

[54] **LIQUID DEVELOPER FOR PLURAL-COLOR ELECTROPHOTOGRAPHY**

[75] Inventors: **Hazime Machida; Zenjiro Okuno**,
both of Tokyo, Japan

[73] Assignee: **Kabushiki Kaisha Ricoh**, Tokyo,
Japan

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[63] Continuation-in-part of Ser. No. 9,971, Feb. 9, 1970, abandoned.

[30] **Foreign Application Priority Data**

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[58] Field of Search..... **252/62.1 L; 96/1.2, 1.5**

[56] **References Cited**

UNITED STATES PATENTS

2,986,521	5/1961	Wielicki.....	252/62.1
3,053,688	9/1962	Grieg	252/62.1 X
3,060,020	10/1962	Grieg	96/1.2
3,060,051	10/1962	Johnson et al.....	96/1.2
3,150,976	9/1964	Johnson	96/1.2
3,212,887	10/1965	Miller et al.	96/1.2
3,337,340	8/1967	Matkin.....	252/62.1 X
3,503,881	3/1970	Shinohara	252/62.1
3,545,969	12/1970	Herrick, Jr. et al.	96/1.5
3,552,959	1/1971	Yamaguchi et al.....	252/62.1 X
3,622,368	11/1971	Okuno et al.	252/62.1 L
3,639,244	2/1972	Machida et al.	252/62.1 L
3,640,751	2/1972	Kasuya et al.....	252/62.1 L

FOREIGN PATENTS OR APPLICATIONS

1,016,072 1/1966 Great Britain..... 252/62.1

Primary Examiner—Benjamin R. Padgett

Assistant Examiner—P. A. Nelson

Attorney, Agent, or Firm—Woodhams, Blanchard and Flynn

[57] **ABSTRACT**

A set of liquid developers for plural-color electrophotography, comprising carrier liquids and toners of four colors separately dispersed in said carrier liquid for each color, said toners being selected from the group consisting of:

a. a toner consisting substantially of coloring agents for four colors and finely divided particles of colorless, transparent organic photoconductive substance colored severally by said four coloring agents;

b. a toner consisting substantially of coloring agents for four colors, finely divided particles of colorless, transparent organic photoconductive substance colored severally by said four coloring agents, and one coating agent coated on the surface of said colored photoconductive substance and selected from the group consisting of hitherto known coating resins for toner and such vinyl polymers as are insoluble in said carrier liquid; and

c. a toner consisting substantially of coloring agents for four colors, finely divided particles of colorless, transparent organic photoconductive substance colored severally by said four coloring agents, and a polymer coated on the surface of said colored photoconductive substance and having an affinity with said carrier liquid.

5 Claims, No Drawings

LIQUID DEVELOPER FOR PLURAL-COLOR ELECTROPHOTOGRAPHY

CROSS REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of application Ser. No. 9 971, filed Feb. 9, 1970 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a set of liquid developers for electrophotography, and particularly a set of liquid developers for use in reproducing a plural-color electrophotograph by a wet-developing process.

2. Description of the Prior Art

The conventional liquid developers for plural-color electrophotography have been prepared by processes in which pigment particles in plural colors are coated for each color with a natural resin or a synthetic resin for imparting a polarity-controlling property and a dispersibility to said particles and the thus coated particles are separately dispersed as the toner in a carrier liquid. And, in case of reproducing a plural-color image of an original on an electrophotographic recording material by employing a set of developers as above, there has been usually applied a method wherein the impression of electrostatic charge, exposure and development are repeated in turn thereby reproducing the color images in the order of, say, black, yellow, magenta and cyan. However, said developers in the prior art have a drawback in reproducing a plural-color image of an original on a recording material such that, in cases where the developers employed contain toners consisting of the pigments or a resin coated thereon having a high electrical resistivity, the electrical resistivity of the first formed image-area becomes higher than that of the non-image area, making it difficult to effect a uniform impression of electrostatic charge on the surface of the recording material at the time of the next impression of electrostatic charge to form another color-image area different from the first one and resulting in impairment of the color balance. In other words, the high electrical resistivity of the image-area hampers the disappearance of the electric charge of the area where a complete disappearance of said electric charge is required after exposure, and, as a result, on the occasion of the next dipping in another developer, the toner adheres to the latter area too, thereby making it difficult to reproduce a plural-color image of the original. On the other hand, a similar phenomenon occurs also in case of reproducing the color images in order as above by employing a set of developers containing toners consisting of pigments or a resin coated thereon having a low electrical resistivity. In other words, a uniform impression of electrostatic charge on the recording material subsequent to formation of the first image-area thereon becomes impossible as in the foregoing case and there takes place a disappearance of the electric charge of the area where a residual charge is required after exposure or decrease in electric potential thereof, and, as a result, on the occasion of the next dipping in another developer, the toner fails to adhere to said area, thereby making it difficult to reproduce a desired plural-color image of the original.

Inasmuch the plural-color electrophotography is supposed to reproduce the color-images of an original by means of superposing toners for plural colors in order as above, certain portions of a once formed image-area

must be adhered to toners for other colors thereon, and, accordingly, the materials of said toners should be also possessed of satisfactory electrostatic characteristics.

Thus, the U.S. Pat. No. 3,060,020 Specification provides a method for reproducing the multi-color images electrographically using the developer powders prepared by mixing a photoconductive zinc oxide powder together with a thermoplastic material and coloring agents for each color. In case of utilizing such developer powders as liquid developer there was entailed a drawback that developer powders, which dispersibility in carrier liquid is inferior, precipitate after a long period of preservation, thereby the function as developer being lost. The images formed onto an electrophotographic copying material using liquid developers dispersed said developer powders in a carrier liquid had also a drawback that they are readily separated from a photoconductive layer owing to its bad adhesiveness to said layer.

In case of effecting color reproduction using such liquid developers, furthermore, it was found that impression and disappearance of electric charge can be made as desired, but in superposing toners for plural colors only the color of the last-adhered toner is predominant and the color tone of the first-adhered toner decreases, entailing dissatisfaction in reproductivity of color tone.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a set of liquid developers for plural-color electrophotography which make up for the shortcomings of conventional developers as described in the foregoing.

