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LIQUID DEVELOPERS FOR DEVELOPING ELECTROSTATIC IMAGES

Tetsuro Otsuka, Takatsuki-shi, Isao Ota, Osaka-shi, and Shinichi Ogo, Moriguchi-shi, Japan, assignors to Matsushita Electric Industrial Co., Ltd., Kadoma, Osaka, Japan

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ABSTRACT OF THE DISCLOSURE

An improved liquid developer consists essentially of a carrier liquid having an electrical resistivity higher than 10^{12} ohm–cm., a finely divided pigment powder dispersed or suspended in the carrier liquid, a control agent and, as an addition for improving visual images in halftone, from 0.01 to 0.3%, optimally 0.03 to 0.1%, by weight of geraniol, linalool, or citronellol.

This invention relates to improved liquid developer for converting an electrostatic latent image into a visual image and for fixing the visual image into a permanent visual record.

It is well known that an electrostatic latent image formed on an insulating photoconductive layer coating on an electrically conductive base can be immediately converted into a visual image by applying an electrically charged pigment powder which is dispersed in an insulating carrier liquid. Such a process is called liquid development and is described in prior literature, especially with electrophotographic plate or paper comprising Se or ZnO as a photoconductive material. However, little attention has been paid to the liquid developer for use in the development of electrostatic latent images on an electrophotographic layer comprising transparent organic photoconductive material. A copending U.S. patent application Ser. No. 526,713, filed Feb. 11, 1966, teaches that latent images on a transparent organic photoconductive layer can be developed satisfactorily by using novel liquid developers. The electrophotographic copies according to the copending application Ser. No. 526,713 are superior in granularity and resolution, but are not so suitable for reproducing a halftone or continuous-tone of an original image. Recent electrostatic photography is requiring a copy superior in reproducing a halftone or continuous-tone.

More pigment powder is deposited in the places of the electrostatic image where sharp voltage contrasts are present. Thus, in central portions of a large image area the voltage contrast between adjacent points are small and pigment powder deposition is proportionally reduced. These edge effects are particularly effective for line copy where letters and drawings containing no large black areas are to be reproduced, but are not desirable for reproducing a halftone or continuous-tone. Various efforts have been directed to an achievement of superior electrophotographic copies in connection with a photoconductive layer comprising Se or ZnO. For example, U.S. Pat. No. 3,032,432 describes that a tone of a visual image on a photoconductive layer is controlled by varying the electrical conductivity of carrier liquid. However, it is well known that an increase in the electrical conductivity of carrier liquid results in impairment of the contrast of the image. So far as we know, there is no disclosure of a superior electrophotographic copy for a photoconductive layer comprising a transparent organic photoconductive material. Particularly, there is no disclosure of a liquid developer composition capable of achieving a picture superior in reproducing a halftone as well as in granularity and resolution when a visual image on a transparent electrophotographic film is enlarged and projected on a screen. The transparent electrophotographic film is produced by coating a transparent base film having a transparent electrically conducting layer (e.g. CuI layer) with a transparent organic photoconductive material comprising photoconductive compounds such as those described it the Hoegl et al. U.S. Pat. No. 3,037,861.

It is an object of this invention to provide an improved liquid developer which is adapted for an electrophotographic layer comprising a transparent organic photoconductive material.

It is another object of this invention to provide an improved liquid developer composition capable of improving a halftone of images on a transparent organic photoconductive layer.

It is a further object of this invention to provide an improved liquid developer composition capable of achieving an excellent contrast as well as a superior halftone of an electrophotographic copy on a transparent organic photoconductive layer.

It has been discovered according to the invention that in a liquid developer consisting essentially of a carrier liquid of an electrical resistivity higher than 10^{12} ohm-cm., a finely divided pigment powder dispersed or suspended in said liquid, a control agent, and an addition of geraniol, linalool or citronellol which dissolves in said carrier liquid, improves visual images in halftone.

According to this invention, an operable additive amount of geraniol linalool or citronellol ranges from 0.01 to 0.3% by weight. The minimum amount of geraniol, linalool or citronellol can be determined by the amount necessary for improving the halftone of reproduced images. Since each of geraniol, linalool or citronellol is an oily liquid, the maximum amount must be controlled from the standpoint of quick drying. The most advantageous amounts are 0.03 to 0.1% by weight.

Said carrier liquid consists preferably of trichlorotrifluoroethane or carbon tetrachloride having an electrical resistivity higher than 10^{12} ohm-cm.

