with a potential of -150V placed 0.5mm apart from the sensitive paper and in the liquid developer under Example 2. As a result, a positive image of continuous gradation could be obtained.

EXAMPLE 4

After leaving the liquid developer prepared according to the Example 2 at room temperature for 20 days, a sensitive paper exposed in the same manner as in the case of Example 1 was developed. The thus obtained positive image differed little from that obtained in Example 2.

EXAMPLE 5

The following components were kneaded:

Phthalocyanine blue (RS 1/16)	1 g
Nitrocellulose/(Daicell Co. Ltd.)	1 g
Drying oil type alkyd resin	50 g
Acetone	20 c.c.

Using the above and according to the same process as in Example 1, a liquid developer for blue image could be obtained.

EXAMPLE 6

Paste for liquid developer prepared by kneading the following constituents:

Phthalocyanine green (finesse green made by Tokyo Ink Co. Ltd.)	1 g
Nitrocellulose (RS 1/16)	1 g
Drying oil type alkyd resin	30 g
Acetone	20 c.c.

By means of the liquid developer prepared from the above paste using the carrier liquid under Example 1, a green image could be obtained.

EXAMPLE 7

Paste for liquid developer prepared by kneading the following components:

Llansa yellow	1 g
Nitrocellulose	0.5 g
Rosin modified alkyd resin	10 g
Acetone	20 c.c.

The liquid developer prepared from this paste using the carrier liquid under Example 1 provides a yellow image.

EXAMPLE 8

Carbon Black	1 g
Vinyl chloride-vinyl acetate copolymer	2 g
Linseed Oil	30 g
Acetone	5 c.c.
Methyl ethyl ketone	15 c.c.

The liquid developer prepared from this paste provided a mild black image.

EXAMPLE 9

Liquid developer prepared by dissolving and dispersing the paste obtained according to Example 1 in the following liquid:

Cyclohexane	100 parts by weight
Soybean oil	15 parts by weight
Soybean lecithin	0.001 parts by weight

This developer provides a black image of mild tone and is suitable for the reproduction of continuous gradation.

EXAMPLE 10

Three types of paste with the following compositions were prepared:

Type I	
Tartrazine	4.5 g
Vinyl chloride-vinyl acetate copolymer	4 g
Drying oil type alkyd resin	30 g
Acetone	20 c.c.
Butyl acetate	80 c.c.

Type II	
Acid violet 7	4.5 g
Vinyl chloride-vinyl acetate copolymer	4 g
Drying oil type alkyd resin	30 g
Acetone	20 c.c.
Butyl acetate	80 c.c.

Type III	
Acid blue 54	4.5 g
Vinyl chloride-vinyl acetate copolymer	4 g
Drying oil type alkyd resin	30 g
Acetone	20 c.c.
Butyl acetate	80 c.c.

1 part in weight of these pastes I, II and III was added respectively and independently to 100 parts in weight of the following liquid while stirring strongly, dissolved and dispersed.

Cyclohexane	90 parts by weight
Linseed oil	10 parts by weight

Three types of developer were thus obtained. In the meantime, three sheets of zinc oxide paper described under Example 1 were charged and thereafter exposed with three sheets of three color decomposition negatives for cyanine, magenta and yellow as prepared from color positives with continuous gradation, and developed by means of the corresponding 3 types of developer. Three sheets thus developed were dried and thereafter pressed against a sheet of gelatine transfer paper one after another under correct registration. As a result, a colored positive image could be obtained. Despite of charge control agent being covered with dyestuff, dye transfer was complete, the dyestuff being covered with charge control agent.

EXAMPLE 11

Selenium was vacuum-evaporated to a thickness of 60 μ on to a flat aluminum plate. This selenium sensitive plate was exposed to corona discharge at +7,000V and after this charging, exposed for 0.2 seconds through a positive line image by means of a 5,500-lux light source.

In the meantime, a paste composed of the following was prepared. In this composition, thermoplastic acrylic resin is the carrier liquid soluble component whereas vinyl chloride-vinyl acetate maleic acid terpolymer is the insoluble component.

