July 26, 1966 G. GOURGÉ 3,262,806

THREE COMPONENT MAGNETIC DEVELOPER FOR ELECTROPHOTOGRAPHIC PURPOSES AND METHOD FOR USING IT

Filed Dec. 13, 1962

FIG. 1

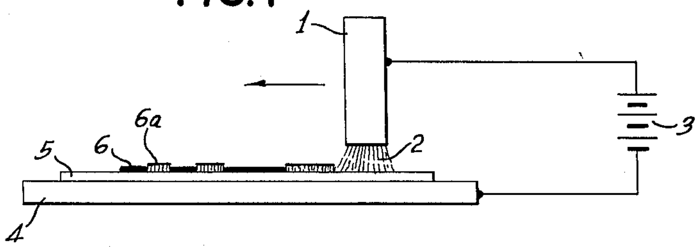
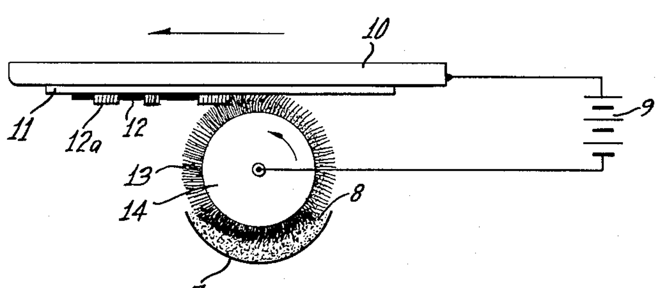


FIG. 2



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United States Patent Office

3,262,806
Patented July 26, 1966

3,262,806

THREE COMPONENT MAGNETIC DEVELOPER FOR ELECTROPHOTOGRAPHIC PURPOSES AND METHOD FOR USING IT

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Filed Dec. 13, 1962, Ser. No. 244,251
Claims priority, application Germany, Dec. 16, 1961, K 45,462
34 Claims. (Cl. 117—17.5)

The toners commonly used in electrophotography comprise natural or synthetic resins in finely divided powder form. When used for the development of latent electrostatic images, such a toner is mixed with somewhat larger particles of a carrier which generally comprises an inorganic material, e.g. iron powder.

Iron powder is particularly effective as a carrier as it can be moved magnetically, for example, by means of a roller magnetized by electric current. The toner present on the surface of the iron powder is thus applied in a desired manner to the surface of the electrostatic image to be developed. Thus, an even application of toner to fairly large solid areas is possible.

The toner and the iron powder become oppositely charged, as the result of the triboelectric effect, in the course of mixing, the toner particles generally assuming a positive or weakly negative charge.

It has been suggested to use toners consisting of two components which have approximately the same grain sizes. One toner component acquires a positive charge during handling and the other toner component acquires a negative charge. The use of these toners gives particularly desirable results with respect to freedom from background and sharpness of images produced therewith.

It is, however, desirable for the advantages of a magnetic system of application to be combined with the good properties of these last-named toners. In this, however, there have been considerable difficulties because reciprocal charging or reversal charging of the three components does not always give reproducible results.

The object of the present invention is a method for developing latent electrostatic images by means of a developer consisting of a carrier and toner, said developer being characterized in that the carrier consists of a magnetically excitable powder which is mixed with a toner consisting of at least two components of about equal grain sizes at least one of which accepts a positive charge and the other a negative charge and that this developer is taken up by a magnetic device which serves as an applicator system for the developer and, simultaneously, as a bias electrode.

The present invention is further concerned with a material for performing the above described process, said material consisting of a carrier and a toner and being characterized in that the carrier consists of a magnetically excitable powder and the toner consists of at least two components of about equal grain sizes one of which accepts a positive charge and the other a negative charge.

The iron powder in the developer according to the invention does not participate with the toner components in the triboelectric charging, but acts, in conjunction with a suitable magnetic applicator, as an applicator system and, if desired, also as a bias electrode.