It is important that said pigment powder does not coagulate even when suspended in said carrier liquid for a time period longer than one week. Operable pigment powder is phthalocyanine blue, black iron oxide (F_3O_4), graphite, zinc oxide, magnesium oxide, or titanium dioxide in a particle size less than 1 micron. Such a pigment powder is charged entirely in the same sign, i.e. positively, by adding 0.001 to 0.3% by weight of said control agent to said carrier liquid.

Specifically, graphite powder can be employed as an excellent pigment powder and produces an entirely satisfactory visual image. Since the graphite powder has a flaky shape in a small dimension, it is easily adhered to the surface of a photoconductive layer when the carrier liquid evaporates off. Furthermore, graphite powder is superior as pigment of the liquid developer which is adapted for an electrophotographic layer comprising an organic photoconductive material such as poly-N-vinylcarbazole. It is more advantageous to use colloidal graphite dispersed in oil commercially available as an "Oildag" (Acheson Colloids Ltd., Prince Rock, Plymouth, Devon, England).

Since a high concentration of pigment powder in the carrier liquid has a tendency to promote the agglomeration of said pigment powder and to elevate the viscosity of the carrier liquid, the electrophotographic layer with-

drawn from the liquid developer may be accompanied by undesirable deposition of excess pigment powder due to its high concentration in the liquid, causing impairment of the visual image. In addition, a very low concentration results in a slow rate of developing process. The following percentages by weight of pigment powder for the liquid developer composition can be employed: Operable amounts of pigment are 0.005 to 0.1% by weight and optimum amounts are 0.01 to 0.05% by weight. Such a low concentration of pigment powder can produce sufficiently a fine visual image in a development time of not more than a few seconds.

Said control agent is to control the polarity of said pigment powder to have the same polarity throughout all the particles of said pigment powder. Optimal control agent according to the invention is a metallic soap selected from the group consisting of cobalt naphthenate, nickel naphthenate, manganese naphthenate or cobalt resinate.

When the pigment particles dispersed in the carrier liquid are subjected to electrophoresis, the particles charged "plus" move to the cathode and the particles charged "minus" to the anode. By this method one can determine the polarity degree of the electrical charges of the pigment particles. An electrophoresis test indicates that the addition of said control agent increases the percentage of the number of pigment particles charged in the same sign, that is, positively.

An increase in the additive amount of metal naphthenate or resinate results in a low electrical resistance of carrier liquid. This is undesirable because of the discharge of an electrostatic latent image. Therefore, the maximum amount of metal naphthenate or resinate must be controlled from the standpoint of the electrical resistivity of the carrier liquid. The minimum amount of metal naphthenate or resinate can be determined by the amount necessary for producing pigment powder charged entirely in the same sign. Optimal amounts of metal naphthenate or resinate are 0.001 to 0.3% by weight. It is a great feature of the invention that uniformity of electrical charges on the powder particles can be achieved by the addition of 0.001 to 0.3% by weight of metallic soap selected from the group consisting of cobalt naphthenate, nickel naphthenate, manganese naphthenate and cobalt resinate where the pigment powder is in a particle size less than 1 micron and the carrier liquid has a high electrical resistivity over 10^{12} ohm-cm.

A visual image entirely satisfactory in halftone is obtained by employing a liquid developer consisting essentially of

(1) trichloro-trifluoroethane or carbon tetrachloride as a carrier liquid,
(2) As a pigment powder, 0.005 to 0.1% by weight of phthalocyanine blue, black iron oxide, graphite, zinc oxide, magnesium oxide, or titanium dioxide in a particle size less than 1 micron,
(3) as a control agent, 0.001 to 0.3% by weight of cobalt naphthenate, nickel naphthenate, manganese naphthenate or cobalt resinate, and
(4) 0.01 to 0.3% by weight of geraniol, linalool or citronellol.

Such a liquid developer according to the invention has a high electrical resistivity more than 10^{12} ohm-cm. and is noninflammable and highly volatile for quick drying. Especially, the liquid developer of the invention is more suitable for a transparent electrophotographic layer comprising, as an organic photoconductive material, poly-N-vinylcarbazole, poly-N-vinylcarbazole derivatives such as poly-3,6-dibromo-N-vinylcarbazole, brominated poly-N-vinylcarbazole or nitrated poly-N-vinylcarbazole, polyacenaphthylene, polyacenaphthylene derivatives such as nitrated polyacenaphthylene, or said material sensitized by activators or dyestuff compounds. The liquid developer of the invention is also useful for developing latent images on a layer comprising an inorganic photoconductive material such as zinc oxide.