The developers under the present invention are applicable to both the electrostatic recording material employed for a method wherein an electrostatic latent image is formed on a recording material by means of an impression of electrostatic charge on said recording material and exposure subsequent thereto and the thus formed latent image is then made into a plural-color visible image through wet-process development and the electrostatic recording material employed for a method wherein an electrostatic latent image corresponding to an original image is directly formed on a recording material and then made into a plural-color visible image through wet-process development.

As for the colored particles to be employed for the material of the toners in the present invention, finely divided particles of colorless, transparent organic photoconductive substances having a high electrical resistivity and provided with a desired color are applicable. And, as for said colorless, transparent organic photoconductive substances, the suitable one includes, for instance, anthracene, imidazole, carbazole, poly-3,6-dibromovinylcarbazole, poly-2,3-dichlorovinylcarbazole, poly-2,4-dichlorovinylcarbazole, poly-3,6-dichlorovinylcarbazole, poly-3-bromo-6-chlorovinylcarbazole, poly-3-bromovinylcarbazole, poly-3-chlorovinylcarbazole, poly-N-vinylcarbazole and polyvinylanthracene, etc.

As for the coloring agent for providing these photoconductive substances with desired colors, either of the inorganic substance and the organic substance will do, and all of those colored substances called pigments and those colored substances called coloring matters are applicable. And, the coloring agents having transpar-

ency are advantageously employed in the present invention. For example, as for the coloring agent for black color, Cyanine Black BX (a manufacture of Sumitomo Kagaku K. K.), Spilon Black (a manufacture of Hodogaya Chemical Industries Ltd., as hereinafter referred to as H Co.), Spirit Black (a manufacture of Orient Chemical Industries Ltd., as hereinafter referred to as O Co.), etc. are applicable. As for the coloring agent for magenta color, Spilon Red (C.I. Solvent Red 8; a manufacture of H Co.), Spilon Orange (C.I. Solvent Orange 5; a manufacture of H Co.), Benzidine Orange (C.I. No. 21110; a manufacture of Sanyo Color Works Ltd., as hereinafter referred to as S Co.), Brilliant Carmine 6B (C.I. No. 15850; a manufacture of S Co.), Scarlet KR (C.I. No. 15865; a manufacture of S Co.), Fast Red (C.I. No. 15865; a manufacture of Dainichi Seika K. K. as hereinafter referred to as D Co.), Monolite Fast Red (a manufacture of Imperial Chemical Industries Ltd., England as herein after referred to as I Co.), etc. are applicable. As for the coloring agent for yellow color, Spilon Yellow (C.I. Solvent Yellow 19; a manufacture of H Co.), Benzidine Yellow GNN (C.I. No. 21100; a manufacture of S Co.), Benzidine Yellow 471 (C.I. No. 21095; a manufacture of D Co.), Monolite Fast Yellow IOG (a manufacture of I Co.), etc. are applicable. As for the coloring agent for cyan color, Victoria Blue (C.I. No. 44045; a manufacture of H Co.), Methylene Blue (C.I. No. 52015; a manufacture of H Co.), Oil Blue (C.I. No. 61555; a manufacture of O Co.), Alkali Blue (C.I. No. 42750; a manufacture of O Co.), Sky Blue (a manufacture of S Co.), Cyanine Blue FG (a manufacture of S Co.), Cyanine Blue NSG (C.I. No. 74250; a manufacture of D Co.), Lignol Blue NCB (a manufacture of Toyo Ink Industries Ltd.), Monastral Fast Blue G (a manufacture of I Co.), Vali Fast Blue (C.I. No. 74350; a manufacture of O Co.), etc. are applicable. As for the coloring agent for green color, Phthalocyanine Green L. L (a manufacture of S Co.), Phthalocyanine Green LX (C.I. No. 42040; a manufacture of S Co.), Seika Light Green Lake No. 4554 (C.I. No. 42040; a manufacture of D Co.), Chromofine Green G (C.I. No. 74260; a manufacture of D Co.), etc. are applicable. As for the coloring agent for other colors than the foregoing, Spilon Violet (C.I. Solvent Violet 2; a manufacture of H Co. for purple color) is applicable.

In the present invention, the toners to be applied comprise the aforesaid highly insulating organic photoconductive substance and coloring agent employed as the toner base and according to the following combinations (a), (b) and (c):

a. a toner consisting substantially of a colorless, transparent organic photoconductive substance and a coloring agent.

b. a toner consisting substantially of a colorless, transparent organic photoconductive substance, a coloring agent and a hitherto known resin for use in coating the toner or at least one polymer selected from the group consisting of compounds expressed by the below-mentioned general formula (1); and

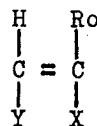
c. a toner consisting substantially of a colorless, transparent organic photoconductive substance, a coloring agent and a polymer which principle component is at least one member of the group consisting of compounds expressed by the below-mentioned general formula (2).

In other words, such developers as prepared by dispersing either one of the toners of said combination in a carrier liquid are included in the present invention.

To begin with, in case of preparing a toner under (a), the coloring agent is first dissolved or dispersed in an appropriate solvent, next a photoconductive substance is dissolved or dispersed therein, and the resultant dispersion is dried and pulverized. In this case, it is desirable to either select a combination of such photoconductive substance and coloring agent as are mutually soluble from among the abovementioned photoconductive substances and coloring agents or select a solvent in which both the photoconductive substance and the coloring agent are soluble. Therefore, such particles as obtained by drying and pulverization of a dispersion prepared by combining either one of such photoconductive substances as polyvinyl anthracene, poly-2,3-dichlorovinyl carbazole, poly-2,4-dichlorovinyl carbazole and polyvinyl carbazole with either one of the oil-soluble coloring agents such as Methylene Blue (a manufacture of H Co.), Victoria Blue (a manufacture of H Co.) and Spilon Red (a manufacture of H Co.) and dissolving the thus combined photoconductive substance and coloring agent in either one of monochlorobenzene, dichlorobenzene and benzene, which are all capable of dissolving both of said photoconductive substance and coloring agent, are suitable as the toner in the present invention. Further, in case where a polymeric photoconductive substance such as N-vinylcarbazole is employed, through effecting suspension polymerization by adding a coloring agent for a desired color at the time of polymerization of said substance, there can be obtained a toner which is provided with said color much more securely and particularly suitable for the developer of the present invention.