The developer according to the invention enables a latent electrostatic image to be developed in such a way that fine lines and large solid areas are simultaneously given perfect development. At the same time, an image practically completely free of background is obtained.

The particle size of the iron powder is normally between 50 and 400μ and preferably between 100 and 300μ.

These two toner components are advantageously such that the toner or toners constituting the component of one polarity at least are soluble in water, alkalis or acids and/or when heated decompose to yield volatile substances or substances readily soluble in these solvents.

Natural and synthetic resins such as colophony, copals, dammar resin, asphalts, colophony-modified phenol resins, ketone resins, maleic resins, coumarone resins, polyacrylic acid resins and polystyrenes are suitable for the toner component which assumes a positive charge. Mixtures of these resins may also be used. Inorganic and/or organic pigments and/or dyestuffs may be added to these resins to impart to them a definite positive polarity. Examples of suitable substances are carbon black, zinc oxide, titanium dioxide, barium sulfate, minium and dyestuffs such as those listed in Schultz's Farbstofftabellen, vol. 1, 7th edition (1931). Also mixtures of such dyestuffs and/or pigments may be used.

Minute quantities of these substances, e.g. 0.5 percent by weight of carbon black, are often sufficient to impart a clearly positive character to the resins. It is also often advantageous to incorporate small quantities of waxes and/or organic compounds of low melting point and their substitution products, e.g. 0.1 to 10 percent, preferably 1 to 5 percent by weight, to the positive toner component to influence in a desirable direction its melting point and adhesive power.

Waxes suitable for this purpose include natural waxes such as carnauba wax, beeswax, Japan wax, montan wax, ceresine and synthetic waxes such as those marketed as A-wax, OP-wax, SPO-wax, V-wax, O-wax, E-wax, Hard Wax H, Hard Wax W, various waxes known as Ruhrwachse, and particularly the products available as Gersthofener waxes with the codings S, L, O, and OP.

Suitable organic compounds of low melting point include, in particular, substituted and unsubstituted aromatic compounds having melting points between 40 and 150° C., for example naphthols, such as 1-naphthol and 2-naphthol, aromatic compounds such as acenaphthene, acylamino compounds such as acetanilide, halogen aromatic compounds such as p-dibromobenzene, amino compounds such as 2,4-diamino toluene, o-phenylene diamine, phenols such as resorcinol, and diphenylamine and derivatives thereof.

Metal resinates are particularly suitable as the toner component which acquires the negative charge. Metal resinates, also known as resin soaps, are resin acid salts of metals of the first to eighth groups of the Periodic System.

Resinates, and mixtures thereof, of aluminum, barium, lead, calcium, cerium, iron, cobalt, copper, magnesium, manganese and zinc are particularly suitable.

In addition to these metal resinates, the negative toner component may include up to 50 percent by weight of resins, such as those above specified for use in the positive toner component. The above mentioned waxes and low-melting organic compounds having melting points between 40 and 150° C. may also be added to the metal resinates.

Dyestuffs and pigments, such as those described for use in the positive toner component may also be added. However, in general, the content of pigments and dyestuffs should not exceed 10 percent of the metal resinates in order to assure preservation of the negative polarity, except in the case of dyestuffs containing metals, of which quantities of up to 50 percent, but preferably not more than 35 percent by weight, may be added.

Examples of dyestuffs containing metals are those which contain in the molecule metals such as copper, zinc, magnesium, iron, sodium or potassium bound in complex form, e.g. complexes such as chlorophyll or copper, zinc or magnesium phthalocyanine or Naphthol Green B. Also useful are double salts of dyestuff molecules, e.g. zinc chloride double salts. Complexes of heteropoly acids, such as phosphoric/molybdic/tungstic acid with dyestuffs, may also be used.

