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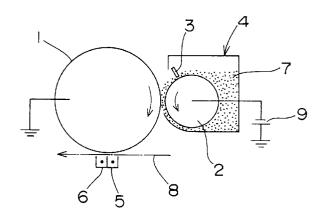
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# (54) Method for contact type development

(57) The method uses a positive charging toner 7 wherein a resin having a trialkylammonio group at the side chain is blended as an electric charge controlling material, in combination with a positive charging photoconductor 1 wherein a single-layer type positive charging organic photosensitive layer is formed on the surface of an electroconductive substrate. Thereby, a good image having a high image density can be formed without causing image fog.

F I G. 1



#### Description

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#### BACKGROUND OF THE INVENTION

The present invention relates to a method for contact type development using a positive charging toner and a positive charging photoconductor, which is used for image forming apparatus such as facsimiles, laser beam printers, etc.

In the image forming apparatus such as facsimiles, laser beam printers, etc., it is necessary to conduct a so-called negative-positive reversal development, comprising adhering a toner to an area, where the potential is decreased by exposure, on the surface of the uniformly charged photoconductor to form a toner image. As an exemplified method thereof, there is a method for contact type development (impression development) using a positive charging photoconductor and a positive charging toner.

In this method for contact type development, firstly, a toner is positively charged by friction with a developing sleeve, to which a negative developing bias has been applied, in a developing apparatus, and then adhered on the surface of the developing sleeve by an image force from a control blade to form an uniform thin layer of the positive charging toner on the surface of the developing sleeve.

On the other hand, the surface of a photoconductor is uniformly charged to the same polarity (positive) as that of the toner by corona charging, etc.. Then, the photoconductor is exposed to laser light, etc. to form an electrostatic latent image. Regarding this electrostatic latent image, the potential of the exposed area should be lower than a developing bias and the potential of the non-exposed area should be higher than the developing bias.

Then, when the thin layer on the surface of the developing sleeve is brought into contact with the electrostatic latent image on the surface of the photoconductor, the toner does not transfer to the photoconductor at the non-exposed area. On the other hand, the toner transfers from the thin layer to the surface of the photoconductor by the potential different from the developing bias, thereby forming a toner image on the surface of the photoconductor.

However, the method for contact type development had the following problem. That is, the potential of the photoconductor is higher than the developing bias at the non-exposed area, as described above, so that an electric charge having a reverse polarity (negative) from the developing sleeve flows into the toner to reverse the charged potential to negative from positive, and the toner of which charged potential is reversed is adhered to the non-exposed area of the photoconductor by the action of the image force, thereby causing so-called image fog, that is, a toner is adhered to the area where no image is formed.

The method has also the following problem. That is, when the negative electric charge from the developing sleeve flows into the thin layer, the charged potential of the toner does not reverse but the amount of charging is decreased, thereby decreasing the potential difference between the toner and photoconductor at the exposed area, which results in decrease of the density at the image area of the image formed.

# SUMMARY OF THE INVENTION

It is a main object of the present invention is to provide a method for contact type development which can form a good image having a high image density without causing image fog.

In order to accomplish the above object, the present inventors have studied intensively about an optimum combination of a positive charging toner and a positive charging photoconductor to be used for the method for contact type development. As a result, it has been found that, by combining a positive charging toner, wherein a resin having a trialkylammonio group at the side chain (hereinafter referred to as an "electric charge controlling resin") is blended as an electric charge controlling material, with a positive charging photoconductor wherein a single-layer type positive charging organic photosensitive layer is formed on the surface of an electroconductive substrate, a good image having a high image density can be obtained without causing image fog.

That is, the method for contact type development of the present invention comprises the steps of:

rubbing a positive charging toner with a developing surface, preferably a sleeve, to which a developing bias is applied, to positively charge the toner, thereby forming a uniform thin layer of the positive charging toner on the developing surface;

charging the surface of a positive charging photoconductor to the same polarity as that of the toner and exposing to light to form an electrostatic latent image having a potential lower than the developing bias;

bringing the thin layer of the positive charging toner on the developing surface into contact with the electrostatic latent image on the surface of the photoconductor to transfer the toner from the thin layer to the surface of the photoconductor, thereby forming a toner image on the surface of the photoconductor; and

transferring the toner image to a material to be printed;

wherein the positive charging toner contains an electric charge controlling resin as an electric charge controlling material, and the positive charging photoconductor comprises an electroconductive substrate and a single-layer type positive charging organic photosensitive layer formed on the surface of the electroconductive substrate.