The monomer or monomers applicable for producing a colored organic photoconductive substance such as aforesaid colored poly-N-vinylcarbazole are at least one monomer selected from the group consisting of N-vinylcarbazole, vinylanthracene, dimethylaminostyrene, 3-bromo-6-chlorovinylcarbazole, orthobromocarbazole, 3,6-dibromovinylcarbazole, 2,3-dichlorovinylanthracene, orthochlorovinylcarbazole, 2,4-dichlorocarbazole and 2-chlorovinylanthracene. The foregoing toners display a distinct electric charge within the below-mentioned carrier liquids, and, besides, the dispersibility thereof has proved satisfactory.

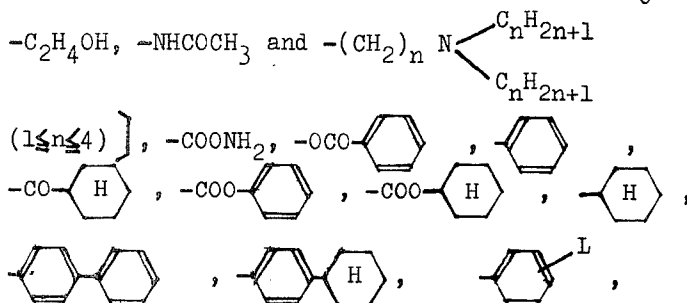
As for the toner under (b) above, it is prepared by employing the toner under (a) as its base and combining therewith a hitherto known resin for use in coating the toner or a polymer comprising at least one member of the group consisting of compounds expressed by the following general formula (1), thereby much more improving the fixability of toner toward an electrostatic recording material, the electrification property of toner and the dispersibility of toner. General Formula (1)



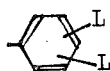
wherein, Y represents a radical selected from the group consisting of —COOH, —H and —Cl;

X represents a radical selected from the group consisting of $-\text{C}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{OCOC}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{OC}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{CN}$, $-\text{COOH}$, $-\text{Cl}$, $-\text{COCl}$, $-\text{COOR}$ [wherein R is selected from the

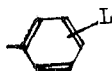
group consisting of $-\text{C}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{CH}_2\text{CH}(\text{O})\text{CH}_2$,



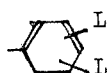
[wherein L is selected from the group consisting of $-\text{CH}_3$, $-\text{NO}_2$, $-\text{NH}_2$, $-\text{N}(\text{CH}_3)_2$, $-\text{COOH}$, $-\text{COOCH}_3$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{Cl}$ and $-\text{Br}$],



(wherein L is identical with said L), $-(\text{CH}_2)_n$



(wherein, L is identical with said L, and $n=1-4$) and $-(\text{CH}_2)_n$



(wherein, L is identical with said L, and $n=1-4$); Ro represents a radical selected from the group consisting of $-\text{H}$ and $-\text{CH}_3$.

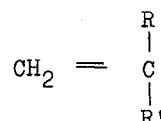
To give concrete examples of such coating resin or polymer, the former includes hitherto known coating agents such as alkyd resin STAYDELITE resin, rosin, linseed oil and phenolmodified resin, and as for the latter, there can be enumerated varieties of substances, such as styrene butadiene copolymer, polybutyl methacrylate, polyoctyl methacrylate, polylauryl methacrylate, polycyclohexyl methacrylate, poly-n-hexyl vinyl ether, polyvinyl butylate, polystearyl vinyl ether, poly-n-amyl vinyl ether, styrene-butyl methacrylate copolymer, styrene-lauryl methacrylate copolymer, hydroxyl ethyl methacrylate-hexyl methacrylate copolymer, glycidyl methacrylate-vinyl stearate copolymer, methacrylate-aminostyrenelauryl methacrylate copolymer, paracyclohexyl methacrylatenitrostyrene-octylacrylate copolymer, octadecyl methacrylateacrylamide copolymer, etc.

In case of preparing a toner under (b), there can be applied either of the following two methods: a method

wherein appropriate toner particles and a coating resin or a polymer are kneaded in the presence of a small quantity of solvent, thereby causing said coating resin or polymer to coat the surface of said particles; and a method wherein a photoconductive substance, a color-

ing agent and a coating resin or polymer are mixed within a solvent and a mixture resulting therefrom is subjected to either spray-drying or pulverization after drying to make it into particles having a grain-size of about $1-5\mu$.

In case of preparing a toner under (c), a polymer consisting of at least one vinyl monomer selected from the group consisting of compounds expressed by the following general formula (2) is coated on the toner under (a). General Formula (2)



wherein, R represents a radical selected from the group consisting of $-\text{H}$ and $-\text{CH}_3$;

R' represents a radical selected from the group consisting of alkyl radicals having 5 to 20 carbon atoms, $-\text{OR}''$ (wherein R'' represents a radical selected from alkyl radicals having 5 to 20 carbon atoms) and $-\text{COOR}'''$ (wherein R''' represents a radical selected from the group consisting of cyclohexyl radical and alkyl radicals having 5 to 20 carbon atoms).

Further, in case of preparing a toner having a composition under (c), such a compound as expressed by the aforementioned general formula (1) may be employed at the same time.