Sulfonic acids and, in particular, carboxylic acids are suitable as alkli-soluble toners, e.g. oxalic acid, adipic acid, tartaric acid, benzoic acid, aminobenzoic acid, chlorobenzoic acid, naphthalic acid, 2-hydroxy-1-naphthoic acid, tetrachlorophthalic acid, anthraquinone carboxylic acid, benzene sulfonic acid, chlorobenzene sulfonic acid, naphthalene sulfonic acid, naphthol sulfonic acid, naphthylaminosulfonic acids, aminonaphthol sulfonic acids, benzidine sulfonic acids, anthracene sulfonic acids, anthraquinone sulfonic acids; and also acid anhydrides such as naphthalic anhydride and phthalic anhydride and acid imides such as naphthalic imide and hydroxynaphthalic imide, sulfonamides such as toluene sulfonamide, naphthalene sulfonamide, naphthalene sulfoanilide and phenyl sulfanilide, imidazoles such as benzimidazole, 2-mercaptobenzimidazole and 2-(4-aminophenyl)-4,5-diphenyl-imidazole, hydroxy compounds such as resorcinol, 4-hydroxydiphenyl and 4-hydroxy-benzophenone, naphthols such as 1-naphthol, purpurogallin, pyrogallol, 2,3-dihydroxynaphthalene and 5-hydroxy-acenaphthene, triazole compounds such as 2,5-diphenyl-1,3,4-triazole and pyrazole compounds such as 3,5-diphenyl pyrazole.

The alkali-soluble organic compounds may be used uncolored or they may be colored with the above-mentioned organic dyestuffs or organic or inorganic pigments.

Resins which are obtained by the polymerization of vinyl chloride with esters of fatty acids such as acetic acid, propionic acid and butyric acid, and which also contain a certain proportion of unsaturated monocarboxylic acids such as crotonic acid and cinnamic acid or unsaturated dicarboxylic acids such as maleic acid, fumaric acid or itaconic acid can also be used as alkali-soluble toners. Such products are commercially available. Styrene and maleic acid interpolymers and resins having a high acid number, e.g. over 150, and of which colophony forms the major part, can also be used.

Suitable acid-soluble toners are solid basic organic compounds such as phenylene diamine, benzidine, diphenylamine, naphthylamine, naphthylene diamine, 5,6-benzoquinoline, 5,6-benzoquinaldine, 4-chloroaniline, 4,4′-diamino-benzophenone and those of the triazole, imidazole and pyrazole compounds above named as alkali-soluble compounds and which, because of the presence of an NH group, are also acid-soluble.

As the water-soluble toners, the salts of the alkali-soluble toners, particularly their alkali metal salts, are suitable, as also are the salts of the acid-soluble toners, particularly with strong inoragnic acids.

Examples are: alkali metal salts of organic aliphatic, aromatic or heterocyclic carboxylic acids or sulphonic acids such as sodium acetate, lithium citrate, sodium/potassium tartrate, sodium benzoate, the sodium salt of naphthalene-1-carboxylic acid, the disodium salt of naphthalene-1,5-disulfonic acid, the potassium salt of anthracene-1-sulfonic acid, the potassium salt of fluorene dicarboxylic acid and the sodium salt of 1-phenyl-5-methyl pyrazole carboxylic acid, water-soluble sulfonimides such as benzoic acid sulfimide and dibenzene sulfonylimide. Lower, water-soluble organic carboxylic acids, di- and tricarboxylic acid and hydroxycarboxylic acids such as oxalic acid, succinic acid, adipic acid, maleic acid, tartaric acid, malic acid, citric aid, salicyclic and resorcyclic acid and water-soluble resins such as polyvinyl alcohols, polyvinyl pyrrolidones and low molecular weight condensation products of melamine-formaldehyde resins can also be used.

Readily decomposable carboxylic acids, such as malonic acid, acetone dicarboxylic acid, citraconic acid and furfural malonic acid, in particular, may be used as toners which decompose under the influence of heat.