The reason why a good image having a high image density can be formed without causing image fog when the positive charging toner is used in combination with the positive charging photoconductor will be assumed as follows.

That is, the electric charge controlling resin wherein a trialkylammonio group is introduced into the side chain has a good compatibility with a fixing resin so that it does not collect on the surface or interior of a toner particle like a normal low-molecular weight electric charge controlling material, for example, dye type electric charge controlling material such as nigrosine dye, etc., but is uniformly dispersed in the toner particle. Therefore, the positive charging toner using the electric charge controlling resin as the electric charge controlling material is superior in charging stability and the negative electric charge from the developing sleeve is not easily flown into so that the charging potential thereof is not easily allowed to reverse from positive to negative or the amount of changing is not easily decreased.

On the other hand, the positive charging toner using the electric charge controlling resin matches well with the single-layer type positive charging organic photosensitive layer formed on the surface of the electroconductive substrate with respect to charging characteristics, etc., so that the toner is efficiently transferred to the exposed area on the surface of the photoconductor from the thin layer on the surface of the developing sleeve, but no toner is transferred at the non-exposed area. As a result, a good image having a high image density can be formed without causing image fog.

Other objects, features and advantages of the present invention will become apparent to those skilled in the art from the following description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1 is a schematic diagram illustrating the apparatus used for measuring a fog density in the Examples of the present invention.

Fig. 2 is a graph illustrating a relation between the charged potential and the fog density of the surface of the photoconductor measured using the apparatus of Fig. 1.

#### DETAILED DESCRIPTION OF THE INVENTION

As described above, the positive charging toner to be used in the present invention is that which contains the electric charge controlling resin, wherein a trialkylammonio group is introduced into the side chain, as the electric charge controlling material. Preferably, the positive charging toner is composed of a toner particle formed by internally adding the electric charge controlling resin and a colorant in a fixing resin, and an external additive (e.g. inorganic fine powder, etc.) to be externally added in the toner particle. The external additive may be used for improving fluidity and the like.

Examples of the fixing resin include styrene resin (homopolymer or copolymer containing styrene or a styrene substitute) such as polystyrene, chloropolystyrene, poly- $\alpha$ -methylstyrene, styrene-chlorostyrene copolymer, styrene-propylene copolymer, styrene-butadiene copolymer, styrene-winyl chloride copolymer, styrene-vinyl acetate copolymer, styrene-maleic acid copolymer, styrene-acrylate copolymer (e.g. styrene-methyl acrylate copolymer, styrene-butyl acrylate copolymer, styrene-phenyl acrylate copolymer, etc.), styrene-methacrylate copolymer (e.g. styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-phenyl methacrylate copolymer, etc.), styrene- $\alpha$ -chloromethyl acrylate copolymer, styrene-acrylonitrile-acrylate copolymer, etc., polyvinyl chloride, low-molecular weight polyethylene, low-molecular weight polypropylene, ethylene-ethyl acrylate copolymer, polyvinyl butyral, ethylene-vinyl acetate copolymer, rosin-modified maleic resin, phenol resin, epoxy resin, polyester resin, ionomer resin, polyurethane resin, silicone resin, ketone resin, xylene resin, polyamide resin and the like. These may be used alone or in combinations thereof.

As the colorant to be contained in the toner particle, there can be used various dyes, pigments, etc. which have hitherto been known. Among them, carbon black is mainly used in case of a black toner.

As the carbon black, there can be used various carbon blacks which have hitherto been known, such as channel black, roller black, disk black, gas furnace black, oil furnace black, thermal black, acetylene black and the like.

The amount of carbon black is not specifically limited. However, since carbon black itself has an electroconductivity, it also plays a role as a control means of electric properties of the toner particle, which take part in charging of the toner particle. Accordingly, it is preferred to set the preferable range of the amount to be added according to the objective performances of the developer. The amount of carbon black to be formulated is preferably about 1 to 9 parts by weight, based on 100 parts by weight of the fixing resin, in view of the charging properties of the developer.