Aforesaid metal naphthenate can be prepared by the reaction of an aqueous solution of metal acetate such as cobalt acetate, nickel acetate or manganese acetate with a basic aqueous solution of naphthenic acid; by the reaction of an aqueous solution of metal nitrate such as cobalt nitrate, nickel nitrate or manganese nitrate with a benzene solution of naphthenic acid; or by heating a mixture of naphthenic acid and metal oxide such as cobalt oxide, nickel oxide or manganese oxide. Since the naphthenic acid is a product of petroleum distillation, it is difficult to exactly define the molecular weight. Actual naphthenic acid comprises materials of various molecular weights. An increase in the molecular weight of naphthenic acid results in a decrease in a weight percent of metal in the total molecular weight of the naphthenate.

A higher weight percentage of metal is preferable for producing a uniformity of electrical charges on the pigment powder particles in the aforesaid liquid developer when the metal naphthenate is soluble in the carrier liquid. An operable metal naphthenate composition comprises 4 to 10% by weight of metal selected from the group consisting of cobalt, nickel or manganese, and a more advantageous metal naphthenate is the metal naphthenate comprising 6 to 8% by weight of the metal. From these facts, it is desirable that the naphthenate compound comprising 4 to 10% by weight of cobalt, nickel or manganese be added to said carrier liquid in an amount of 0.001 to 0.3% by weight. Furthermore, the addition of metal naphthenate to the carrier liquid causes the following effect: The dispersion of the pigment powder in the carrier liquid becomes more stable and homogeneous, and acccordingly satisfactory visual images can be rapidly developed even in the low concentration of the pigment powder according to this invention. Although cobalt resinate (or rosinate) is valuable similarly to aforesaid naphthenate, it has been difficult to exactly determine a weight percentage of cobalt metal.

The dispersion of pigment powder in the liquid developer of the invention is also maintained satisfactorily for a long time by adding a small amount of oil into the dispersion system. Any oil which has a high electrical resistivity and is inert to the liquid developer constituents, can be employed for the above mentioned purposes, for example, petroleum oil, mineral oil, olive oil, silicone oil, chlorinated diphenyl, etc. The amount of oil in the liquid developer is advantageously less than 1% by weight because a large amount of oil results in a slow drying of the photoconductive layer and impairs the visual image by the oil remaining as smears on the layer.

When one uses, for example, colloidal graphite as the pigment powder, which is commercially available as an "Oildag" consisting of 10% by weight of fine graphite powder and 90% by weight of petroleum oil, one finds that the resulting developer shows a very stable graphite dispersion and no settling or agglomeration of the graphite particles takes place for a great many days.

A visual image can be fixed immediately by adding a fixing agent into the liquid developer of the invention. The fixing agent is required to dissolve in the carrier liquid and to cure easily when the carrier liquid evaporates off. In addition, it is important that an addition of a fixing agent does not lead to a decrease in electrical resistivity of the carrier liquid and does not influence the polarity of the electrical charges of the pigment powder such as graphite. In view of the solubility of fixing agent, a different carrier liquid needs a different fixing agent. Any resin or rosin satisfying the above requirements can be employed. An advantageous fixing agent is chlorinated triphenyl for a carrier liquid of trichloro-trifluoroethane, and chlorinated triphenyl or polystyrene for a carrier liquid of carbon tetrachloride. The amount of ad-

ditive fixing agent must be controlled from the standpoint of avoiding the impairment of the image when the electrophotographic layer is withdrawn from the liquid developer. It is advantageous to use 0.05 to 0.5% by weight of chlorinated triphenyl or polystyrene where the carrier liquid is trichloro-trifluoroethane or carbon tetrachloride. It has been well known that resinous materials for use in a fixing agent in the conventional developers are partially soluble or entirely insoluble in trichloro-trifluoroethane. According to the prior art, complete fixing of the pigments has been achieved by softening the surface of a transparent electrophotographic film having a visual image thereon. Such a prior method is practically undesirable because impairment of the developed image frequently takes place due to the addition of a liquid which softens constituent materials of a transparent organic photoconductive layer. Chlorinated triphenyl is soluble in trichloro-trifluoroethane and is an excellently effective resinous material for fixing of the pigment powder on a transparent electrophotographic film.