The developer according to the invention may include at least one organic resin-type toner component which assumes a positive charge and at least one inorganic toner component which assumes a negative charge, the particle sizes being approximately equal.

Suitable inorganic toner components which assume a negative charge are salts such as potassium sulfate, calcium sulfate, ammonium chloride, sodium chloride, potassium bromide, copper sulfate, aluminum/potassium sulfate and sodium sulfate; oxides, e.g. iron oxide, titanium dioxide, zinc oxide, aluminum oxide and copper oxide; silicates, e.g. kieselguhr, silical gel, talcum and glass powder; borates, e.g. sodium metaborate and potassium borate; and carbonates such as calcium carbonate, magnesium carbonate and potassium carbonate.

The organic toner components are advantageously prepare as follows: the pulverized starting materials are ground together very finely; the mixture is heated to melting and stirred until a high degree of homogeneity is attained and the melt is then cooled. Alternatively, the fusible starting materials may be liquified by heating. The other components are then stirred in and the mixture is cooled. The resultant mass is finely ground and screened and, for the toner, screen fractions with an average particle size of about 1 to 100μ, preferably of about 10 to 30μ are used.

The inorganic toner substances are likewise finely ground and screened and average particle sizes of about 1 to 100μ, preferably 1 to 10μ and/or 10 to 20μ are used. The toner component which acquires a negative charge may be mixed with the one which acquires a positive charge in proportions of about 1:1 to 20:1 by weight. Approximately equal proportions of the two types of toner are preferable.

The developer may contain 1 part by weight of toner to 15–50 parts by weight of iron powder. Particularly good results are obtained with proportions of 1 part of toner to 15–25 parts by weight of iron powder.

A general principle is that with relatively fine iron powder, of particle size 50–100μ, a larger quantity of toner is necessary than is required in a mixture with fairly coarse iron filings, e.g. of particle size 300–400μ.

To develop latent electrophotographic images, the developer may be withdrawn from a trough by means of a rotating magnetic roller and passed over the surface of the exposed photoconductive material. The iron powder releases the toner and a visible image is formed, which may be fixed.

The quality of the image is influenced not only by the proportions of the components of the developer and the particle size of the iron powder but also by the type of magnetic applicator used. Advantageously, magnetic brushes which are as "soft" as possible are used, e.g. those constituted by permanent or electrically excited bar magnets. These can be arranged in a plane or in radial formation on a rotating roll. Magnetic rolls excited by electrical windings in grooves parallel to the axis are also very suitable. Images free of background are obtained in which even very large solid image areas are homogeneously developed with a covering layer of developer. At the same time, the finest lines are sharply reproduced.

The invention will be further illustrated by reference to the accompanying drawings in which:

FIGURE 1 schematically illustrates a device for magnetic brush development using a bias electrode, and

FIGURE 2 schematically illustrates a device for magnetic brush development using a permanent electromagnetic roller.

Referring to FIGURE 1, a permanent magnet **1** has a plurality of brush-like bristles **2** of the developer mixture of the invention adhered thereto. A battery **3**, or other source of biasing voltage, is connected with the permanent magnet **1** and a supporting plate **4** of high conductivity. An electrophotographic material **5**, having a photoconductive layer on the top thereof and a latent electrostatic image on the photoconductive layer, is developed with positively charged toner in the image areas

6, and developed with the negatively charged toner in the image areas **6a**.

Referring to FIGURE 2, a container **7** holds a quantity of the developer mixture **8** of the invention and a battery or other source of biasing voltage **9** is connected with the axle of the permanent electromagnetic roller **14** and the supporting plate **10** of high conductivity. An electrophotographic material **11**, having a photoconductive layer on the downwardly facing side and a latent electrostatic image on the photoconductive layer, is developed in the image areas **12** with positively charged toner and in the image areas **12a** with negatively charged toner. The toner is applied to the latent electrostatic image by means of the brush-like bristles **13** of the developer mixture of the invention which are magnetically adhered to the roller **14**.