As the electric charge controlling material, there can be used an electric charge controlling resin wherein a trialky-lammonio group corresponding to a quaternary ammonium salt is introduced into the side chain, as described above. Examples of the electric charge controlling resin include compounds wherein a trialkylammonio group represented by the formula:

$$\begin{array}{c|c} R^{1} R^{2} R^{3} \\ & \downarrow / \\ & N^{+}X^{-} \end{array}$$

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(wherein  $R^1$ ,  $R^2$  and  $R^3$  are the same or different and indicate a straight or branched chain alkyl group having 1 to 6 carbon atoms, such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, tert-butyl group, pentyl group or hexyl group; and X is F, Cl, Br, I,  $ClO_4$ ,  $PF_4$  or  $BF_4$ ) as the side chain is introduced into a suitable polymer main chain.

As the main chain of the electric charge controlling resin, there can be used various polymer main chains. As described above, the compatibility between the electric charge controlling resin and fixing resin is particularly important in view of charging properties of the toner so that it is preferred to use the polymer main chain having a good compatibility with the polymer to be used as the fixing resin. Among them, it is more preferred to use the same polymer main chain as the polymer to be used as the fixing resin.

For example, when the styrene-acrylic resin such as styrene-acrylate copolymer, styrene-methacrylate copolymer, etc. is used as the fixing resin, it is preferred to use the same styrene-acrylic resin as the main chain of the electric charge controlling resin. When the main chain is the styreneacrylic resin, the trialkylammonio group is substituted on whole or partial ester moiety of acrylate or methacrylate. It is preferable that the portion of acrylate or methacrylate component in styrene-acrylic resin is 10 to 50 mol %.

Examples of the side chain may be a carbon chain such as methyl group, ethyl group, as well as the ester moiety of acrylate or methacrylate.

The electric charge controlling resin may be formulated in the amount of 0.1 to 10 parts by weight, preferably 0.5 to 5 parts by weight, based on 100 parts by weight of the fixing resin.

Various additives such as release agents (anti-offset agents), etc. may be added to the toner particle, in addition to the colorants and electric charge controlling materials.

Examples of the release agent (anti-offset agent) include aliphatic hydrocarbons, aliphatic metal salts, higher fatty acids, fatty acid esters or partially saponified material thereof, silicone oil, various waxes and the like. Among them, aliphatic hydrocarbons having a weight-average molecular weight of about 1000 to 10000 are preferred. Examples thereof include low-molecular weight polypropylene, low-molecular weight polyethylene, paraffin wax, low-molecular weight olefin polymer of an olefin unit having not less than 4 carbon atoms, and they may be suitably used alone or in combination thereof.

The release agent may be internally added in the amount of 0.1 to 10 parts by weight, preferably 0.5 to 8 parts by weight, based on 100 parts by weight of the fixing resin.

The toner particle can be produced by uniformly melting and kneading a mixture, obtained by uniformly premixing the above respective components with a dry-blender, Henschel mixer, ball mill, etc., using a kneading apparatus such as Banbury mixer, roll, single- or twin-screw extruder, etc., cooling the resulting kneaded mixture, followed by pulverizing and optional classifying. It can also be produced by a suspension polymerization method.

It is preferred that the particle size of the toner particle is not more than 10  $\mu$ m for the purpose of enhancing the image quality of the image to be formed. The construction of the present invention can also be used for a normal toner particle having a particle size of larger than 10  $\mu$ m.

As the external additive to be externally added to the toner particle, there can be used various external additives which have hitherto been used, such as inorganic fine powder, fluorine plastic particle and the like. Among them, silica surface treatments containing hydrophobic or hydrophilic silica fine particles (e.g. ultrafine particulate silica anhydride, colloidal silica, etc.) are suitably used.

The amount of the external additive to be externally added is not specifically limited and it may be the same as a conventional amount. For example, it is preferred to formulate the external additive in the amount of about 0.1 to 3.0 parts by weight, based on 100 parts by weight of the toner particle. In some case, the amount of the external additive may deviate from this range.