In case of preparing a toner by employing a vinyl monomer expressed by the general formula (1) or a vinyl compound expressed by the general formulas (1) and (2), a polymer consisting of at least one vinyl compound expressed by the general formula (1) or consisting of at least one vinyl compound expressed by the general formula (1) along with at least one vinyl compound expressed by the general formula (2) is first prepared and thus prepared polymer is treated in the same way as the coating resin in case of preparing a toner under (b), whereby the desired toner is obtained. Further, it will do to carry out polymerization upon adding a photoconductive substance and a coloring agent when preparing said polymer. Moreover, through either polymerization upon adding a monomer which is

to form a photoconductive substance consisting of a polymer, such as N-vinyl carbazole, vinyl anthracene, dimethylaminostyrene, orthobromovinyl carbazole, 2,3-chlorovinyl anthracene, orthochlorovinyl carbazole, 2,4-dichlorovinyl carbazole, 3,6-dichlorovinylcarbazole, 2-chlorovinyl anthracene, 3,6-dibromovinylcarbazole and 3-bromo-6-chlorovinylcarbazole, to a vinyl compound expressed by said general formulas, or suspension polymerization upon adding a coloring agent in addition to the foregoing monomer, there can be obtained a toner consisting of a polymer chemically bonded to a photoconductive substance and contributing to the polarity-controllability as well as dispersibility thereof.

The present invention relates to a set of liquid developers for plural-color electrophotography wherein the toners have been separately dispersed in a carrier liquid for each color. As for the carrier liquid to be employed, any of the liquid hydrocarbons of normal paraffin family, isoparaffin family, olefin family and Naphtha No. 6 family hitherto known as the carrier liquid for developers for use in the wet-process developing method or said liquid hydrocarbons containing an aromatic hydrocarbon as well is applicable, and these hydrocarbons are all possessed of an electrical resistivity not less than $10^9 \Omega \cdot \text{cm}$ and a dielectric constant not greater than 3. To give concrete examples of hydrocarbons having said properties, there are manufactures of ESSO Standard Oil Co. sold under tradenames of Naphtha No. 6, Solvesso 100, Isopar H, Isopar G and Isopar L along with a manufacture of Mobile Oil Co. sold under the tradename of Pegasol AS-100. And, it will do to employ these manufactures either individually or upon mixing two or more thereof.

In order to form a colored image on an electrophotographic copying material by the use of the set of four color developer liquids according to the present invention, the following developing process is applicable:

a. Negative charge from corona discharge is impressed onto the entire surface of a photoconductive layer of the copying material, said layer being formed by dispersing zinc oxide in a resinous binder, and this is followed by the exposing of the photoconductive layer, through a colored original and a blue filter which is laid underneath of said original, to light. The resultant copying material having an electrostatic latent image is then subjected to the first development by the immersion of said copying material into a developer liquid containing dispersed therein yellow toners;

b. After drying the resultant copying material having a yellow image, the photoconductive layer of said copying material is again impressed with negative charge. Thereafter, the copying material is exposed, through the same colored original and a green filter laid under-

copying material is once again impressed with negative charge and exposed, through the same colored original and a red filter laid underneath thereof, to light, and then subjected to the third development by the immersion of said copying material into a developer liquid containing dispersed therein cyan toners;

d. Thereafter, the resultant copying material is dried and impressed with negative charge according to the same procedure as described above, and, subsequently, exposure is effected, through the same colored original without using a filter, to light. The exposed copying material is then subjected to the fourth development by the immersion of said copying material into a developer liquid containing dispersed therein black toners.

When reproducing a colored original through the above-mentioned process, the toners contained in the developer have a colorless, transparent organic photoconductive substance as base material, and therefore when interposing toners for multi colors for the purpose of reproducing the colored original the electric charge impressed on the copying material after formation of images thereon is permitted to be uniform in both image and non-image areas and when exposing the copying material to light the disappearance of electric charge impressed on the desired area can be effected rapidly and completely, whereby it is made possible to fix desired toners for multi colors in turn onto desired areas of the copying material and furthermore transparency of said toners prevents the colors of last superposed toners from being predominant in the toner-superposed area.

Because of their containing toners consisting of a colorless, transparent organic photoconductive substance having a high electrical resistivity as the toner base, the above-described developers under the present invention are capable of rendering the electrification property of an image-area and a non-image area uniform when impressed with electrostatic charge subsequent to formation of the image on a recording material on the occasion of superposing colors for reproducing a plural-color image, and also capable of causing the electric charge on a desired portion of a recording material to disappear rapidly and completely in case where a recording material impressed with electrostatic charge is subjected to exposure, so that it is possible to cause a toner for a desired color to fix onto a desired portion of said recording material in order. Thus, a plural-color original can be faithfully reproduced without impairing the color-balance.

In applying a set of four color developer liquids of our invention to the respective developments, colors in each development may be employed in various color sequence as shown in the undermentioned Table 1.

Table 1

Development Sequence	Developer liquid No.							
	1	2	3	4	5	6	7	8
First	yellow	magenta	magenta	cyan	cyan	black	black	black
Second	cyan	yellow	cyan	magenta	yellow	yellow	cyan	magenta
Third	magenta	cyan	yellow	yellow	magenta	magenta	magenta	cyan
Fourth	black	black	black	black	black	cyan	yellow	yellow

neath thereof, to light. Then, the exposed copying material is subjected to the second development by the immersion of said copying material into a developer liquid containing dispersed therein magenta toners;

c. The resultant copying material having a yellow image and a magenta image is dried, and then this

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE 1

A solution was prepared by adding 1 kg of N-vinyl carbazole to 10 kg of a buffer solution (viz., a solution prepared by dissolving 2.88g to caustic soda, 11.18g of

potassium chloride and 9.28g of boric acid in 6 litres of distilled water) and dissolving therein by heating at 70°C. Then, to said solution was added another solution prepared by dissolving 20g of Victoria Blue in 100 ml of monochlorobenzene, and the mixture was thoroughly stirred. To a solution thus prepared was added still another solution prepared by dissolving 2.5g of azobisisobutyronitrile (viz., a reaction initiator) in 50 ml of monochlorobenzene, and, while stirring at a high speed, 5g of bentonite was added as well. Subsequently, while stirring, the resultant mixed solution was heated up to a temperature of about 90°C, and, by means of maintaining said temperature for four hours, said solution was caused to effect suspension polymerization, whereby there was prepared photoconductive particles colored in blue. Then, these particles were washed in water, cleansed with methanol and dried. The dried particles were further treated with monochlorobenzene, and thereafter were resuspended within n-hexane and dried, thereby producing finely divided particles of cyan color. By dispersing about 10g of thus produced particles in 1,000 ml of Naphtha No. 6, there was obtained a developer containing a cyan-color toner.