A liquid developer of the present invention can be prepared as follows: A mixture of a small amount of aforesaid carrier liquid, aforesaid pigment powder in a particle size less than 1 micron, and aforesaid oil in a given composition is ballmilled for about 10 hours to form a homogeneous paste. The paste so produced is added to the carrier liquid such as trichloro-trifluoroethane or carbon tetrachloride in a given weight ratio, in which carrier liquid there are dissolved metallic soap such as metal naphthenate, and geraniol, linalool or citronellol in a given weight percentage, respectively. The resulting suspension is stirred by means of an ultrasonic vibrator to obtain a well dispersed liquid developer. A fixing agent such as chlorinated triphenyl or polystyrene is added to the liquid developer prior to the ultrasonic vibration when it is necessary to fix permanently a visual image. The liquid developer of the present invention is a positively charged liquid developer which selectively deposits on a negatively charged electrostatic latent image.

The novel liquid developer of the present invention can be applied to an electrostatic latent image produced by any of the known procedures recognized in the prior art. For example, uniform positive or negative charges are applied on a transparent electrophotographic film by any of the known means such as corona discharge. Then, the electrophotographic film is exposed to a pattern of light and shadow illumination whereby the illuminated areas are discharged and a charge image pattern remains on the layer which is developed to a visual image by a liquid developer of the present invention. When the electrophotographic film having a latent image pattern thereon is immersed into the novel liquid developer for a few seconds, the pigment powder particles selectively deposit either on the charged or on the discharged areas depending on the polarity of charges imparted on the photoconductive layer so that the image patterns are immediately rendered visible. Because of the highly volatile character of the carrier liquid of the developer composition, quick drying can be achieved and a superior visual image can be simultaneously fixed, by a fixing agent dissolved in the carrier liquid, into a permanent record when the layer is dried. By using the liquid developers of the present invention, satisfactorily superior permanent visual images can be obtained even where a long electrophotographic film is required to be continuously developed on condition that the film be submerged in the liquid developer for a few seconds. The image produced on the transparent electrophotographic film by this developer gives a satisfactory visual pattern when enlarged and projected onto a screen. The visual pattern is superior not only in reproducing a halftone of an original image but in resolution and granularity.

The following examples of specific new compositions are given by way of illustration and should not be construed as limitative. In these examples, "g." signifies gram(s) and "ml." signifies milliliter(s).

EXAMPLE 1

Twenty grams of graphite powder in a particle size less than 1 micron, 50 g. of oil and 200 ml. of carbon tetrachloride are milled for 10 hours in a ball mill. Two milliliters of the graphite powder suspension is diluted by 500 ml. of carbon tetrachloride, in which there are dissolved 0.2 g. of cobalt naphthenate containing 8 percent by weight of cobalt metal and 0.5 g. of citronellol or geraniol.

The amount of cobalt naphthenate available is in a range of 0.01 to 2 g. for 500 ml. of carbon tetrachloride. Any cobalt naphthenate comprising 4 to 10% by weight percentages of cobalt metal can lead to the same result.

When transparent electrophotographic film carrying a negatively charged electrostatic latent image is submerged in the resulting liquid developer for a few seconds, a black visual image of the pattern is produced on the photoconductive layer and it is a direct (or positive) print of the original. When it is necessary to fix permanently the visual image on the layer, 1 g. of polystyrene is additively dissolved in 500 ml. of the developer. In this case the visual image is sufficiently fixed simultaneously when the carrier liquid is evaporated. Polystyrene is useful as a fixing agent for a carrier liquid such as carbon tetrachloride.

EXAMPLE 2

Thirty grams of finely divided graphite powder, 100 ml. of oil and 200 ml. of trichloro-trifluoroethane are blended in a ball mill to form a homogeneous paste. Five grams of the paste so produced is dispersed in one liter of trichlorotrifluoroethane which contains in solution 0.4 g. of manganese naphthenate with 8% by weight of manganese metal metal and 1 ml. of linalool.

When the resulting liquid developer is applied to a transparent organic photoconductive layer bearing an electrostatic latent image in a similar way to that described in Example 1, a black visual image is produced successfully on the layer.

There are two possible methods to obtain the visual image permanently fixed on the photoconductive layer. One is the method of again submerging the photoconductive layer bearing the visual image into liquid carbon tetrachloride containing in solution only 0.1 to 0.2% by weight of polystyrene. This method has the defect that the development and the fixing involve two different steps. The other developer is prepared by dissolving additively 0.4 g. of chlorinated triphenyl in 300 ml. of the above obtained developer. Employment of this developer produces a permanently fixed visual image on the photoconductive layer simultaneously with developing and drying of the layer. Chlorinated triphenyl is an effective resinous fixing agent soluble in a carrier liquid, especially when the carrier liquid is trichloro-trifluoroethane and the pigment powder is finely divided graphite particles.