As described above, the positive charging photoconductor to be used in combination with the positive charging toner is composed by forming the single-layer type positive charging organic photosensitive layer on the surface of the electroconductive substrate. Such a single-layer type positive charging organic photosensitive layer may be composed by formulating the electric charge generating material and electric charge transferring material in the layer of the binding resin.

Examples of the binding resin include synthetic resins which have hitherto been known, such as styrene polymer, acrylic polymer, styrene, acrylic copolymer, ethylene, vinyl acetate copolymer, olefin polymer (e.g. polypropylene, ion-

omer, etc.), polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, polyester, alkyd resin, polyamide, polyurethane, epoxy resin, polycarbonate, polyarylate, polysulfon, diaryl phthalate, silicone resin, ketone resin, polyvinyl butyral, polyether, phenol resin, photosetting resin (e.g. epoxy acrylate, etc.). These binding resins can be used alone or in combination thereof.

Among the above binding resins, there can be suitably used styrene polymer, acrylic polymer, styrene, acrylic copolymer, polyester, alkyd resin, polycarbonate, polyacrylate and the like. Among them, so-called bisphenol type polycarbonates derived from bisphenols represented by the formula (2):

$$HO \longrightarrow C \longrightarrow OH \qquad (2)$$

$$R^{5}$$

(wherein R<sup>4</sup> and R<sup>5</sup> are the same or different and indicate a hydrogen atom or a lower alkyl group such as methyl group, ethyl group and the like; and R<sup>4</sup> and R<sup>5</sup> may be bonded together with a carbon atom of the main chain to form a cyclo ring such as cyclohexane ring) and phosgene can be used, most preferably.

Examples of the electric charge generating material to be contained in the layer of the binding resin include selenium, selenium-tellurium, amorphous-silicon, pyrylium salt, azo pigments, bisazo pigments, anthanthrone pigments, phthalocyanine pigments, indigo pigments, therene pigments, toluidine pigments, pyrazoline pigments, perylene pigments, quinacridone pigments and the like. They may be used alone or in combination thereof so that the resulting photoconductor may have a sensitivity within a desired absorption wavelength range.

Among them, phthalocyanine pigments (e.g. X-type metal-free phthalocyanine, oxotitanylphthalocyanine, etc.), perylene pigments represented by the formula (3):

$$R^6-N$$
 $N-R^7$  (3)

(wherein R<sup>6</sup> and R<sup>7</sup> are the same or different and respectively indicate an alkyl, cycloalkyl, aryl or aralkyl group having not more than 18 carbon atoms which may have a substituent) are particularly preferred.

Examples of the alkyl group include methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isopoutyl group, sec-butyl group, tert-butyl group, 2-ethylhexyl group and the like. Examples of the cycloalkyl group include cyclohexyl group and the like. Examples of the aryl group include phenyl group, napthyl group, tolyl group xylyl group, ethylphenyl group and the like. Examples of the aralkyl group include benzyl group, phenethyl group and the like. Further, examples of the substituent which may be substituted on these groups include lower alkyl groups such as methyl group, ethyl group, etc.; alkoxy groups such as methoxy group, ethoxy group, etc.; halogen atoms such as chlorine, iodine, bromine, etc.

The electric charge transferring material preferably includes an electron transferring material superior in electric transferring properties and a hole transferring material superior in hole transferring properties. Examples of the electron transferring material include electron attractive materials such as paradiphenoquinone derivative, benzoquinone derivative, naphthoquinone derivative, trinitrofluorenoneimine derivative, tetracyanoethylene, tetracyanoquinodimethane, chloroanil, bromoanil, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, etc., high-molecular compounds of electron attractive materials mentioned above, and the like.

Among the above electron transferring materials, paradiphenoquinone derivatives represented by the formula (4):

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$$\mathbb{R}^{8}$$
 $\mathbb{R}^{9}$ 
 $\mathbb{R}^{10}$ 
 $\mathbb{R}^{11}$ 

(wherein  $R^8$ ,  $R^9$ ,  $R^{10}$  and  $R^{11}$  are the same or different and indicate a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group or an alkoxy group) are suitably used. Among them, unsymmetrical paradiphenoquinone derivatives such as paradiphenoquinone derivatives wherein two substituents of the substituents  $R^8$ ,  $R^9$ ,  $R^{10}$  and  $R^{11}$  indicate a lower straight-chain alkyl group and other two substituents indicate a branched alkyl, cycloalkyl, aryl or aralkyl group are used, most preferably, because they are superior in electron transferring properties and solubility to the binding resin.