On the other hand, in accordance with the method of preparing a developer as set forth above, a developer containing black-color toner, a developer containing yellow-color toner and a developer containing magenta-color toner were also prepared by employing Spirit Black, Spilon Yellow and Spilon Red, respectively, in lieu of Victoria Blue employed in preparing the foregoing cyan-color toner.

By employing a set of liquid developers for plural-color electrophotography comprising black, yellow, magenta and cyan colors prepared as above, and applying conventional processes to a commercialized electrophotographic copying paper (viz., a copying paper having a photoconductive layer formed by binding zinc oxide on a supporting paper with a resinous binder), a plural-color image was reproduced. To be precise, namely, negative charge was first impressed on the photoconductive layer of the copying paper, then the photoconductive layer was exposed to light through a colored original and a blue filter which is laid underneath of said original and thereafter the copying material was dipped into the liquid developer containing dispersed therein yellow-color toner to thereby reproduce a yellow-color image on the copying paper. Magenta and cyan-color images were reproduced respectively on the copying paper by the following steps, i.e., impression of electric charge, exposure to light through a green filter, dipping into a developer containing magenta-color toner, additional impression of electric charge, exposure to light through a red filter, and dipping into a developer containing cyan-color toner. Then, a black-color image was reproduced on the copying paper by impressing negative electrostatic charge on the photoconductive layer of the copying paper having yellow, magenta and cyan color images, thereafter exposing the copying paper to white light through a color original using no filter and dipping said copying paper into a developer containing black-color toner. Clear-colored copied images were thus obtained which reproduced original images with high fidelity.

EXAMPLE 2

0.1 kg of a mixture, prepared by kneading—
poly-2, 4-dichlorovinyl carbazole 1 kg,
chlorobenzene 5 kg and
Spilon Yellow 100 g,

was resuspended within 15 kg of n-hexane, whereby finely divided particles of yellow-color were obtained.

Then, by dispersing 50g of thus obtained particles in 1,000 ml of Isopar H, a developer containing a yellow-color toner was prepared.

On the other hand, by employing the same composition as above except for employment of Cyanine Black BX as a coloring agent for black-color, Vali Fast Blue as a coloring agent for cyan-color and Fast Red as a coloring agent for magenta-color, respectively, in lieu of said Spilon Yellow, there were prepared developers respectively containing black-color toner, cyan-color toner and magenta-color toner.

When a set of liquid developers for plural-color electrophotography thus obtained was applied for copying a colored original onto an electrophotographic copying paper by the use of the developers in the order of black-yellow-magenta-cyan, there was obtained a clear-cut colored image which faithfully reproduced said original.

The efficiency of a set of liquid developers for plural-color electrophotography thus prepared proved equal to that of developers in Example 1.

EXAMPLE 3

A mixture, prepared by kneading—
polyvinyl anthracene powder 1 kg,
polystyrene-butadiene resin 0.5 kg,
Brilliant Carmine 6B 50 g and
toluene 3 kg

was subjected to spray-drying with a spray-dryer, whereby finely divided particles of magenta-color having a grain-size of about 1μ were obtained. By dispersing 20g of said particles in 1,000 ml of Naphtha No. 6/Solvesso 100 (mixing ratio: 6/4), a developer containing a magenta-color toner was prepared.

On the other hand, by employing the same composition except for employment of Spilon Black as a coloring agent for black-color, Lignol Blue NCB as a coloring agent for cyan-color and Monolite Fast Yellow IOG as a coloring agent for yellow-color, respectively, in lieu of said Brilliant Carmine 6B, there were prepared developers containing black-color toner, cyan-color toner and yellow-color toner, respectively.

Further, for the purpose of testing a performance of the liquid developers according to the invention, a set of control liquid developers was prepared in accordance with the same procedure as described above except that 1 kg of zinc oxide powder was used in place of the polyvinyl anthracene powder referred to in the above preparation of the respective liquid developers of the present invention.

Comparative tests were carried out by the methods described below to compare the aforesaid liquid developers as regards their toners dispersion stability in the carrier liquid, fixing ability to a photoconductive layer of copying paper and reproducibility of a color tone of a colored original.

1. Dispersion Stability:

The magenta-color toner containing developer according to our invention was poured into a measuring sedimentation tube 10 mm in diameter and 300 mm in length till the surface of said toner comes up to 300 mm. The same was left stand respectively for 7 days, one month and three months to measure at each termination the graduation to which the uppermost surface of the sedimented toner came up.

It is to be noted that the larger the value of graduation, the more superior the dispersion stability. The same measurement was effected concerning the control developer containing a magenta-color toner. Thus obtained dispersion stability test results will be shown in Table-2.

Table 2

	after 7 days	after one month	after three months
Developer according to our example	250 mm	200 mm	150 mm
Control developer	140 mm	50 mm	40 mm

2. Fixing Ability:

By using the same liquid developer according to the invention as used in the aforesaid test-(1), an electrophotographic copying paper (which is a copying paper for use in the electrophotographic copying machine sold under the trademark Electron Recopy BS-1 manufactured by Kabushiki Kaisha RICOH) and Electron Recopy BS-1, copied image consisting of magenta toner was formed on the copying paper.

The toner concentration of the copied image was measured by a densitometer manufactured and sold under the trade name of Narumi NSG-III type of Narumi Shokai Kabushiki Kaisha, both before and after 50 and 300 erasing strokes respectively were applied to the image using a reciprocating erasure tester. The erasure tester was provided with an eraser named "LION" (manufactured by Fukui Kabushiki Kaisha) having a sectional area of 10 mm × 10 mm. The tester is designed for rubbing the image with the eraser reciprocally 100 times per minute under a load of 600 g. From the test results, the undermentioned value was calculated:

$$\frac{\text{Image concentration after erasure}}{\text{Image concentration before erasure}} \times 100$$

Then, by the same method as described above, the copied image formed with the control liquid developer containing magenta color toner was tested in like fashion and the same calculation was made.