If suitable photoconductors are used, particularly organic photoconductors which can be charged both negatively and positively, positive images can be obtained from positive as well as from negative masters with the same toner.

If the colored toner component of the developer acquires a positive charge, negative charging of the layer and exposure thereof behind a positive master will cause toner to become deposited in the image parts.

To obtain a positive image from a negative master, on the other hand, the same photoconductive coating is positively charged and exposed behind a negative master so that a latent image is first obtained in which the image parts are no longer charged while in the other parts the positive charge is preserved to a greater or lesser extent. To develop such a latent image, the colored, positively charged component of the toner must be caused to settle in the charge-free parts. For this purpose, a positive bias voltage, with respect to the conductive support of the photoconductive layer, is applied to the magnetic brush. In the electric field formed between the magnetic brush and the layer, the positive toner particles are preferentially deposited on the charge-free parts while the other toner component of the developer settles on the positively charged parts of the latent image. The level of the bias applied is determined by the potentials remaining after exposure in the image parts and the image-free parts. If too low a bias is selected, insufficient toner is deposited on the image parts.

In the development process just described, where the colored component of the toner adheres to the image parts which are still charged after exposure, images completely free of background are obtained. Exposure must of course be adequate, because otherwise—particularly if a master of poor contrast has been used—residual charges will be left on the image-free parts which may result in a disturbing background upon the application of toner. But even then, images completely free of background can also be produced if a bias of the same polarity as the charge on the coating is applied to the magnetic brush.

The processes for application of the toner that have just been described can of course also be employed with a developer in which the colored component assumes a negative charge if charging and exposure conditions are reversed.

The above described advantageous results obtained when development is carried out with the developer and process provided by the invention acquire particular significance when the copy is to be further processed to a printing plate. For this purpose, the fixed copy is wiped over with acids or alkaline agents to remove the photoconductive coating and, where appropriate, the toner layer in the parts that are to be made water-acceptant, and the support is bared. Consequently, substances are used for the photoconductive coating which are soluble in acids or alkalis.

For example, in the case of an electrophotographic material, the photoconductive coating of which is soluble in alkalis, and a developer, the toner of which acquires a positive charge and is likewise soluble in alkalis, if a negative charge is applied to the photoconductive coating, a printing plate is obtained after development, fixing, and alkaline treatment which is a reversed image of the master. If direct images are required, the coating is given a positive charge and the process is in other respects the same. If, with the same developer, an acid-soluble substance is used as the toner which assumes a negative charge, this developer can also be used for electrophotographic material the photoconductive coating of which is soluble in acids. If the coating is negatively charged, direct images are obtained, while with positive charging, reversed images are obtained.

After the electrophotographic image has been developed and fixed, it is converted into a printing plate by treatment with an alkaline or an acid liquid, according to the solubility properties of the photoconductive coating. In the parts which are to be made water-acceptant, according to the type of development, the image parts or the image-free parts of the photoconductive coating, including any toner or decomposition product thereof that may be present thereon, are washed away and the support is bared. It is made water-acceptant either during this treatment or by after-treatment. The support may be bared by wiping with the liquid, e.g. with a soaked cotton pad, or the plate may be immersed in a bath of the liquid, or rolls or other mechanical devices may be used to apply the liquid.

After the treatment with alkali or acid, the printing plate is rinsed down with water and inked up with greasy ink. When the plate has been set up in a machine, long runs of prints can be produced.

Both the charged and uncharged parts of the image are covered during development with one or other of the toners; as a result, particularly fine, sharp contours are obtained so that it is possible also for fine line screens to be produced.