Examples of the alkyl group include the respective groups described above.

On the other hand, examples of the hole transferring material include the following compounds:

pyrene, N-ethylcarbazole, N-isopropylcarbazole, N-methyl-N-phenylhydrizino-3-methylidene-9-carbazole, N,N-diphenylhydrazino-3-methylidene-9-ethylcarbazole, N,N-diphenylhydrazino-3-methylidene-10-ethylphenoxazine;

hydrazone salts such as p-diethylaminobenzaldehyde-N,N-diphenylhydrazone, p-diethylaminobenzaldehyde- $\alpha$ -naphthyl-N-phenylhydrazone, p-pyrrolidinobenzaldehyde-N,N-diphenylhydrazone, 1,3,3-trimethylindolenine- $\omega$ -aldehyde-N,N-diphenylhydrazone, p-diethylbenzaldehyde-3-methylbenzazolinone-2-hydrazone, etc.;

2,5-bis(p-diethylaminophenyl)-1,3,4-oxadiazole;

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pyrazolines such as 1-phenyl-3-(p-diethylaminostyryl)-5-(p-diethylaminophenyl)pyrazoline, 1-[quinonyl(2)]-3-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminophenyl)pyrazoline, 1-[pyridyl(3)]-3-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-5-(p-diethylaminostyryl)-4-methyl-5-(p-diethylaminophenyl)pyrazoline, 1-[pyridyl(2)]-3-( $\alpha$ -methyl-p-diethylaminostyryl)-3-(p-diethylaminophenyl)pyrazoline, 1-phenyl-3-(p-diethylaminostyryl)-4-methyl-5-(p-diethylaminophenyl)pyrazoline, 1-phenyl-3-(p-diethylaminostyryl)-4-methyl-5-(p-diethylaminophenyl)pyrazoline, etc.;

oxazoles such as 2-(p-diethylaminostyryl)-3-diethylaminobenzoxazole, 2-(p-diethylaminophenyl)-4-(p-diethylaminophenyl)-5-(2-chlorophenyl)oxazole, etc.;

thiazoles such as 2-(p-diethylamino-styryl)-6-diethylaminobenzothiazole, etc.;

triarylmethane compounds such as bis(4-diethylamino-2-methylphenyl)phenylmethane, etc.;

polyarylalkanes such as 1,1-bis(4-N,N-diethylamino-2-methylphenyl)heptane, 1,1,2,2-tetrakis(4-N,N-diethylamino-2-methylphenyl)ethane, etc.:

benzidine compounds such as N,N'-diphenyl-N,N'-bis(methylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(ethylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(propylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(butylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(tert-butylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(tert-butylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(2,4-dimethylphenyl)benzidine, N,N'-diphenyl-N,N'-bis(chlorophenyl)benzidine, etc.;

triphenylamine, poly-N-vinylcarbazole, polyvinylpyrene, polyvinylanthracene, polyvinylacridine, poly-9-vinylphenylanthracene, pyrene-formaldehyde resin, ethylcarbazole formaldehyde resin, etc.

Among the above hole transferring materials, benzidine compounds represented by the formula (5):

(wherein R<sup>12</sup> and R<sup>13</sup> are the same or different and indicate a lower alkyl group such as methyl group, ethyl group, etc.; and R<sup>14</sup>, R<sup>15</sup>, R<sup>16</sup> and R<sup>17</sup> are the same or different and indicate an alkyl, cycloalkyl, aryl or aralkyl group having not more than 18 carbon atoms) and carbazolehydrazone compounds represented by the formula (6):

$$R^{18}$$
  $C=N-N$   $R^{20}$   $R^{21}$ 

(wherein R<sup>18</sup> is a hydrogen atom, an alkyl group or an acyl group; R<sup>19</sup> is a divalent organic group such as alkylene group, etc.; R<sup>20</sup> and R<sup>21</sup> are the same or different and indicate an alkyl, cycloalkyl, aryl or aralkyl group having not more than 18 or less carbon atoms; and i is an integer of 1 to 3) among hydrazole salts are used, most preferably, because they are superior in hole transferring properties and solubility to the binding resin.