The fixing ability (adhesiveness) of the toner to the photoconductive layer is directly proportional to the thus calculated value. The test results are given in Table-3.

Table 3

	Fixing Ability (%)	
	After 50 erasure	After 300 erasure
Image formed with the developer of our invention	70	45
Image formed with the control developer	35	20

As is clear from the results in Tables-2 and -3, the developer according to our invention is recognized superior in both dispersion stability and adhesiveness to photoconductive layer in comparison with control developer using zinc oxide.

3. Reproducibility of Color Tone:

Next, using, as original, a color step tablet having colors of black, blue, green, red, cyan, magenta, yellow and white (transparent), and as developer, a set of developers according to our invention and a set of control developers, color images were reproduced on marketed electrophotographic copying papers according to the same procedure disclosed in Example 2 to survey a difference in color tone between images reproduced

in both cases of using our developer and control one. Thus obtained results were as mentioned below.

Negative electrostatic charge was impressed on a photoconductive layer of a copying paper, then same was exposed to white light through said plural-color original, and dipped into a developer containing black color toner to thereby form a copied black color image area. A copied black color image was similarly reproduced using a control developer containing black color toner. So far as said copied black color image areas are concerned, there could find no difference between our invention and the control example. Next, electrostatic charge was impressed on the copying paper having the thus copied color image, then same was exposed to light through a blue filter interposed between the plural-color original and said copying paper and dipped into a developer containing yellow color toner to thereby form a copied yellow color image area. The yellow color toner was, in both cases of our invention and the control example, adhered to the copied black color image area and to areas of the copying paper corresponding to red and yellow color areas of the original. In the copied black color image area there was recognized that the yellow color toner adhered onto the black color toner and the adhered amount was substantially same in degree between our invention and the control example. When making comparison in color tone between both copied black image areas, it was recognized that the copied black color image area of the control example was more predominant in yellow than ours.

Next, electrostatic charge was impressed on the copying paper having thus formed copied black and yellow color image areas, then same was exposed to light through a green filter interposed between the plural-color original and said copying paper and dipped into a developer containing magenta color toner to thereby form a copied magenta color image area. The magenta color toner adhered to the copied black color image area and to areas of the copying paper corresponding to blue, red and magenta color areas of the original in both the control example and our invention. In the copied black and red color image areas there was recognized that the magenta color toner adhered onto the yellow color toner which formed the copied yellow color image area, but the adhered amount was substantially same in degree in both the control example and our invention. In observing the color tone of the respective image areas, it was recognized that the copied black color image area of the control example was more predominant in red than ours, and that the copied red color image area of the control example was more predominant in magenta than ours. Then, electrostatic charge was impressed on the copying paper having thus formed the respective copied image areas, same was exposed to light through a red filter interposed between the plural-color original and said copying paper and dipped into a developer containing cyan color toner to thereby form a copied cyan image area.

The cyan toner adhered to the copied black color image area and to areas of the copying paper corresponding to blue, green and cyan color areas of the original. It was recognized that in the black and blue color areas the cyan color toner adhered onto the magenta color toner which formed the copied magenta color image area and in the green color area the cyan color toner adhered onto the yellow color toner which

formed the copied yellow color image area, but the adhered amount was substantially same in degree in both our invention and the control example. When comparing the present invention with the control example in respect of the color tone of the respective color image areas there was recognized that the copied black color image area of the control example was cyanic black, while that of our invention almost deep-black, and that the copied blue and green color image areas of the control example were all predominant in cyan color as compared with those of our invention.

As described above, comparing the present invention with the control example it was recognized that the amounts of adhered toners in the respective color image areas was almost equal in both cases, but in the color-imposed portions of the control example the color of the uppermost toner was predominant and that of the undermost toner decreased, especially the four-color imposed portion thereof was not colored in deep-black but most predominant in blue color. Contrary to this, in the copied color image according to our invention it was recognized that the color of the uppermost toner did not become unnaturally predominant and that of the undermost toner was displayed with no decrease, thereby permitting obtainment of a copied color image extremely superior in reproductivity of color tone from the original color image.

This phenomenon may be analyzed as hereinafter, that is, in an inorganic photoconductive substance such as a zinc oxide powder, which lacks transparency, the color of the under portion of the formed image is decreased by the toner for the color of the upper portion thereof, while in an organic photoconductive powder, which is transparent, such does never take place, thereby producing superior color tone reproducibility.

For the purpose of obtaining a set of liquid developers for plural-color electrophotography, it is desirable in the present invention to fix the mixing ratio of a coloring agent to an organic photoconductive substance in toner in the range of from 1 to 100 parts by weight of said agent against 100 parts by weight of said substance. And concerning the coating agent it is preferable to coat 1 part by weight of toner having a composition as described above with 0.1 to 10 parts by weight of the coating agent.

EXAMPLE 4

A mixture, prepared by mixing—
 Anthracene 3 kg,
 styrene 1 kg,
 butyl acrylate 2 kg and
 benzoyl peroxide 10 g,

was heated at a temperature ranging from 90°C to 100°C in an atmosphere of nitrogen gas, thereby effecting polymerization reaction. A mixture prepared by kneading upon adding 10g of phthalocyanine blue and 100 g of toluene to 100 g of the products from said polymerization was subjected to spray-drying with a spray-dryer, whereby, a cyan-color toner having a grain-size of about 1 μ was prepared.

On the other hand, in accordance with the foregoing method of preparing a toner, a black-color toner, a yellow-color toner and a magenta-color toner were respectively prepared by employing Spilon Black, Benzidine Yellow GNN and Scarlet KR, respectively, in lieu of the foregoing phthalocyanine blue. Subsequently,

about 15g each of these four color toners was separately dispersed in 1,000 ml each of Naphtha No. 6, whereby a set of liquid developers for plural-color electrophotography were prepared.