EXAMPLE 3

Thirty grams of finely divided graphite powder having an average particle size of 0.5 micron, and 100 g. of oil are mixed in 200 ml. of trichloro-trifluoroethane and then blended in a ball mill to obtain a homogeneous paste.

When 1 g. of the paste so produced is dispersed in 300 ml. of trichloro-trifluoroethane in solution containing 0.1 g. of nickel naphthenate involving 8% by weight of nickel metal and 0.3 g. of linalool, a positively charged liquid developer is obtained. As in Example 1, an electrostatic latent image is rendered visible in the development time of a few seconds. The visible image on the photoconductive layer can be immediately fixed by adding 0.3 g. of chlorinated triphenyl in 300 ml. of the resultant developer.

EXAMPLE 4

A liquid developer is prepared by mixing 2 g. of "Oildag" with 1 liter of trichloro-trifluoroethane containing in solution 0.1 g. of cobalt napthenate, 1 ml. of citronellol and 2 g. of chlorinated triphenyl. The resulting developer is a very stable graphite dispersion and no

settling or agglomeration of the graphite particles takes place for a great many days.

The image is developed in similar way to that of Example 1. The developer so prepared has excellent developing quality and moreover the preparation of this developer is a very simple procedure. The visual image produced by the developer has high quality, both on continuous tone and on line copy. Although the pigment concentration is very low, the development time is less than several seconds. When a transparent organic photoconductive layer having an electrostatic latent image is submerged in the liquid developer for three seconds, the maximum optical density of the obtained visual image is more than 2, and the developer makes it possible to obtain a resolution of more than 100 line paris per millimeter on line copy.

The visual image is fixed simultaneously when the electrophotographic layer is withdrawn from the developer.

EXAMPLE 5

Two hundred milliliters of trichloro-trifluoroethane, 200 g. of "Oildag" consisting of 10% by weight of fine graphite powder and 90% by weight of petroleum oil, and 20 g. of cobalt napthenate involving 8% by weight of cobalt metal are milled together in a ball mill until blending is complete. Five grams of the paste so produced is completely dispersed in 1 liter of trichloro-trifluoroethane, in which liquid are dissolved 0.1 mg. of cobalt napthenate and 1 ml. of linalool.

The visual image is developed in a similar way to that of Example 1. The resultant developer is a useful liquid developer for developing a negatively charged electrostatic latent image on a transparent organic photoconductive layer and for projecting the obtained visual pattern onto a screen.

EXAMPLE 6

A liquid developer is prepared by suspending 3 g. of "Oildag" in 1 liter of trichloro-trifluoroethane or carbon tetrachloride comprising 0.5 g. of cobalt resinate and 1 ml. of geraniol, linalool or citronellol. The resulting developer is a stable dispersion and selectively deposits on a negatively charged electrostatic latent image.

We claim:

1. A liquid developer composition for developing electrostatic latent images, consisting essentially of carrier liquid having high electrical resistivity, 0.005 to 0.1 percent by weight of finely divided pigment powder dispersed or suspended in said liquid, 0.001 to 0.3 percent by weight of metallic soap which dissolves in said liquid and is selected from the group consisting of cobalt naphthenate, nickle naphthenate, manganese naphthenate, and cobalt resinate, 0.01 to 0.3 percent by weight of an organic material selected from the group consisting of geraniol, linolool and citronellol, and 0 to 1 percent by weight of an insulating oil.

2. A liquid developer composition for developing electrostatic latent images, according to claim 1, in which said carrier liquid is selected from the group consisting of trichloro-trifluoroethane and carbon tetrachloride.

3. A liquid developer composition for developing electrostatic latent images according to claim 1, in which said pigment powder is finely divided powder in a particle size less than 1 micron and is a member selected from the group consisting of phthalocyanine blue, black iron oxide, graphite, zinc oxide, magnesium oxide and titanium dioxide.

4. A liquid developer composition for developing electrostatic latent images according to claim 1, which further comprises as a fixing agent, 0.05 to 0.5 percent by weight of chlorinated triphenyl.

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GEORGE F. LESMES, Primary Examiner

J. P. BRAMMER, Assistant Examiner

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