Examples of the alkyl, cycloalkyl, aryl and aralkyl group include the respective groups described above. Examples of the acyl group include formyl group, acetyl group, propionyl group, butyryl group, valeryl group and the like. Examples of the alkylene group include ethylene group, propylene group, butylene group and the like.

Among the respective components, the amount of the electric charge generating material is not specifically limited, but is preferably about 0.1 to 5 % by weight, particularly about 0.25 to 2.5 % by weight, based on the total amount (total amount of solid content) of the respective components constituting the single-layer type positive charging organic photosensitive layer. Further, the amount of the electron transferring material is preferably about 5 to 50 % by weight, particularly about 10 to 40 % by weight, based on the total amount of the solid content. Further, the amount of the hole transferring material is preferably about 5 to 50 % by weight, particularly about 10 to 40 % by weight, based on the total amount of the solid content. It is preferred to contain the electron transferring material and hole transferring material in the weight ratio of 1:9 to 9:1, particularly 2:8 to 8:2.

The single-layer type positive charging organic photosensitive layer is formed as follows. That is, the above respective components are dispersed/mixed with a suitable solvent using a roll mill, a ball mill, an atriter, a paint shaker, a supersonic dispenser, etc. to prepare a coating solution for photosensitive layer, which is applied on the surface of an electroconductive substrate by a dip coating method, a bar coating method, a spray coating method, a flow coating method, spin coating method, etc., followed by drying.

The concentration of the solid content of the coating solution can be suitably adjusted according to the method of coating onto the surface of the electroconductive substrate, and is preferably 5 to 50 % by weight.

Various additives such as antioxidants, radical scavengers, singlet quenchers, ultraviolet absorbers, softeners, surface modifiers, antifoamers, bulking agents, thickners, dispersion stabilizers, wax, acceptors, donors, etc. can be appropriately contained in the coating solution, in addition to the above respective components, within such a range as not to exert a deleterious influence on characteristics of the photoconductor.

Further, when steric hindering phenolic antioxidants are contained in the amount of about 0.1 to 50 % by weight based on the total amount of the solid content, the durability of the photosensitive layer can be improved without exerting a deleterious influence on characteristics of the photoconductor.

As the conductive substrate, there can be used any substrate of various materials having the electroconductivity in various forms which fit to the structure of an image forming apparatus, such as drum, plate, sheet, etc. Examples of the material for the electroconductive substrate include metals or alloy such as aluminum, copper, tin, platinum, gold, silver, vanadium, molybdenum, chromium, cadmium, titanium, nickel, indium, stainless steel, brass, etc.; plastic materials vapor-deposited or laminated with the above metal; glass materials coated with aluminum iodide, tin oxide, indium oxide, etc. Among them, there can be suitably used aluminum, particularly aluminum which has been subjected to anodizing so that the anodized film may become 1 to 50  $\mu$ m, because no interference fringe is produced occurs.

As the solvent for preparing the coating solution, there can be used various organic solvents, and examples thereof include alcohols such as methanol, ethanol, isopropanol, butanol, etc.; aliphatic hydrocarbons such as n-hexane, octane, cyclohexane, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; halogenated hydrocarbons such as dichloromethane, dichloroethane, carbon tetrachloride, chlorobenzene, etc.; ethers such as dimethyl ether, diethyl ether, tetrahydrofuran, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, etc.; ketones such as acetone, methyl ethyl ketone, cyclohexanone, etc.; esters such as ethyl acetate, methyl acetate, etc.; dimethylformamide, dimethylsulfoxide, etc. These solvents may be used alone or in combination thereof according to the solubility of the above respective materials.

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# **EXAMPLES**

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# Production of positive charging toner I

100 Parts by weight of a styrene-acrylic resin as the fixing resin, 7.5 parts by weight of an electric charge controlling resin [resin (trade name of FCA-201-PZ manufactured by Fujikura Kasei Co., Ltd.) wherein a trialkylammonio group is introduced into the side chain of the styrene-acrylic resin)], 5 parts by weight of carbon black as the colorant and 2.5 parts by weight of polypropylene wax as the release agent were mixed and, after melting and kneading, the mixture was pulverized and classified to prepare a toner particle having an average particle size of 9 µm.