If a toner mixture is used from which at least one toner can be easily removed during or after fixing, it is possible for this effect to be exploited particularly in the case of printing plates. It is also possible for two toners with quite widely differing softening or melting points to be used, e.g. with a difference in melting point of 20 to 200° C., preferably 50 to 150° C. If the toner of higher melting point is used as the one which is later removed, this prevents broadening in the contours of the toner of lower melting point, so that there is a further increase in the sharpness of the printing plates.

The developers described are advantageously used for the development of printing plates from which one toner, together with a part of the coating, is to be removed. It is also possible, particularly if one toner is colorless, for any other electrostatic image to be developed. It is immaterial by what means the electrostatic image has been produced, e.g. by the action of visible light, X-rays, UV or infra-red light on suitably sensitive layers or by direct electronic production of the image on an insulating layer or by the transfer of an electrostatic image to an insulating layer.

The invention will be further illustrated by reference to the following specific examples:

Example 1

20 parts by weight of iron powder having a range of particle size of 100–150μ are mixed with 1 part by weight of toner of average particle size 10–15μ. The toner used consists of two components:

(a) 10 parts by weight of a powdered colorless interpolymer consisting of 85 percent of vinyl chloride, 14 percent of vinyl acetate and 1 percent of maleic acid and

(b) 3 parts by weight of a toner obtained from 3 parts by weight of polystyrene of low melting point, 3 parts by weight of a maleinate resin, 0.3 part by weight of spirit-soluble nigrosine and 0.1 part by weight of Pigment Deep Black, by melting these constituents together, grinding and screening.

The resultant developer, in which toner component (a) acquires a negative charge and toner component (b) acquires a positive charge, is taken up from a trough by means of an electrically excited magnetic roll. The magnetic brush, constituted by the iron powder adhering to the roll and carrying the toner on its surface, is grounded.

This developer is brought, in this form, into contact with a latent electrostatic image on the surface of a photoconductive insulating layer supported on an aluminum foil which had been charged before exposure to −300 volts. The black, positively charged toner component is attracted by the negatively charged image and the colorless, negative toner component is repelled by the image but adheres to the uncharged edges of the black image. The image is fixed by heating to about 160° C. The resultant smear-fast copy is free of background while the large-area solid image parts are homogeneously colored.

To convert the image into a printing plate, it is wiped over with a solution of 10 percent monoethanolamine, 5 percent sodium silicate and 85 percent by weight polyethylene glycol. This alkaline solution dissolves the image-free parts of the coating and also the alkali-soluble toner adhering to the edges of the image. After a brief rinsing with water, the image is inked up with greasy ink and used for printing in an offset machine. The plate has a long printing run and produces prints free from defects.

Example 2

25 parts by weight of iron powder having a range of particle size of 50–100μ produced by a spraying process, are mixed with one part by weight of toner of average particle size 10–15μ. The toner consists of two components:

(a) 10 parts by weight of finely pulverized 5-chloro-2-methyl-benzimidazole and

(b) 10 parts by weight of a mixture of 4 parts by weight of polystyrene, 3 parts by weight of colophony, 2 parts by weight of carbon black and 1 part by weight of spirit-soluble nigrosine.

The developer so produced is used to develop a latent electrostatic image on an aluminum foil carrying a photoconductive insulating layer which had been charged to −300 volts and exposed imagewise by the contact process under a positive master and the image is fixed. A sharp and clearly defined image of the master is formed.

If the exposure were insufficient, i.e. if the entire charge had not leaked away in the image-free parts, the latent electrostatic image could still be developed without background by means of this developer if a negative bias (about 80 volts) with regard to the support is applied to the magnetic brush during development.

The fixed toner image can be converted into a printing plate by wiping over with a solution containing, by weight, 0.5 percent monoethanolamine, 60 percent glycerine and 39.5 percent ethylene glycol. After being sprayed down with water, the image is inked up with greasy ink, after which printing can be performed. With a printing plate of this type, long runs are possible and the prints reproduce fine lines sharply and clearly.