Further, by applying such combinations of materials as shown in the following Table 4 and in accordance with the method of preparing developers of the present example, two sets of liquid developers for plural-color electrophotography were prepared.

Table 4

Devel- oper No.	Photocon- ductive Substance	Material for Toner			Carrier Liquid
		Vinyl Compound	Reaction Initiator	Color- ing Agent	
1	vinyl	styrene		Methyl- ene Blue	Naphtha No. 6
	anthracene (3 kg)	(0.75 kg)		Cyanine Black BX	Naphtha No. 6
		Lauryl metha- crylate (1.25 kg)	azobis- isobutyl- nitrile (10 g)	Brilliant Carmine 6B	Naphtha No. 6
				Benzidine Yellow 471	Naphtha No. 6
2	vinyl anthracene (3 kg)	butyl metha- crylate (1 kg)		Brilliant Carmine 6B	Naphtha No. 6/ Solvesso 100 6/4
			azobis- isobutyl- nitrile (4.5 g)	Spilon Black	Naphtha No. 6/ Solvesso 100 6/4
		metha- crylic acid (0.3 kg)		Spilon Yellow	Naphtha No. 6/ Solvesso 100 6/4
				Cyanine Blue	Naphtha No. 6/ Solvesso 100 6/4

It is noted in this connection that, in case where the toner for each color in the present example was prepared without employing a spray-dryer but prepared through the process comprising the steps that the coloring agent was added and mixed with the products from polymerization reaction, the solvent was removed thereafter, and said polymerization-reaction products thus treated were pulverized, the toner thus obtained was equal to that obtained through spray-drying.

Each set of developers prepared as above was employed for reproducing a plural-color image under the same operation as described in Example 1, and, as a result, there was obtained a satisfactory plural-color image from any and every set thereof.

EXAMPLE 5

A mixture consisting of—
 orthochlorovinyl carbazole 1.5 kg,
 vinyl toluene 0.5 kg,
 octylmethacrylate 1.0 kg,
 azobisisobutyronitrile 6.5 kg,
 dichlorobenzene 100 ml,
 Methylene Blue 14 g and
 buffer solution 18 kg
 (having the same
 composition as in
 Example 1)

was caused to effect suspension polymerization through the same polymerizing operation as in Example 4. Then, 20 g of a cyan-color toner thus obtained was dispersed in 1,000 ml of Naphtha No. 6 as a carrier liquid, whereby a cyan-color developer was obtained.

On the other hand, by employing coloring agents for black-color (Spilon; Spirit Black), coloring agents for yellow-color (Benzidine Yellow GNN; Benzidine Yellow 471) and coloring agents for magenta-color (Fast Red; Benzidine Orange) respectively in lieu of Methylene Blue among the foregoing materials for toner and in accordance with the foregoing method of preparing a toner, a black-color toner, a yellow-color toner and a magenta-color toner were respectively prepared. Further, the respective toner was separately dispersed in 1,000 ml of carrier liquid for each color, whereby liquid developers for plural-color electrophotography were obtained.

For the purpose of testing a performance of the liquid developer according to the invention, a control liquid developer was prepared in accordance with the same procedure as described above except that 1.5 kg of zinc oxide powder was used in place of the orthochlorovinyl carbazole referred to in the above preparation of the liquid developer containing a cyan-color toner of the present invention.

Comparative tests were carried out in accordance with the same methods as described in tests-(1) and -(2) in Example 3. The test results of the dispersion stability in the carrier liquid and the fixing ability to a photoconductive layer of copying paper are given respectively in Table-5 and Table-6.

In the comparative tests, the liquid developer containing cyan-color toner according to our invention was employed for comparison with the control liquid developer containing cyan-color toner using zinc oxid.

Table 5 (Dispersion stability)

	After 7 days	After one month	After three months
Developer according to our invention	300 mm	300 mm	250 mm
Control developer	200 mm	75 mm	50 mm

Table 6

	Fixing Ability (%)	
	After 50 erasure	After 300 erasure
Image formed with the developer of our invention	90	70
Image formed with the control developer	50	35

As is clear from the results in Tables-5 and -6, the developer according to our invention is recognized superior in both dispersion stability and adhesiveness to photoconductive layer in comparison with control developer using zinc oxide.

What is claimed is:

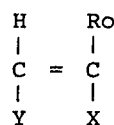
1. In a set of liquid developers for plural-color electrophotography, in which each developer comprises a toner dispersed in a carrier liquid, said carrier liquid being a liquid hydrocarbon having an electric resis-

tance of at least $10^9 \Omega \cdot \text{cm}$ and a dielectric constant of not greater than 3, said set of liquid developers comprising separate liquid developers respectively containing as the only toner present therein

- a magenta-color toner consisting essentially of finely divided particles of photoconductive substance colored with a magenta-coloring agent;
- a cyan-color toner consisting essentially of finely divided particles of photoconductive substance colored with a cyan-coloring agent;
- a black-color toner consisting essentially of finely divided particles of photoconductive substances colored with a black-coloring agent;
- a yellow-color toner consisting essentially of finely divided particles of photoconductive substance colored with a yellow-coloring agent, the improvement which comprises: the photoconductive substance in each of said toners is a colorless, transparent photoconductive substance selected from the group consisting of anthracene, imidazole, carbazole, poly-3,6-dibromovinylcarbazole, poly-2,3-dichlorovinylcarbazole, poly-2,4-dichlorovinylcarbazole, poly-3,6-dichlorovinylcarbazole, poly-3-bromo-6-chlorovinylcarbazole, poly-3-bromovinylcarbazole, chlorovinylcarbazole, poly-N-vinylcarbazole, polyvinylanthracene, polyvinylcarbazole, polydimethylaminostyrene, polyorthobromocarbazole, poly-2,3-dichlorovinylanthracene, polyorthochlorovinylcarbazole, poly-2,4-dichlorocarbazole, and poly-2-chlorovinylanthracene.