To 100 parts by weight of the toner particle, 0.3 parts by weight of a hydrophobic silica as the external additive was added to prepare a positive charging toner.

# Production of positive charging toner II

According to the same manner as that described in the production of the positive charging toner I except for adding 7.5 parts by weight of metal-free phthalocyanine in place of the electric charge controlling resin, a positive charging toner was produced.

# Production of positive charging toner III

According to the same manner as that described in the production of the positive charging toner I except for adding 5.0 parts by weight of a nigrosine dye in place of the electric charge controlling resin, a positive charging toner was produced.

# 25 Production of positive charging photoconductor:

5 Parts by weight of metal-free phthalocyanine as the electric charge generating material, 40 parts by weight of N,N'-diphenyl-N,N'-bis(2,4-dimethylphenyl)benzidine as the hole transferring material, 40 parts by weight of 3,3',5,5'-tet-raphenyldiphenoquinone as the electron transferring material and 100 parts by weight of polycarbonate as the binding resin were mixed and dispersed with 800 parts by weight of dichloromethane as the solvent using a paint shaker to prepare a coating solution. Then, this coating solution was applied on an aluminum tube by a dip coating method, followed by hot-air drying in a dark place at 60 °C for 60 minutes to produce a positive charging photoconductor drum having a single-layer type positive charging organic photosensitive layer of 15 μm in film thickness.

# 35 Test of image characteristics

As shown in Fig. 1, an image forming apparatus using a contact type developing apparatus 4 equipped with a developing sleeve 2 and a control blade 3 in combination with transfer and release chargers 5, 6 was used for the positive charging photoconductor drum 1 produced above in order to carry out the test.

A positive charging toner **7** was charged in the developing apparatus **4** and a DC voltage (developing bias) of -200 to -900 V was applied from a bias power **9** to the developing sleeve **2** while rotating the drum **1** and developing sleeve **2** at the state where the drum **1** is grounded (0 V) to produce a potential difference between them.

Then, a paper was passed through a carrier passage shown by a chain line with the arrow 8 in Fig. 1 at the state where a predetermined potential difference is maintained, and transfer and release chargers 5, 6 were operated to print out.

Then, the fog density of the surface of the printed paper was measured using a reflection densitometer (TC-6D, manufactured by Tokyo Denshoku Co., Ltd.). The results are shown in Fig. 2.

On the other hand, a test was carried out for comparison according to the same manner as that described above except for using an aluminum tube having no photosensitive layer on the surface in place of the above positive charging photoconductor drum 1.

Incidentally, the combination of the drum 1 with the positive charging toner 7 is as follows.

	Toner <b>7</b>	Drum <b>1</b>
Example 1	1	D1
Comp. Example 1	II	D1

Continuation of the Table on the next page

(continued)

	Toner <b>7</b>	Drum <b>1</b>
Comp. Example 2	Ш	D1
Comp. Example 3	1	D2
Comp. Example 4	II	D2
Comp. Example 5	Ш	D2

In the above table, the symbol in the column of "Drum 1" is as follows. 10

D1: positive charging photoconductor drum

D2: aluminum tube

As is apparent from the results of Fig. 2, it was confirmed that the fog density could be decreased only in Example 1 wherein the positive charging toner produced in the production of the positive charging toner I was used in combination with the positive charging photoconductor drum having the positively charged type organic photosensitive layer and the fog density was increased to cause image fog in other combinations, at the state corresponding to the non-exposed area at the time of contact developing where the effective potential difference between the drum 1 and sleeve 2 was 400 V or more

#### Claims

A method for contact type development, comprising the steps of:

rubbing a positive charging toner with a developing surface, to which a developing bias is applied, to positively charge the toner, thereby forming a uniform thin layer of the positive charging toner on the developing surface:

charging the surface of a positive charging photoconductor to the same polarity as that of the toner and exposing to light to form an electrostatic latent image having a potential lower than the developing bias;

bringing the thin layer of the positive charging toner on the developing surface into contact with the electrostatic latent image on the surface of the photoconductor to transfer the toner from the thin layer to the surface of the photoconductor, thereby forming a toner image on the surface of the photoconductor; and

transferring the toner image to a material to be printed;

wherein said positive charging toner contains, as an electric charge controlling material, a resin having a side chain comprising a trialkylammonio group, and said positive charging photoconductor comprises an electroconductive substrate and a single-layer type positive charging organic photosensitive layer formed on the surface of the electroconductive substrate.