Example 3

1 part by weight of a toner consisting of equal parts by weight of a finely pulverized 4-amino-anisole-2-sulfonic acid and a colored interpolymer of vinyl chloride, vinyl acetate and maleic acid are mixed with 30 parts by weight of iron filings having an average particle size of 150–200μ.

This developer is used as described in Example 1 and Example 2 to develop a latent electrostatic image on a photoconductive insulating coating supported on an aluminum foil produced by contact exposure behind a master after the insulator layer has been positively charged to 130 volts.

After fixing, a full-tone background-free image is obtained which can be converted into a printing plate as described in Example 1 and Example 2.

Example 4

15 parts by weight of iron powder, produced by a spray process and subsequent grinding and having a particle size range of 50 to 100μ, are mixed with 1 part by weight of a toner of an average particle size of 5–15μ. The toner consists of two components:

(a) 10 parts by weight of kieselguhr and

(b) 10 parts by weight of a colored resin mixture of polystyrene of low melting temperature, maleinate resin and "Pigment Red B."

A photoconductive insulating coating on a paper support of adequate electrical conductivity is charged to −340 volts and then imagewise exposed by the contact process under a negative master. The resultant electrostatic latent image is made visible by applying the developer by a magnetic brush which is given a negative bias of −300 volts. The resultant image is free of background. The finest line drawings are exactly and sharply reproduced. Also, large solid areas of 100 $cm.^2$, and more can be covered completely homogeneously and uniformly with toner particles.

Example 5

1 part by weight of the toner mentioned in Example 2, having a particle size of 10 to 20μ, is mixed with 25 parts by weight of iron filings having a particle size of 100 to 200μ. This developer is applied by a magnetic applicator to a latent electrostatic image, produced by the reflex process, on a zinc oxide coating supported on a paper foil. The developed toner image can be transferred to another surface to produce a copy which is a sharp and background-free reproduction of the master.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. A method of developing an electrostatic latent image which comprises applying to the image a developer comprising a mixed toner the components of which are powders having approximately equal particle sizes, one component being capable of acquiring a positive charge and consisting essentially of resin, and the other component being capable of acquiring a negative charge and consisting essentially of an inorganic substance, and an iron powder carrier, and fixing the deposited resin powder.

2. A method of developing an electrostatic latent image which comprises applying to the image developer comprising a mixed toner the components of which are powders having approximately equal particle sizes, one component being capable of acquiring a positive charge and consisting essentially of resin, and the other component being capable of acquiring a negative charge and consisting essentially of an inorganic substance, and an iron powder carrier, by means of a magnetic device which serves also as a bias electrode, and fixing the deposited resin powder.

3. A method according to claim 2 in which the toner component capable of acquiring a positive charge is a mixture of a resin and a wax.

4. A method according to claim 2 in which the toner component capable of acquiring a positive charge is a mixture of a resin and an organic compound having a melting point in the range of about 40–150° C.

5. A method according to claim 2 in which the toner component capable of acquiring a negative charge is selected from the group consisting of inorganic silicates, metal oxides, and inorganic metal salts and inorganic ammonium salts.

6. A method according to claim 2 in which the toner

component capable of acquiring a charge of one polarity is soluble in a liquid.

7. A method according to claim 6 in which the soluble component is selected from the group consisting of sulfonic and carboxylic acids.

8. A method according to claim 6 in which the soluble component is a conjoint polymer of a vinyl halide with an ester of a fatty acid and an unsaturated carboxylic acid.

9. A method according to claim 6 in which the soluble component is a solid, basic organic compound.

10. A method according to claim 6 in which the soluble component is selected from the group consisting of imidazoles, hydroxy aromatic compounds, triazoles and pyrazoles.

11. A method according to claim 6 in which the soluble component is an alkali metal salt of an acid selected from the group consisting of sulfonic and carboxylic acids.