Titanium dioxide (rutile type)	0.5 g
Thermoplastic acrylic resin (Hitaloid 1105, made by Hitachi Kasei Kogyo Co. Ltd)	30 g
Vinyl chloride-vinyl acetate maleic acid terpolymer	1.5 g
Methyl ethyl ketone	20 c.c.

1 part by weight of this paste was dissolved and dispersed in 100 parts by weight of solvent naphtha containing 5 percent of soybean oil while agitating strongly, thus preparing liquid developer. The above-mentioned exposed selenium plate was processed in this liquid developer and a positive image involving little white fog could be obtained.

EXAMPLE 12

Liquid developer similar to the one mentioned under Example 11 except that nitrocellulose (RS 1/2) is employed instead of vinyl chloride-vinyl acetate maleic acid copolymer as the charge control agent. In this case, nitrocellulose (RS 1/2) is the carrier liquid insoluble component and serves as the charge control agent.

EXAMPLE 13

Carbon Black	1 g
Vinyl chloride-vinyl acetate-maleic acid terpolymer	1 g
Resin modified phenolformaldehyde resin	5 g
Ethyl acetate	40 cc

1 gram of this paste was dissolved and dispersed in the liquid having the following composition:

Kerosene	15 cc
Cyclohexane	80 cc
Linseed oil	5 cc

This developer provides a black image of mild tone and is suitable for the reproduction of continuous gradation.

What is claimed is:

1. A process for the preparation of an electrophotographic liquid developer comprising kneading together (1) a coloring material in fine particle form, said coloring material being insoluble in a nonpolar carrier liquid, (2) a charge control agent consisting of a material selected from the group consisting of a vinyl chloride polymer or nitro-cellulose which is insoluble in said carrier liquid, and (3) a material selected from the group consisting of thermoplastic acrylic resin, drying oil type alkyd resin, nondrying oil type alkyd resin, epoxy ester, rosin modified alkyd resin, phenol-modified alkyd resin, styrenated alkyd resin, rosin modified phenol-formaldehyde resin, phenol-formaldehyde resin, epoxy ester of vegetable oil fatty acids, and glycol ester of long chain fatty acids and mixtures thereof, and (4) a liquid selected from the group consisting of acetone, butyl acetate, methyl ethyl ketone, and ethyl acetate to obtain a paste as raw material, and dissolving said paste and dispersing said paste in said carrier liquid selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, chlorinated-fluorinated hydrocarbons, and fluorinated hydrocarbons and having a volume resistivity of over $10^9 \Omega \text{ cm}$ and a specific dielectric constant of below 3.5, containing not more than 20 percent and not less than 0.5 percent by weight of a dispersion stabilizer selected from the group consisting of vegetable oils, resins and mixtures thereof whereby a stable dispersion of toner particles comprising said coloring material covered by said charge control agent is obtained, said toner particles being very fine and containing substantially uniform negative electric charges.

2. A process as claimed in claim 1 wherein the vinyl chloride polymer is a vinyl chloride-vinyl acetate copolymer.

3. A process as claimed in claim 1 wherein the vinyl chloride polymer is a vinyl chloride-vinyl acetate-maleic acid terpolymer.

4. A process as claimed in claim 1 wherein the vinyl chloride polymer is a vinyl chloride-vinyl acetate-vinyl alcohol terpolymer.

5. A method as in claim 1 wherein said paste is dispersed in said carrier liquid by passing ultrasonic waves through said liquid.

6. The method as in claim 1 where said vegetable oils are selected from the group of linseed oil, tung oil, soybean oil, peanut oil, and sesame oil.

11

7. The method as in claim 1 wherein said coloring material is selected from the group consisting of inorganic pigments, organic pigments, water-soluble dyes, and alcohol-soluble dyes.

8. A method as in claim 1 wherein said coloring material is selected from the group consisting of carbon black, black iron oxide, nickel oxide, chrome oxide, cobalt ferrite, titanium ox-

12

ide, zinc oxide, mercury iodide, mercury sulfide, lead oxide, cadmium sulfide, pulverized sulfur, metallic powders and organic pigments.

9. The method as in claim 1 wherein said carrier liquid is selected from the group consisting of heptane, hexane, kerosene, cyclohexane, gasoline and light oil.

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