- 2. A method for contact type development according to claim 1, wherein the positive charging toner comprises a fixing 40 resin, the resin having a side chain comprising a trialkylammonio group, and a colorant.
  - 3. A method for contact type development according to claim 2, wherein the resin having a side chain comprising a trialkylammonio group is compatible with the fixing resin.
  - A method for contact type development according to claim 2 or 3, wherein the fixing resin is selected from a styrene-acrylate copolymer and a styrene-methacrylate copolymer, and the resin having a side chain comprising a trialkylammonio group has a main chain of the same chemical structure as that of the fixing resin and the side chain comprises the trialkylammonio group bonded to an ester moiety.
  - A method for contact type development according to any of claims 2 to 4, wherein the resin having a side chain comprising a trialkylammonio group is blended in an amount of 0.1 to 10 parts by weight for 100 parts by weight of the fixing resin.
- 6. The method for contact type development according to any preceding claim, wherein the single-layer type positive 55 charging organic photosensitive layer comprises a binding resin, an electric charge generating material and an electric charge transferring material, and the electric charge generating material is at least one of a phthalocyanine pigment and a perylene pigment and, further, the electric charge transferring material is a paradiphenoquinone

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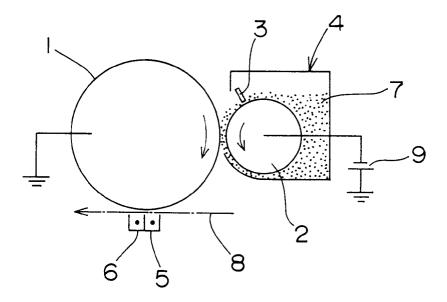
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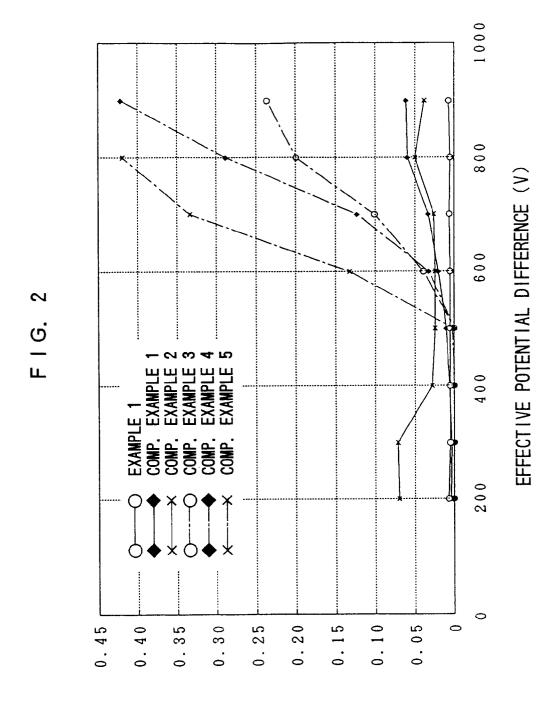
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derivative.

- 7. A positive charging toner comprising a fixing resin, a colorant and an electric charge controlling resin having a side chain comprising a trialkylammonio group, which is usable in the method for contact type development of claim 1.
- **8.** A positive charging toner according to claim 7, wherein the resin having a side chain comprising a trialkylammonio group is compatible with the fixing resin.
- 9. A positive charging toner according to claim 8, wherein the fixing resin is selected from a styrene-acrylate copolymer and a styrene-methacrylate copolymer, and the resin having a side chain comprising a trialkylammonio group has a main chain of the same chemical structure as that of the fixing resin and the side chain comprises the trialkylammonio group bonded to an ester moiety.
- **10.** A positive charging toner according to any of claims 7 to 9, wherein the resin having a side chain comprising a trialkylammonio group is blended in an amount of 0.1 to 10 parts by weight for 100 parts by weight of the fixing resin.

FIG. 1





FOG DENSITY