12. A method according to claim 2 in which one toner component capable of acquiring a charge of one polarity decomposes upon heating to a material soluble in a liquid.

13. A method according to claim 2 in which the toner component capable of acquiring a negative charge is mixed with the toner component capable of acquiring a positive charge in proportions of about 1:1 to 20:1 by weight.

14. A method according to claim 2 in which the developer contains one part by weight of toner to 15–50 parts by weight of iron powder.

15. A method according to claim 2 in which the resin is in admixture with a dyestuff.

16. A method according to claim 2 in which the resin is in admixture with a pigment.

17. A method for the preparation of a printing plate which comprises developing an electrostatic latent image on a supported photoconductive coating by contacting the image with a developer comprising a mixed toner the components of which are powders having approximately equal particle sizes, one component being capable of acquiring a positive charge and consisting essentially of resin, and the other component being capable of acquiring a negative charge and consisting essentially of an inorganic substance, and an iron powder carrier, fixing the deposited resin powder and removing the photoconductive coating from the support in the resin-free areas.

18. A method for the preparation of a printing plate which comprises developing an electrostatic latent image on a supported photoconductive coating by contacting the image with a developer comprising a mixed toner the components of which are powders having approximately equal particle sizes, one component being capable of acquiring a positive charge and consisting essentially of resin, and the other component being capable of acquiring a negative charge and consisting essentially of an inorganic substance, and an iron powder carrier, by means of a magnetic device which serves also as a bias electrode, fixing the deposited resin powder and removing the photoconductive coating from the support in the resin-free areas.

19. An electrophotographic developer comprising a mixed toner the components of which are powders having approximately equal particle sizes, one component being capable of acquiring a positive charge and consisting essentially of resin, and the other component being capable of acquiring a negative charge and consisting essentially of an inorganic substance, and an iron powder carrier.

20. An electrophotographic developer according to claim 19 in which the toner component capable of acquiring a positive charge is a mixture of a resin and a wax.

21. An electrophotographic developer according to claim 19 in which the toner component capable of acquiring a positive charge is a mixture of a resin and an organic compound having a melting point in the range of about 40–150° C.

22. An electrophotographic developer according to claim 19 in which the toner component capable of acquiring a negative charge is selected from the group consisting of inorganic silicates, metal oxides, and inorganic metal salts and inorganic ammonium salts.

23. An electrophotographic developer according to claim 19 in which one toner component capable of acquiring a charge of one polarity is soluble in a liquid.

24. An electrophotographic developer according to claim 23 in which the soluble component is selected from the group consisting of sulfonic and carboxylic acids.

25. An electrophotographic developer according to claim 23 in which the soluble component is a conjoint polymer of a vinyl halide with an ester of a fatty acid and an unsaturated carboxylic acid.

26. An electrophotographic developer according to claim 23 in which the soluble component is a solid, basic organic compound.

27. An electrophotographic developer according to claim 23 in which the soluble component is selected from the group consisting of imidazoles, hydroxy, aromatic compounds, triazoles and pyrazoles.

28. An electrophotographic developer according to claim 23 in which the soluble component is an alkali metal salt of an acid selected from the group consisting of sulfonic and carboxylic acids.

29. An electrophotographic developer according to claim 19 in which one toner component capable of acquiring a charge of one polarity decomposes upon heating to a material soluble in a liquid.

30. An electrophotographic developer according to claim 19 in which the toner component capable of acquiring a negative charge is mixed with the toner component capable of acquiring a positive charge in proportions of about 1:1 to 20:1 by weight.

31. An electrophotographic developer according to claim 19 containing 1 part by weight of toner to 15–50 parts by weight of iron powder.

32. An electrophotographic developer according to claim 19 in which the resin is in admixture with a dyestuff.

33. An electrophotographic developer according to claim 19 in which the resin is in admixture with a pigment.

34. A method according to claim 2 in which the magnetic device is a rotating magnetic roller.

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