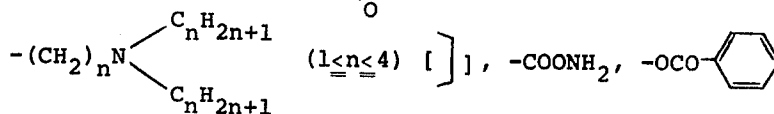
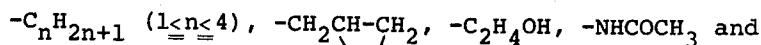
2. A set of liquid developers for plural-color electrophotography according to claim 1, wherein said toners are respectively coated with a coating agent selected from the group consisting of:

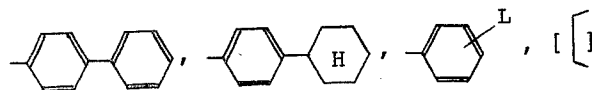
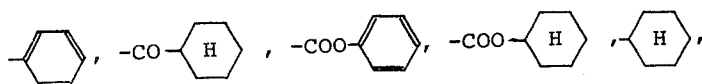
- a polymer comprising at least one monomer selected from the group consisting of vinyl monomers expressed by the below-mentioned formula (1);
- a polymer comprising at least one vinyl monomer selected from the group consisting of monomers expressed by the below-mentioned formula (2); and
- a copolymer comprising at least one monomer selected from the group consisting of vinyl monomers expressed by the below-mentioned formula (1) and at least one monomer selected from the group consisting of vinyl monomers expressed by the below-mentioned formula (2); Formula (1)



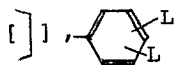
wherein, Y is selected from the group consisting of $-\text{COOH}$, $-\text{H}$ and $-\text{Cl}$;

X is selected from the group consisting of $-\text{C}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{OCOC}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{OC}_n\text{H}_{2n+1}$ ($1 \leq n \leq 4$), $-\text{CN}$, $-\text{COOH}$, $-\text{Cl}$, $-\text{COCl}$, $-\text{COOR}$ wherein R is selected from the group consisting of



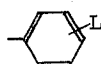


wherein L is selected from the group consisting of
 $-\text{CH}_3$, $-\text{NO}_2$, $-\text{NH}_2$, $-\text{N}(\text{CH}_3)_2$, $-\text{COOH}$,
 $-\text{COOCH}_3$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{Cl}$ and Br

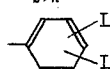


[(wherein L is identical with said L)],

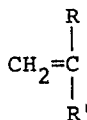
$-(\text{CH}_2)_n$



[(wherein L is identical with said L, and
 $n=1\sim 4$)]₂ and $-(\text{CH}_2)_n$



Ro is selected from the group consisting of $-\text{H}$ and
 $-\text{CH}_3$, Formula (2)



wherein, R is selected from the group consisting of $-\text{H}$
and $-\text{CH}_3$;

R' is selected from the group consisting of alkyls hav-
ing 5 to 20 carbon atoms, $-\text{OR}''$ wherein R'' is se-
lected from the alkyls having 5 to 20 carbon atoms,
and $-\text{COOR}'''$ wherein R''' is selected from the
group consisting of cyclohexyl and alkyls having 5
to 20 carbon atoms.

3. A set of liquid developers for plural-color electro-
photography according to claim 2, wherein said toners
are respectively composed of said coloring agent and
products of the copolymerization reaction of:

a. a monomer for forming said organic photoconduc-
tive substance selected from the group consisting of
of 3,6-dibromovinylcarbazole, 2,3-
dichlorovinylcarbazole, 2,4-
dichlorovinylcarbazole, 3,6-
dichlorovinylcarbazole, 3-bromo-6-
chlorovinylcarbazole, 3-bromovinylcarbazole, 3-
chlorovinylcarbazole, N-vinylcarbazole, vinylan-
thracene, vinylcarbazole, dimethylaminostyrene,
orthobromocarbazole, 2,3-
dichlorovinylanthracene, orthochlorovinylcar-
bazole, 2,4-dichlorocarbazole and 2-
chlorovinylanthracene; and

b. at least one monomer selected from the group con-
sisting of monomers expressed by said formula (1)
and monomers expressed by said formula (2), the
products of said copolymerization reaction being
separately colored with said coloring agents for
each color.

4. A set of liquid developers for plural-color electro-
photography according to claim 1, wherein each said
toner consists essentially of 100 parts by weight of said
photoconductive substance and 1 to 100 parts by
weight of said coloring agent.

5. A set of liquid developers for plural-color electro-
photography according to claim 2, wherein each said
toner consists essentially of 100 parts by weight of said
photoconductive substance and 1 to 100 parts by
weight of said coloring agent, and the amount of said
coating agent coated on each said toner is in the range
of from 0.1 to 10 parts by weight of said coating agent
per one part by weight of said toner.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3 870 644

Dated March 11, 1975

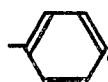
Inventor(s) Hazime Machida and Zenjiro Okuno

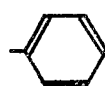
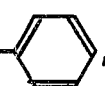
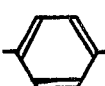
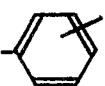
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Please cancel Col. 16, line 64 through Col. 17, line 28 and replace with the following:

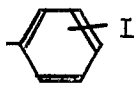
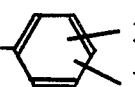
--- $-C_nH_{2n+1}$ ($1 \leq n \leq 4$), $-CH_2CH(CH_2O)-$, $-C_2H_4OH$, $-NHCOCH_3$ and

$-(CH_2)_nN \begin{matrix} C_nH_{2n+1} \\ C_nH_{2n+1} \end{matrix}$ ($1 \leq n \leq 4$), $-COONH_2$, $-OCO-$ , ,

-CO-H, -COO-H, H, ,

-, -H, L, wherein L

is selected from the group consisting of $-CH_3$, $-NO_2$, $-NH_2$, $-N(CH_3)_2$, $-COOH$, $-COOCH_3$, $-OH$, $-OCH_3$, $-Cl$ and

Br, L, $-(CH_2)_n$ L, and $-(CH_2)_n$ L; ---.

Signed and Sealed this

twenty-eight Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks