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Description

The present invention relates to a toner for the full color development, which is used in the overlapped state with other various toners. More particularly, the present invention relates to a toner for the full color development, the developing property and transfer quantity of which are made substantially equal to those of other toners to provide an excellent image reproducibility.

In the fields of the electrophotography and electrostatic printing, toners are used for visualizing electrostatic latent images formed on image carriers. In these toners, a resin having desirable electroscopic and binding properties, for example, a styrene resin or a polyester resin, is used as the resin medium, and carbon black or other organic or inorganic coloring pigment is used as the coloring agent.

The full color development in which magenta, cyan, yellow and black color toners are overlapped to form an image has been recently proposed and worked.

In this full color development, a multiple-color original is exposed to light through a color-separating filter, this operation is repeated a plurality of times by using cyan, yellow and magenta color developers and a black toner, and toner images are thus overlapped to obtain a multiple-color image. Organic pigments are used as coloring agents for cyan, yellow and magenta toners used for this full color development, and carbon black is used for a black toner.

Fig. 1 is a diagram illustrating developing and transfer zones of an image-forming apparatus for obtaining a full color image. In this apparatus, an electrostatic latent image formed on a photosensitive drum 1 by appropriate means is visualized by a developer in any of developing devices 3a, 3b, 3c and 3d of a vertically movable developing unit 2 and is then transferred by a transfer charger 5 onto a transfer material held on a transfer drum 4 by a gripper 6, from which electricity is removed by an electricity-removing charger 7. Furthermore, a toner image developed by a developer in another developing device of the devices 3a, 3b, 3c and 3d is transferred onto the transfer material by the transfer charger, and third and fourth color images are similarly transferred. Thus, a predetermined number of color images are transferred onto the transfer material held on the transfer drum 4, and the transfer material is delivered to a fixing step (not shown) to form a multiple-color image.
In general, in the above-mentioned transfer step, an operation of transferring a toner of a different color onto a toner layer transferred on a transfer material is carried out. At this operation, it sometimes happens that the charge of the toner already transferred on the transfer material reduces the working transfer electric field at the transfer of the subsequent toner and therefore, an image having a desired hue cannot be reproduced. For obviating this disadvantage, there is sometimes adopted a method in which the transfer voltage is gradually elevated at the transfer step or the transfer voltage is elevated at the transfer to the third and subsequent toners where the toner layer becomes thick.
However, since behaviors of toners at the practical transfer step are delicate and complicated, even if a predetermined transfer voltage is applied and the value of the transfer voltage is elevated in the later stage, scattering of the toners or sufficient transfer is often caused because the respective color toners are different in various characteristics (such as charging characteristics and electric characteristics), and no satisfactory results can be obtained in formation of a toner image of a desirable hue.

Japanese Unexamined Patent Publication No. 01-32981 proposes a method in which the quantity of the charge of a toner to be developed and transferred is made larger than the absolute value of the already developed and transferred toner to compensate the reduction of the working transfer electric field and stabilize the transfer operation. According to this method, if it is intended to adopt common development conditions (charge characteristics of the photosensitive material, the development bias voltage and the sliding contact state between the photosensitive material and the developer carrier), since toners are extremely different in the charge characteristics, development unevenness (insufficient density of the solid portion, thickening of line and dot images and formation of toner dusts in the peripheral portion of the image area) is caused or scattering of toners is caused in the machine, and a shear in the hue and a fog are often observed in the formed image.

EP-A-0275636 describes colour toners and 2-component developers and relies on strictly controlled particle size, freeness from agglomeration, melting characteristics, chromaticity, triboelectric chargeability and optical toner concentration detection characteristics for good performance.

The present invention has been completed under the above-mentioned background, and it is a primary object of the present invention to provide a toner for the full color development, in which the difference of electric characteristics from those of other toners to be overlapped is diminished to make developing and transfer characteristics of the toner substantially equal to those of other toners, whereby a full color image can be formed under substantially common developing and transfer conditions without shear in the hue or density unevenness in the formed image.

Another object of the present invention is to provide a toner for the full color development, in which desired characteristics can be stably maintained under set developing and transfer conditions and the change of the hue is reduced.

In accordance with the present invention, there is provided a toner for the full color development which comprises a coloring agent incorporated in a binder resin and is used in the state overlapped with other toners differing in the kind of the coloring agent, wherein the electroconductivity of the binder resin is in the range of from 1.0×10^{-9} to 5.0×10^{-9} (S/cm).

In this toner for the full color development, a charge-controlling agent is incorporated in the binder resin and the charge-controlling agent is a zinc compound of salicylic acid.

Furthermore, in accordance with the present invention, there is provided a magenta toner comprising a binder resin, a charge-controlling agent and a coloring agent, wherein the electroconductivity of the binder resin is in the range of from 1.0×10^{-9} to 5.0×10^{-9} (S/cm), the charge-controlling agent is composed mainly of a zinc compound of salicylic acid and the coloring agent comprises a quinacridone pigment as the main component.

Furthermore, in accordance with the present invention, there is provided a cyan toner comprising a binder resin, a charge-controlling agent and a coloring agent, wherein the electroconductivity of the binder resin is in the range of from 1.0×10^{-9} to 5.0×10^{-9} (S/cm), the charge-controlling agent is composed mainly of a zinc compound of salicylic acid and the coloring agent comprises a copper phthalocyanine pigment as the main component.

Furthermore, in accordance with the present invention, there is provided a yellow toner comprising a binder resin, a charge-controlling agent and a coloring agent, wherein the electroconductivity of the binder resin is in the range of from 1.0×10^{-9} to 5.0×10^{-9} (S/cm), the charge-controlling agent is composed mainly of a zinc compound of salicylic acid and the coloring agent comprises a benzidine pigment as the main component.

Brief Description of the Drawing

Fig. 1 is a diagram showing developing and transfer zones of an image-forming apparatus, which illustrates the principle of the full color development.

The present invention is based on the finding that if a binder resin having an electroconductivity of 1.0×10^{-9} to 5.0×10^{-9} (S/cm) is used, various color toners for the full color development, which are very akin to one another in electric characteristics, are obtained and a good image reproducibility is obtained by the full color development using these toners.

In the full color development, a cyan toner, a magenta toner, a yellow toner and a black toner are mainly used in the overlapped state to form a full color image.

In the present invention, it is important that the electroconductivity of the binder resin should be in the range of from 1.0×10^{-9} to 5.0×10^{-9} (S/cm), and it is especially preferred that the electroconductivity of the binder resins be in the range of from 1.0×10^{-9} to 3.0×10^{-9} (S/cm). If the electroconductivity of the binder resin is below the above-mentioned range, a great difference of the electroconductivity is produced among toners to be overlapped. For example, as shown in Experiment 1-3 given hereinafter, if a binder resin having such a low electroconductivity as 3.2×10^{-10} S/cm is used, carbon black raises up the electroconductivity of the entire toner to 1.2×10^{-9} S/cm, while other toners such as cyan, magenta and yellow toners show an electroconductivity of an order of 10×10^{-10} S/cm, and coloring agents fail to show such a prominent increase of the electroconductivity as attained by carbon black. Therefore, differences of the electroconductivity are produced among the overlapped toners.

In contrast, if a binder resin having an electroconductivity included within the above-mentioned range, no difference of the electroconductivity is found among the magenta, cyan and yellow toners, for example, as shown in Experiments 1-1 and 1-2. If the full color development is carried out by using toners, among which there is no difference of the electroconductivity, the development and transfer characteristics are substantially the same among the respective color toners, and scattering of toners or fogging of images is not caused and the developed toner quantities become constant. Furthermore, at the transfer step, the respective toners become akin to one another in the transfer characteristics, and the hue and image density can be stabilized.

On the other hand, if the electroconductivity of the binder resin exceeds the above-mentioned range, even if charges are applied to toners, escape of the charges is accelerated and the charging state becomes unstable, scattering of toners or fogging of images is caused.

In the present invention, it is preferred that the binder resin having the above-mentioned electroconductivity be excellent in the light-transmitting property. Namely, since a toner for the full color development should not inhibit coloration of other toner on a transfer sheet it is desired that the binder resin should have a light-transmitting property. Accordingly, a resin having an electroconductivity included within the above-mentioned range and a certain light-transmitting property is used as the binder of a toner for the full color development. Of course, two or more of resins having such properties can be used in combination. In the case where a mixture of at least two binder resins is used, the electroconductivity of the resin mixture should be within the above-mentioned range.

The binder resin of the toner for the full color development may be the same as or different from binder resins of other toners to be simultaneously used. If different binder resins are used, each of them should satisfy the above requirement of the electroconductivity.

In the present invention, it is preferred that a zinc compound of salicylic acid be used as the charge-controlling agent. Charge-controlling agents have been incorporated into toners from old so as to control the charging state, and especially, negative charge-controlling agents are often used. However, most of known charge-controlling agents not only change the charge quantity of the toner but also greatly change other electric characteristics such as the electroconductivity. If such charge-controlling agents are used, disadvantages as mentioned above are often brought about.

However, if a zinc compound of salicylic acid is used in combination with the above-mentioned binder resin, not only the inherent action of controlling the charging property but also the action of reducing changes of other electric characteristics can be attained, and these actions can be maintained for a long period and the toner for the full color development can be advantageously used.

The zinc compound of salicylic acid can be a zinc salt or complex of salicylic acid. Preferably, the zinc compound of salicylic acid is incorporated in an amount of 1.0 to 5.0% by weight, especially 1.5 to 4.0% by weight, based on the resin.

One of characteristic features of the present invention is that a copper phthalocyanine pigment is used as the cyan coloring agent. Most of conventional cyan coloring agents are defective in that they have influences on the charge-controlling agents or the sharpness of the color of the toner is degraded when they are used in combination with the binder resin and charge-controlling agent. However, the copper phthalocyanine pigment has no substantial influences on the binder resin and charge-controlling agent and the hue of the pigment is not degraded by the binder resin and charge-controlling agent. Accordingly, the copper phthalocyanine pigment can be incorporated into the toner in the state where the above-mentioned actions of the electroconductivity and charging property are effectively maintained. Accordingly, when a copper phthalocyanine pigment is used as the coloring agent, a cyan toner suitable for the full color development can be provided.

One of characteristic features of the present invention is that a quinacridone pigment is used as the magenta coloring agent. Most of conventional magenta coloring agents are defective in that they have influences on the charge-controlling agents or the sharpness of the color of the toner is degraded or a shear of the hue is caused when they are used in combination with the binder resin and charge-controlling agent. However, the quinacridone pigment has no substantial influence on the binder resin and charge-controlling agent and the hue of the pigment is not degraded by the binder resin and charge-controlling agent. Accordingly, the quinacridone pigment can be incorporated into the toner in the state where the above-mentioned actions of the electroconductivity and charging property are effectively maintained. Accordingly, when a quinacridone pigment is used as the coloring agent, a magenta toner suitable for the full color development can be provided.

One of characteristic features of the present invention is that a benzidine pigment is used as the yellow coloring agent. Most of conventional yellow coloring agents are defective in that they have influences on the charge-controlling agents or the sharpness of the color of the toner is degraded when they are used in combination with the binder resin and charge-controlling agent. However, the benzidine pigment has no substantial influences on the binder resin and charge-controlling agent and the hue of the pigment is not degraded by the binder resin and charge-controlling agent. Accordingly, the benzidine pigment can be incorporated into the toner in the state where the above-mentioned actions of the electroconductivity and charging property are effectively maintained. Accordingly, when a benzidine pigment is used as the coloring agent, a yellow toner suitable for the full color development can be provided.

The toner for the full color development according to the present invention will now be described in detail.

The toner of the present invention is a toner for the full color development, which is used in the state where the toner is overlapped on other toners differing in the color on an image on a transfer sheet. Namely, the present invention is directed to a toner forming a basic color in the full color development. Basic toners for the full color development include four toners, that is, magenta, cyan, yellow and black toners. In the full color development, these toners are developed in order in the overlapped state, and the hue and image quality of an original are reproduced. Each of these toners comprises a coloring agent and, if desired, a charge-controlling agent in a binder resin, and a known toner additive can be further incorporated in or added to the toner.

Binder Resin

In the present invention, it is important that the resin used as the binder resin should have an electroconductivity of 1.0×10^{-9} to 5.0×10^{-9} (S/cm), preferably 1.0×10^{-9} to 3.0×10^{-9} (S/cm), as pointed out hereinbefore.

Moreover, a resin having an excellent light-transmitting property is preferably used.

As the resin having such characteristics, polyester polystyrene, polyacrylic, polyether, polyamide and polyolefin resins can be used singly or in the form of mixture of two or more of them.

In specific examples of the polyester resin, a aromatic dicarboxylic acid or a fatty acid is included as the acid component. As examples of the acid component, there can be mentioned terephthalic acid, isophthalic acid, naphthalene-dicarboxylic acid, maleic acid, fumaric acid, succinic acid, adipic acid, sebacic acid and cyclohexane-dicarboxylic acid. Terephthalic acid is mainly used. As the diol component, there can be mentioned, for example, ethylene glycol, propylene glycol, diethylene glycol, butanediol, cyclohexane dimethanol, hexylene glycol, triethylene glycol, glycerol, mannitol and pentaerythritol.

Specific examples of the styrene resin include polymers obtained by polymerizing such monomers as styrene, α-methylstyrene, vinyltoluene, α-chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, ethylstyrene and divinylstyrene singly or in combination.

As the acrylic resin, there can be used, for example, polymers obtained by polymerizing such monomers as ethyl acrylate, methyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, acrylic acid and methacrylic acid singly or in combination. As the comonomer other than the above-mentioned monomers, there can be used ethylenically unsaturated acids and anhydrides thereof, such as maleic anhydride, fumaric acid, maleic acid, crotonic acid and itaconic acid.

Polymers comprising vinyl-n-butyl ether, vinylphenyl ether, vinylcyclohexanyl ether or the like can be used as the vinyl ether resin.

Known resins derived from a diamine and a dicarboxylic acid and resins formed by polymerizing a lactam, such as nylon 6, can be used as the polyamide resin.

Polymers formed by polymerizing ethylene, propylene, butene-1, pentene-1, methylpentene-1 or the like can be mentioned as the olefin resin.

The foregoing resins can be used singly, or two or more of the foregoing resins can be combined so that the above-mentioned electroconductivity is attained, and resulting mixtures can be used as the binder resin.

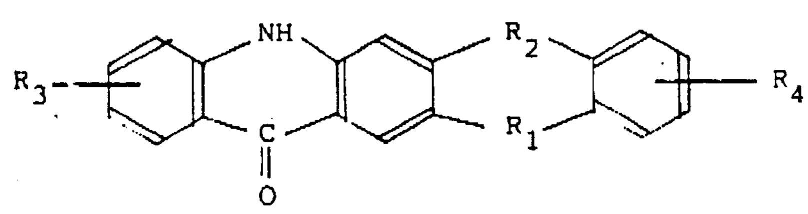
In the present invention, in view of the electroconductivity, light-transmitting property and viscosity characteristics, a polyester resin is preferably used.

Coloring Agent

Known coloring agents used in this field can be used in the present invention. The coloring agent to be contained in the coloring resin is roughly divided magenta, cyan, yellow and black pigments.

As the magenta coloring agent, there can be mentioned red coloring agents such as red iron oxide, cadmium red, red lead, cadmium mercury sulfide, Permanent Red 4R, Permanent Red FNG, Lithol Red, Pyrazolone Red, Watching Red calcium salt, Lake Red D, Brilliant Carmine 6B, Eosine Lake, Rhodamine Lake, Brilliant Carmine 3B and Spiron Red, violet coloring agents such as manganese violet, Fast Violet B and Methyl Violet Lake, and orange coloring pigments such as chrome orange, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange RK, Benzidine Orange G and Indathrene Brilliant Orange GK.

In the present invention, for attaining the foregoing objects, a quinacridone pigment is preferably used as the magenta coloring agent. A typical example of the quinacridone pigment is represented by the following general formula:

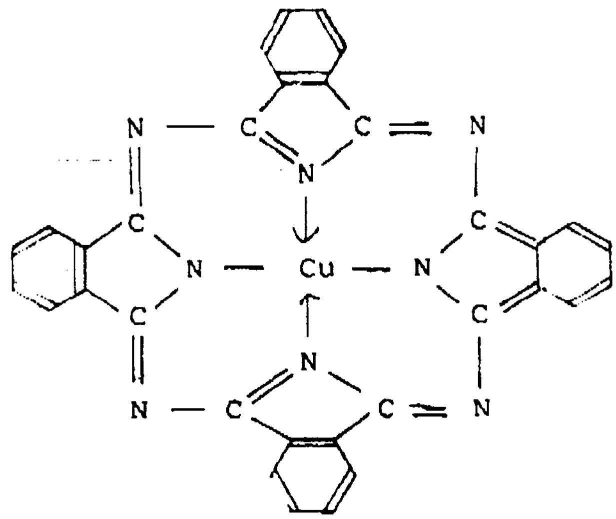


wherein R_1 and R_2 represent an imino group or a carbonyl group, and R_3 and R_4 represent a hydrogen atom, a lower alkyl group or a halogen atom.

As specific examples of the quinacridone pigment, there can be mentioned C.I. Pigment Red 122 and C.I. Pigment Violet.

As the cyan coloring agent, there can be mentioned iron blue, cobalt blue, Alkali Blue Lake, Phthalocyanine Blue, metal-free Phthalocyanine Blue, partially chlorinated Phthalocyanine Blue, Fast Sky Blue and Indanthrene Blue BC.

In order to attain the foregoing objects, a copper phthalocyanine pigment is preferably incorporated as the cyan coloring agent into the binder resin. The copper phthalocyanine pigment is represented by the following formula:



and the benzene nucleus of the structural formula can be substituted with an alkyl group or a halogen atom.

As specific examples of the copper phthalocyanine pigment, there can be mentioned Phthalocyanine Blue, Helliogen Blue G and Fast Sky Blue.

As the yellow coloring agent, there can be mentioned chrome yellow, zinc yellow, cadmium yellow, naples yellow, Naphthol Yellow S, Hansa Yellow G. Hansa Yellow 10G, Benzidine Yellow G. Benzidine Yellow GR, Quinoline Yellow Lake, Permanent Yellow NGG and Tartrazine Lake.

In order to attain the foregoing objects, a benzidine pigment is preferably incorporated as the yellow coloring agent into the binder resin. As specific examples of the benzidine pigment, there can be mentioned Benzidine Yellow G and Benzidine Yellow GR.

As the black coloring agent, there can be mentioned carbon black, lamp black and aniline black.

A coloring agent as mentioned above is incorporated into the binder resin at a weight ratio of from 1/100 to 30/100, especially from 3/100 to 20/100.

Charge Controlling Agent

A charge-controlling agent can be incorporated into the binder resin for controlling the charging of the toner. A known charge-controlling agent can be used in the present invention. For example, there can be mentioned oil-soluble dyes such as Nigrosine Base (C.I. 50415), Oil Black (C.I. 26150) and Spiron Black, metal salts of naphthenic acid, metal soaps, metal-containing azo dyes, pyrimidine compounds and metal compounds of alkylsalicylic acids. A zinc salt or zinc complex of salicylic acid and a zinc salt or zinc complex of an alkylsalicylic acid are preferably used as the charge-controlling agent. It is preferred that the charge-controlling agent be incorporated in the binder resin in an amount of 1.0 to 5.0% by weight based on the binder resin.

The toner for the full color development, prepared from the foregoing components, preferably has such a particle size that the median diameter based on the volume, measured by a Coulter Counter, is 5 to 20 μm, especially 8 to 15 μm. The particles may have an indeterminate shape formed by melt-kneading and pulverization, or a spherical shape formed by the dispersion or suspension polymerization. The flowability of the toner can be improved by sprinkling inorganic fine particles such as hydrophobic silica fine particles or organic fine particles composed of a polymer or the like on the surface of the toner.

In the case where the above-mentioned toner is used as a two-component type development by mixing it with a magnetic carrier, any of known magnetic carriers used in this field can be used, but use of ferrite particles capable of forming a soft magnetic brush is generally preferred.

According to the present invention, by using a resin having an electroconductivity of 1.0×10^{-9} to 5.0×10^{-9} (S/cm) as the binder resin of a toner for the full color development, the differences of electric characteristics among toners to be used in the overlapped state can be reduced. By this reduction of the differences of the electric characteristics, developing conditions for the respective toners can be made substantially equal, and therefore, the difference of the transfer quantity among the respective toners can be diminished and toners for the color development, which are excellent in the image reproducibility, can be provided.

The present invention will now be described in detail with reference to the following examples.

(Experiment 1)

Experiment 1-1

A toner having an average particle size of 10 µm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 1.5×10^{-9} as the binder resin, 5 parts by weight of carbon black as the coloring agent and 2 parts by weight of a zinc/salicylic acid complex as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 1.8×10^{-9} S/cm.

Cyan, magenta and yellow toners were prepared in the same manner as described above except that 5 parts by weight of a copper phthalocyanine pigment, 5 parts by weight of a quinacridone pigment and 3.5 parts by weight of a benzidine pigment were used as the coloring agent, respectively. These cyan, magenta and yellow toners had electroconductivities of 1.5×10^{-9} S/cm, 1.6×10^{-9} S/cm and 1.5×10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers, and these developers were subjected to the development and transfer tests by using a full color electrophotographic copying machine where the imagewise light exposure was carried out by using a semiconductor laser light source. The developed toner quantity and transfer efficiency of each toner were determined by using a 20% original (A4 size original having an image area of 20%), and the full color image density and chroma (stabilized hue) were determined by using a color photo original. The developing and transfer conditions adopted were as follows.

Developing Conditions

Photosensitive drum: organic photosensitive material for negative charging

Surface voltage of photosensitive material: - 700 to - 850 V

Development bias voltage: direct current bias voltage of - 500 to - 650 V and alternating current bias voltage of - 150 to - 650 V (frequency: 1 KHz)

Developing sleeve peripheral speed/photosensitive drum peripheral speed: 2.5 to 4.0

Transfer Conditions

Electricity-removing charger: - 5 kV to + 500 V (2 KHz)

Transfer charger: 5.5 kV to 6.2 kV (for 1st to 3rd colors) and 6.0 kV to 6.5 kV (for 4th color)

Experiment 1-2

Black, cyan, magenta and yellow toners were prepared in the same manner as described in Experiment 1-1 except that 100 parts by weight of a mixture of polymethyl methacrylate (MMA) and polyethyl acrylate (EA), which had an electroconductivity of 2.7×10^{-9} S/cm, was used as binder resin. By using these toners, the full color development was carried out in the same manner as described in Experiment 1-1. These black, cyan, magenta and yellow toners had electroconductivities of 2.9×10^{-9} S/cm, 2.7×10^{-9} S/cm, 2.6×10^{-9} S/cm and 2.6×10^{-9} S/cm, respectively.

Experiment 1-3

Toners were prepared in the same manner as described in Experiment 1-1 except that a polyester resin having an electroconductivity of 3.2×10^{-10} S/cm was used as the binder resin, and by using these toners, the full color development was carried out in the same manner as described in Experiment 1-1. These black, cyan, magenta and yellow toners had electroconductivities of 1.2×10^{-9} S/cm, 3.1×10^{-10} S/cm, 3.2×10^{-10} S/cm and 3.1×10^{-10} S/cm, respectively.

Experiment 1-4

Toners were prepared in the same manner as described in Experiment 1-1 except that a polyester resin having an electroconductivity of 8.9 x 10^{-10} s/cm was used as the binder resin, and by using three toners, the full color development was carried out in the same manner as described in Experiment 1-1. These black, cyan, magenta and yellow toners had electroconductivities of 3.5 x 10^{-9} S/cm, 8.8 x 1^{-10} S/cm, 8.9 x 10^{-10} S/cm and 8.7 x 10^{-10} S/cm, respectively.

Experiment 1-5

Toners were prepared in the same manner as described in Experiment 1-1 except that a polyester resin having an electroconductivity of 5.8 x 10^{-9} S/cm was used as the binders resin, and by using these toners, the full color development was carried out in the same manner as described in Experiment 1-1. These black, cyan, magenta and yellow toners had electroconductivities of 6.0 x 10^{-9} S/cm, 5.9 x 10^{-9} S/cm, 5.8 x 10^{-9} S/cm and 5.8 x 10^{-9} S/cm, respectively.

The results obtained in Experiments 1-1 through 1-5 are shown in Table 1.

Table 1

Experiment No.	Electroconductivity of Resin (S/cm)	Electroconductivity of Toner (S/cm)				Developed Toner Quantity (mg)				Transfer Efficiency (%)				Image Reproducibility
		black	cyan	magenta	yellow	black	cyan	magenta	yellow	black	cyan	magenta	yellow	
1-1	1.5×10^{-9}	1.8×10^{-9}	1.5×10^{-9}	1.6×10^{-9}	1.5×10^{-9}	82	79	81	78	82	76	75	78	○
1-2	2.7×10^{-9}	2.9×10^{-9}	2.9×10^{-9}	2.6×10^{-9}	2.6×10^{-9}	76	75	76	74	77	78	77	76	○
1-3	3.2×10^{-10}	1.2×10^{-9}	3.1×10^{-10}	3.2×10^{-10}	3.1×10^{-10}	80	60	61	58	78	69	68	65	X
1-4	8.9×10^{-10}	3.5×10^{-9}	8.8×10^{-10}	8.9×10^{-10}	8.7×10^{-10}	77	70	69	68	78	69	70	69	Δ
1-5	5.8×10^{-9}	6.0×10^{-9}	5.9×10^{-9}	5.8×10^{-9}	5.8×10^{-9}	84	82	83	81	66	67	66	65	X

Note ○: good, Δ: fair, X: bad

Incidentally, in Table 1, the developed toner quantity is the value obtained when a 20% original (A4 size original having an image area of 20%) for each color was used, and the image reproducibility represents the result of the general evaluation of the image density, the sharpness and the like, obtained when a color photo original was used.

From the results shown in Table 1, it is seen that when the full color development was carried out by using the toners of Experiments 1-1 and 1-2 where the respective toners were akin to one another in the developed toner quantity and transfer efficiency, the obtained full color images were sharp and faithful to the original.

It also is seen that when the full color development was carried out by using the toners of Experiments 1-3, 1-4 and 1-5 where the color toners were different from one another in the developed toner quantity and transfer efficiency, the original could not be reproduced faithfully and obtained full color images were poor in the sharpness.

(Experiment 2)

Experiment 2-1

Toners were prepared in the same manner as described in Experiment 1-1 except that a polyester resin having an electroconductivity of 1.6 x 10^{-9} S/cm was used as the binder resin, and by using these toners, the full color development was carried out in the same manner as described in Experiment 1-1. These black, cyan, magenta and yellow toners had electroconductivities of 1.8 x 10^{-9} S/cm, 1.6 x 10^{-9} S/cm, 1.6 x 10^{-9} S/cm and 1.5 x 10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers. By using these two-component developers, the full color development was carried out by using a full color electrophotographic copying machine where the imagewise light exposure was conducted by using a semiconductor laser light source, in the same manner as described in Experiment 1-1. The change of the image quality was examined in first to 1000th copies.

Experiment 2-2

Black and yellow toners were prepared in the same manner as described in Experiment 2-1, and cyan and magenta toners were prepared in the same manner as described in Experiment 2-1 except that 2 parts by weight of a metal-containing monoazo dye was used as the charge-controlling agent.

These black, cyan, magenta and yellow toners had electroconductivities of 1.8 x 10^{-9} S/cm, 2.2 x 10^{-9} S/cm, 2.1 x 10^{-9} S/cm and 1.5 x 10^{-9} S/cm, respectively.

By using these toners, the full color development was carried out in the same manner as described in Experiment 2-1.

The results obtained in Experiments 2-1 and 2-2 are shown in Table 2.

From the results shown in Table 2, it is seen that when toners comprising a zinc/salicylic acid complex as the charge-controlling agent were used, even if the copying operation was carried out continuously, the developing and transfer characteristics were not changed and a good image quality could be maintained. It also is seen that when toners comprising a metal-containing monoazo dye as the charge-controlling agent were used, the developing and transfer characteristics were changed and the image reproducibility was reduced.

Table 2

Experiment No.		2-1		2-2	
Electroconductivity of Resin(S/cm)		1.6×10^{-9}		1.6×10^{-9}	
Charge-Controlling Agent	black	zinc/salicylic acid complex		zinc/salicylic acid complex	
	cyan	ditto		metal-containing monoazo dye	
	magenta	ditto		ditto	
	yellow	ditto		zinc/salicylic acid complex	
Electroconductivity of Toner(S/cm)	black	1.8×10^{-9}		1.8×10^{-9}	
	cyan	1.6×10^{-9}		2.2×10^{-9}	
	magenta	1.6×10^{-9}		2.1×10^{-9}	
	yellow	1.5×10^{-9}		1.5×10^{-9}	
Developed Toner Quantity(mg)		first copy	1000th copy	first copy	1000th copy
	black	83	82	80	81
	cyan	78	79	82	87
	magenta	80	80	81	86
	yellow	78	79	78	78
Transfer Efficiency (%)					
	black	78	77	77	77
	cyan	76	76	76	71
	magenta	76	76	76	71
	yellow	75	76	76	76
Image Reproducibility		○	○	△	X

Note ○ : good
△ : fair
X : bad

(Experiment 3)

Experiment 3-1

A toner having an average particle size of 8.5 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 1.6×10^{-9} as the binder resin, 5 parts by weight of a quinacridone pigment as the coloring agent and 2 parts by weight of a zinc/salicylic acid complex as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 1.6×10^{-9} S/cm.

Black, cyan and yellow toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of a copper phthalocyanine pigment and 4 parts by weight of a benzidine pigment were used as the coloring agent, respectively. These black, cyan and yellow toners had electroconductivities of 1.8 x 10^{-9} S/cm, 1.7 x 10^{-9} S/cm and 1.6 x 10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers, and these developers were subjected to the development and transfer tests by using a full color electrophotographic copying machine where the imagewise light exposure was carried out by using a semiconductor laser light source in the same manner as described in Experiment 1-1. The change of the image quality in first to 1000th copies was examined.

Experiment 3-2

A toner having an average particle size of 9.0 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 4.2 x 10^{-9} as the binder resin, 5 parts by weight of a quinacridone pigment as the coloring agent and 2 parts by weight of a zinc/salicylic acid complex as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 4.2 x 1^{-9} S/cm.

Black, cyan, magenta and yellow toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of a copper phthalocyanine pigment and 3.5 parts by weight of a benzidine pigment were used as the coloring agent, respectively. These black, cyan and yellow toners had electroconductivities of 4.2 x 10^{-9} S/cm, 4.1 x 10^{-9} S/cm and 4.2 x 10^{-9} S/cm, respectively. By using these toners, images were formed in the same manner as described in Experiment 3-1.

Experiment 3-3

Toners were prepared in the same manner as described in Experiment 3-2 except that a polyester resin having an electroconductivity of 8.9 x 10^{-10} S/cm was used as the binder resin. The obtained magenta, black, cyan and yellow toners had electroconductivities of 9.3 x 10^{-10} S/cm, 9.6 x 10^{-10} S/cm, 9.2 x 10^{-10} S/cm and 9.3 x 10^{-10} S/cm, respectively. By using these toners, the full color development was carried out in the same manner as described in Experiment 3-1.

Experiment 3-4

A magenta toner having an electroconductivity of 9.8 x 10^{-9} S/cm and an average particle size of 8.5 μm was prepared in the same manner as described in Experiment 3-1 except that a polyester having an electroconductivity of 1.3 x 10^{-9} S/cm was used as the binder resin and 2 parts by weight of a metal-containing azo dye was used as the charge-controlling agent.

Black, cyan and yellow toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of a copper phthalocyanine pigment and 5 parts by weight of a benzidine pigments were used as the coloring agent, respectively, and the charge-controlling agent was changed to a zinc compound of salicylic acid for the cyan and yellow toners. These black, cyan and yellow toners had electroconductivities of 9.6 x 10^{-9} S/cm, 1.2 x 10^{-9} S/cm and 1.3 x 10^{-9} S/cm, respectively. By using these toners, the full color development was carried out in the same manner as described in Experiment 3-1.

Experiment 3-5

AS toner having an average particle size of 8.5 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 5.5 x 10^{-9} as the binder resin, 4 parts by weight of a quinacridone pigment as the coloring agent and 2 parts by weight of a metal-containing azo dye as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 5.5 x 10^{-9} S/cm.

Black, cyan and yellow toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of copper phthalocyanine pigment and 5 parts by weight of a benzidine pigment were used as the coloring agent, a polyester having an electroconductivity of 3.9 x 10^{-9} S/cm was used as the binder resin and 2 parts by weight of a zinc/salicylic acid complex was used as the charge-controlling agent. These black, cyan and yellow toners had electroconductivities of 4.0 x 10^{-9} S/cm, 3.9 x 10^{-9} S/cm and 3.8 x 10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers, and these developers were subjected to the development and transfer tests by using a full color electrophotographic copying machine where the imagewise light exposure was carried out by using a semiconductor laser light source.

The results obtained in Experiments 3-1 through 3-5 are shown in Table 3.

Table 3

Experiment No.	3-1	3-2	3-3	3-4	3-5
Electroconductivity of Resin (S/cm)					
magenta	1.6×10^{-9}	4.2×10^{-9}	8.9×10^{-10}	1.3×10^{-9}	5.5×10^{-9}
black	ditto	ditto	ditto	ditto	3.9×10^{-9}
cyan	ditto	ditto	ditto	ditto	ditto
yellow	ditto	ditto	ditto	ditto	ditto
Electroconductivity of Toner (S/cm)					
magenta	1.6×10^{-9}	4.2×10^{-9}	9.3×10^{-10}	9.8×10^{-9}	5.5×10^{-9}
black	1.8×10^{-9}	4.2×10^{-9}	9.6×10^{-10}	9.6×10^{-9}	4.0×10^{-9}
cyan	1.7×10^{-9}	4.1×10^{-9}	9.2×10^{-10}	1.2×10^{-9}	3.9×10^{-9}
yellow	1.6×10^{-9}	4.2×10^{-9}	9.3×10^{-10}	1.3×10^{-9}	3.8×10^{-9}
Charge-Controlling Agent					
magenta	zinc/salicylic acid complex	zinc/salicylic acid complex	zinc/salicylic acid complex	metal-containing azo dye	metal-containing azo dye
black	ditto	ditto	ditto	ditto	zinc/salilcylic acid complex
cyan	ditto	ditto	ditto	zinc/salicylic acid complex	ditto
yellow	ditto	ditto	ditto	ditto	ditto

Experiment No.	3-1 first copy	3-1 1000th copy	3-2 first copy	3-2 1000th copy	3-3 first copy	3-3 1000th copy	3-4 first copy	3-4 1000th copy	3-5 first copy	3-5 1000th copy
Developed Toner Quantity (mg)										
magenta	82	81	86	87	70	70	78	77	88	92
black	83	82	87	86	75	76	79	78	85	85
cyan	81	81	87	86	70	70	80	83	84	83
yellow	82	81	86	86	71	70	81	84	85	84
Transfer Efficiency (%)										
magenta	79	78	69	69	82	81	79	78	69	63
black	78	77	68	67	79	79	81	80	70	70
cyan	79	77	69	68	81	81	78	75	71	70
yellow	79	78	69	67	82	81	77	74	70	71
Image Characteristics										
density unevenness	○	○	○	○	X	X	△	X	○	△
sharpness	○	○	○	○	△	△	△	X	△	X

Note ○: good, △: fair, X: bad

(Experiment 4)

Experiment 4-1

A toner having an average particle size of 8.5 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 1.5 x 10^{-9} as the binder resin, 5 parts by weight of a copper phthalocyanine pigment as the coloring agent and 2 parts by weight of a zinc/salicylic acid complex as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 1.6 x 10^{-9} S/cm.

Black, magenta and yellow toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of a quinacridone pigment and 4 parts by weight of a benzidine pigment were used as the coloring agent, respectively. These black, magenta and yellow toners had electroconductivities of 1.7 x 10^{-9} S/cm, 1.6 x 10^{-9} S/cm and 1.6 x 10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers, and these developers were subjected to the full color development by using a full color electrophotographic copying machine where the imagewise light exposure was carried out by using a semiconductor laser light source in the same manner as described in Experiment 1-1. The change of the image quality in first in 1000th copies was examined.

Experiment 4-2

A toner having an average particle size of 8.5 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 5.5 x 10^{-9} as the binder resin, 5 parts by weight of a copper phthalocyanine pigment as the coloring agent and 2 parts by weight of a metal-containing azo dye as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 5.5 x 10^{-9} S/cm.

Black, magenta and yellow toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of a benzidine pigment and 5 parts by weight of a quinacridone pigment were used as the coloring agent, respectively, 100 parts by weight of a polyester resin having an electroconductivity of 3.9 x 10^{-9} S/cm was used as the binder and 2 parts by weight of a zinc/salicylic acid complex was used as the charge-controlling agent. These black, magenta and yellow toners had electroconductivities of 4.0 x 10^{-9} S/cm, 3.8 x 10^{-9} S/cm and 3.8 x 10^{-9} S/cm, respectively. By using these color toners, the full color development was carried out in the same manner as described in Experiment 1-1.

The results obtained in Experiments 4-1 and 4-2 are shown in Table 4.

Table 4

Experiment No.		4-1		4-2	
Electroconductivity of Resin (S/cm)	cyan	1.5×10^{-9}		5.5×10^{-9}	
	black	ditto		3.9×10^{-9}	
	magenta	ditto		ditto	
	yellow	ditto		ditto	
Electroconductivity of Toner (S/cm)	cyan	1.6×10^{-9}		5.5×10^{-9}	
	black	1.7×10^{-9}		4.0×10^{-9}	
	magenta	1.6×10^{-9}		3.8×10^{-9}	
	yellow	1.6×10^{-9}		3.8×10^{-9}	
Charge-Controlling Agent	cyan	zinc/salicylic acid complex		metal-containing azo dye	
	black	ditto		zinc/salicylic acid complex	
	magenta	ditto		ditto	
	yellow	ditto		ditto	
Developed Toner Quantity (mg)		first copy	1000th copy	first copy	1000th copy
	cyan	80	79	88	89
	black	82	82	85	84
	magenta	80	80	84	83
	yellow	81	80	85	83
Transfer Efficiency (%)	cyan	79	79	68	63
	black	79	78	70	71
	magenta	78	78	71	72
	yellow	78	78	70	72
Image Characteristics					
density unevenness		○	○	△	X
sharpness		○	○	△	X

Note ○ : good

△ : fair

X : bad

(Experiment 5)

Experiment 5-1

A toner having an average particle size of 9.0 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 3.8×10^{-9} as the binder resin, 5 parts by weight of a benzidine pigment as the coloring agent and 2 parts by weight of a zinc/salicylic acid complex as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 3.9 x 10^{-9} S/cm.

Black, cyan and magenta toners were prepared in the same manner as described above except that 5 parts by weight of carbon black, 5 parts by weight of a copper phthalocyanine pigment and 5 parts by weight of a quinacridone pigment were used as the coloring agent, respectively, 100 parts by weight of a polyester having an electroconductivity of 3.5 x 10^{-9} S/cm was used as the binder resin and 2 parts by weight of a zinc/salicylic acid complex was used as the charge-controlling agent. These black, cyan and magenta toners had electroconductivities of 3.7 x 10^{-9} S/cm, 3.6 x 10^{-9} S/cm and 3.6 x 10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers, and these developers were subjected to the full color development in the same manner as described in Experiment 1-1. The change of the image quality in first to 1000th copies was examined.

<u>Experiment 5-2</u>

A toner having an average particle size of 8.5 μm was prepared by melt-kneading 100 parts by weight of a polyester resin having an electroconductivity of 5.5 x 10^{-9} as the binder resin, 4 parts by weight of a benzidine pigment as the coloring agent and 2 parts by weight of a metal-containing azo dye as the charge-controlling agent, cooling the melt and pulverizing and classifying the solid. The electroconductivity of the obtained toner was 5.6 x 10^{-9} S/cm.

Black, cyan and magenta toners were prepared in the same manner a described above except that 5 parts by weight of carbon black, 5 parts by weight of a copper phthalocyanine pigment and 5 parts by weight of a quinacridone pigment were used as the coloring agent. respectively, and 2 parts by weight of a zinc/salicylic acid complex was used as the charge-controlling agent. These black, cyan and magenta toners and electroconductivities of 4.0 x 10^{-9} S/cm, 3.9 x 10^{-9} S/cm and 3.8 x 10^{-9} S/cm, respectively.

These toners were mixed with a known magnetic ferrite carrier to form two-component developers, and these developers were subjected to the full color development by using a full color electrophotographic copying machine where the imagewise light exposure was carried out by using a semiconductor laser light source in the same manner as described in Experiment 1-1.

The results obtained in Experiments 5-1 and 5-2 are shown in Table 5.

Table 5

Experiment No.		5-1		5-2	
Electroconductivity of Resin (S/cm)	yellow	3.8×10^{-9}		5.5×10^{-9}	
	black	3.5×10^{-9}		3.9×10^{-9}	
	cyan	ditto		ditto	
	magenta	ditto		ditto	
Electroconductivity of Toner (S/cm)	yellow	3.9×10^{-9}		5.6×10^{-9}	
	black	3.7×10^{-9}		4.0×10^{-9}	
	cyan	3.6×10^{-9}		3.9×10^{-9}	
	magenta	3.6×10^{-9}		3.8×10^{-9}	
Charge-Controlling Agent	yellow	zinc/salicylic acid complex		metal-containing azo dye	
	black	ditto		zinc/salicylic acid complex	
	cyan	ditto		ditto	
	magenta	ditto		ditto	
		first copy	1000th copy	first copy	1000th copy
Developed Toner Quantity (%)	yellow	86		88	89
	black	85		85	84
	cyan	84		84	85
	magenta	84		85	85
Transfer Efficiency (%)	yellow	70		67	61
	black	71		70	71
	cyan	71		71	72
	magenta	71		70	71
Image Characteristics	density unevenness	○		△	X
	sharpness	○		△	X

Note ○: good, △: fair, X: bad

Claims

1. A toner comprising a colouring agent incorporated in a binder resin for use in full colour development by overlapping with other toners comprising different kinds of colouring agent, wherein the electroconduc-

tivity of the binder resin is in the range of from 1.0 x 10^{-9} to 5.0 x 10^{-9} (S/cm).

2. A toner according to claim 1 comprising as charge-controlling agent a zinc compound of salicylic acid.

3. A toner according to claim 2 wherein the colouring agent comprises a quinacridone pigment as the main component.

4. A toner according to claim 2 wherein the colouring agent comprises a copper phthalocyanine pigment as the main component.

5. A toner according to claim 2 wherein the colouring agent comprises a benzidine pigment as the main component.

6. Use of a toner according to any one of claims 1 to 5 in full colour development by overlapping the toner with other toners comprising different kinds of colouring agent.

7. Use of a magenta toner according to claim 3, a cyan toner according to claim 4 and a yellow toner according to claim 5 in full colour development by overlapping the magenta, cyan and yellow toners.

Patentansprüche

1. Toner, umfassend ein in einem Binderharz eingebautes Farbmittel, zur Verwendung in der totalen Farbentwicklung durch Überlappung mit anderen Tonern, die verschiedene Arten von Farbmitteln umfassen, dadurch gekennzeichnet, daß die elektrische Leitfähigkeit des Binderharzes im Bereich von 1.0 x 10^{-9} bis 5.0 x 10^{-9} (S/cm) liegt.

2. Toner nach Anspruch 1, dadurch gekennzeichnet, daß er als Ladungskontrollmittel eine Zinkverbindung von Salicylsäure umfaßt.

3. Toner nach Anspruch 2, dadurch gekennzeichnet, daß das Farbmittel ein Cuinacridon-Pigment als Hauptkomponente umfaßt.

4. Toner nach Anspruch 2, dadurch gekennzeichnet, daß das Farbmittel ein Kupferphthalocyanin-Pigment als Hauptkomponente umfaßt.

5. Toner nach Anspruch 2, dadurch gekennzeichnet, daß das Farbmittel ein Benzidin-Pigment als Hauptkomponente umfaßt.

6. Verwendung eines Toners nach einem der Ansprüche 1 bis 5 in der totalen Farbentwicklung durch Überlappen des Toners mit anderen Tonern, die verschiedene Arten von Farbmitteln enthalten.

7. Verwendung eines Magenta-Toners nach Anspruch 3, eines Cyan-Toners nach Anspruch 4 und eines Gelb-Toners nach Anspruch 5 in der totalen Farbentwicklung durch Überlappung der Magenta-, Cyan- und Gelb-Toner.

Revendications

1. Toner comprenant un agent colorant incorporé à une résine liante, destiné à être utilisé pour le développement en couleur par recouvrement avec d'autres toners ayant d'autres sortes d'agents colorants, et dont la résine liante a une conductivité électrique comprise entre 1,0 x 10^{-9} et 5,0 x 10^{-9} S/cm.

2. Toner selon la revendication 1, comprenant comme agent de réglage de charge une composé de zinc de l'acide salicylique.

3. Toner selon la revendication 2, dont l'agent colorant a comme constituant principal un pigment de quinacridone.

4. Toner selon la revendication 2, dont l'agent colorant a comme constituant principal un pigment de phta-

locyanine de cuivre.

5. Toner selon la revendication 2, dont l'agent colorant a comme constituant principal un pigment de benzidine.

6. Utilisation d'un toner selon l'une des revendications 1 à 5 pour le développement en couleur par mise en recouvrement de ce toner avec d'autres toners ayant d'autres sortes d'agents colorants.

7. Utilisation d'un toner magenta selon la revendication 3, d'un toner cyan selon la revendication 4 et d'un toner jaune selon la revendication 5 pour le développement en couleur par mise en recouvrement de ces toners magenta, cyan et jaune.

FIG. 1