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YOSHIKI HAYASHI ET AL
FLEXIBLE TRANSPARENT ELECTROPHOTOGRAPHIC FILM AND METHOD
OF DEVELOPMENT OF SAID FILM
Filed Oct. 4, 1965

3,438,773

FIG. 1

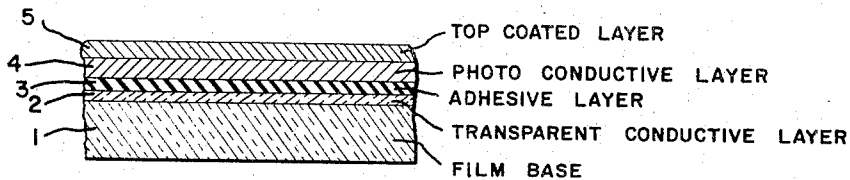
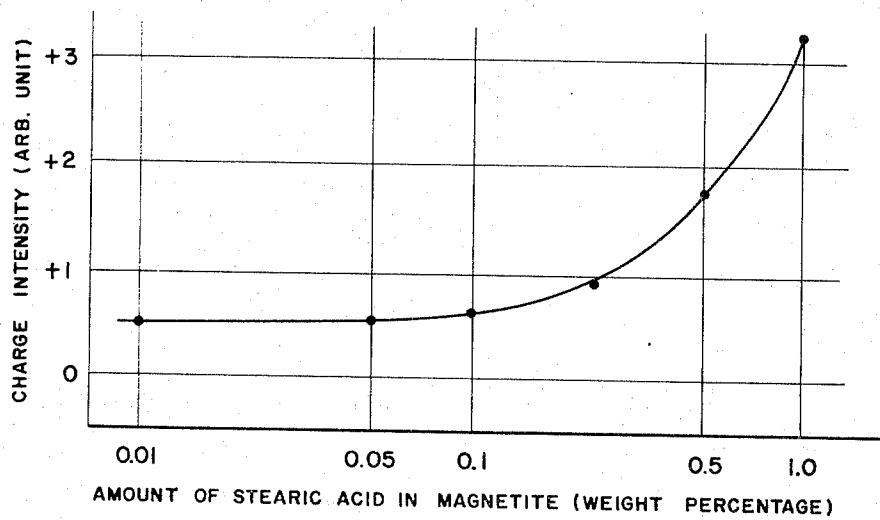


FIG. 2



*Yoshiki Hayashi and
Shikofumi Odo*

INVENTORS

BY Wendert, Lind & Bonack,

ATTORNEYS

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FLEXIBLE TRANSPARENT ELECTROPHOTOGRAPHIC FILM AND METHOD OF DEVELOPMENT OF SAID FILM**Yoshiki Hayashi, Hirakata-shi, and Hikofumi Oido, Osaka-fu, Japan, assignors to Matsushita Electric Industrial Co., Ltd., Osaka, Japan**

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13 Claims

ABSTRACT OF THE DISCLOSURE

Flexible and transparent electrophotographic film characterized by less fog and high resolution covering half tone is prepared with a polyvinylacetate adhesive layer of from 3 to 7 μ in thickness between a transparent conductive layer and an organic photoconductive layer. Toner is brushed onto a top coating layer having a latent electrostatic image by means of a "magnetic brush" which reveals an image immediately as the brush is swept across the top coated layer.

The present invention is concerned with electrophotographic materials, i.e. materials useful in carrying out electrophotographic processes.

More especially, the present invention is concerned with the constitution of electrophotographic films having a high transmittance and with toner compositions applicable to said films for the purpose of visible presentation of latent electrostatic images.

Electrostatic processes for graphic reproduction and photography have been developed by many investigators for a long period of time, their goals being mainly limited to graphic reproductions on opaque papers. The best-known system, called "xerography" has been disclosed in Journal of the Optical Society of America, vol. 38, No. 12, December 1948. However, transparent photography by an electrostatic process has not been achieved successfully, for the reason that transparent photographs, usually projected in large magnification onto a screen, require higher resolution, less fog and an exact reproduction covering half tone. It is important for obtaining excellent images that the toner consist of finely dispersed pigment powder. Prior toner compositions, usually containing resin binder, have a tendency to aggregate during developing and fixing.

It is an object of the present invention to provide an electrophotographic image with high resolution, less fog and an exact reproduction covering half tone.

It is another object of the invention to provide compositions of toner producing visual images formed of finely dispersed particles.

It is a further object of the invention to provide transparent electrophotographic film constitutions characterized by less fog and high resolution covering half tone.

It is a still further object of the invention to provide a method of fixing toner in excellent images.

These and other objects of this invention will become apparent upon consideration of the following description taken together with accompanying drawings in which:

FIG. 1 is a cross-sectional view, on a highly exaggerated scale, of a transparent electrophotographic film in accordance with this invention, and FIG. 2 is a graphical illustration of an effect of additive amount of surface active agent on the charge intensities of toners in accordance with this invention.

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Referring to FIG. 1, a transparent conductive layer 2 is coated on a transparent film base 1, and is laminated firmly to an organic photoconductive layer 4 through the medium of an adhesive 3. The organic photoconductive layer 4 is coated with a transparent resin 5 having a toner-fixing capacity which is established upon curing the resin by heating or by treating with vapors of an appropriate organic solvent. It is an additional feature of this invention that the film is provided with a top coat layer 5 which fixes an imaged toner pigment. According to the prior art, electrophotographic film comprising a top coat layer for fixing is not known; moreover, the toner itself has heretofore contained a resin for fixing imaged pigment. It has heretofore been believed that a top coated layer of non-photoconductive material on the photoconductive material layer would act to lower the electrophotographic light sensitivity and the resolution of image. It has been discovered, according to the present invention, that a suitable non-photoconductive material of the top coated layer does not lower the sensitivity and/or the resolution.

It is necessary that the top coated layer consist of a resin which has a specific electrical resistivity higher than 10^{10} ohm-cm. and a thickness less than 15μ and that it easily cures into a transparent layer for fixing a toner pigment by means of heating or treating with vapors of a resin-soluble solvent. According to the invention, copolymer of vinyl chloride and vinyl acetate is preferable for the production of the top coated layer. The preferable thickness is of 5 to 10μ .

The transparent conductive layer is required to exhibit 60 to 95% of transmittance in incandescence and a surface resistivity lower than 10^6 ohms. A thin layer of vacuum evaporated metal such as copper or chromium can be employed. A thin layer of cuprous iodide in a thickness of 200 to 800 m μ is most preferable for this purpose and can be prepared as follows: Copper is vacuum-evaporated on a sheet of commercial transparent cellulose acetate film and is iodized with iodine vapor in a similar way to that of the prior art; cf. method described in U.S. Pat. No. 2,756,165, patented July 24, 1956. The thickness of the cuprous iodide layer can be controlled by checking its transmittance. Any defects, such as pin holes and scratches, must be avoided because they give undesirable defects to resultant images.

A transparent adhesive to laminate the cuprous iodide layer and organic photoconductive layer plays an important role on the quality of image. Polyvinyl acetate in a solvent inert to cuprous iodide and to the base material is preferable for obtaining an excellent resultant image, and is coated on the cuprous iodide layer by a per se well known method, for example, by roller coating, spraying or squeezing in a thickness of 3 to 7μ .

The photoconductive layer can be formed of any material having photoconductivity characterized by a dark electric resistivity higher than 10^{10} ohm-cm. It is necessary that the surface of the photoconductive layer be as smooth as that of plate glass. A thin layer of vacuum evaporated inorganic photoconductive material, such as selenium or cadmium sulfide, can be employed but is of inferior transparency. Many organic materials having photoconductivity are superior to said inorganic materials from the standpoint of transparency. Organic polymeric materials, such as poly-N-vinylcarbazole, polyacacenaphthylene and polyvinyl triphenylpyrazoline can be employed without addition of binders. The following are operable only when accompanied by the addition of binders for formation of transparent thin layers: oxadiazole compounds, leuco malachitegreen, tetrahydroimidazole derivatives, pyrazoline derivatives, 4,5-diphenyl imidazolthion derivatives and 1,3,4-triazole derivatives. It

is preferable that the photoconductive layer be formed of poly-N-vinylcarbazole having incorporated therein a small amount of Rhodamin 6G and 2-methyl-anthraquinone in a thickness of 20μ . The coating method for the poly-N-vinylcarbazole solution is the same as that of polyvinyl acetate adhesive solution.

In connection with the novel constitution of the electro-photographic film, the toner compositions of this invention are characterized by an elimination of i.e. absence of, resin for fixing the pigment powders. According to this invention, the toner comprises pigment powders and organic compounds which are employed to achieve uniform distribution of the electrostatic charge of the toner pigment. Since a conventional toner contains resin, such as coumarone-indene resin, piccopale resin or polystyrol, for fixing the pigment powders, these pigment powders have a tendency to aggregate during curing of the resin and result in an inferior image. This disadvantage is removed by using a top coated layer in the film constitution as described above and eliminating the resin in the toner compositions. This is a great feature of this invention.

The toner is brushed onto the top coating layer having a latent electrostatic image by means of a "magnetic brush" which reveals the image immediately as the brush is swept across the top coated layer. The magnetic brush is per se art-known and consists of a permanent magnet carrying at one end a mass of iron powder loaded with the toner pigment. According to the present invention, it has been discovered that fogs of the visual images are reduced by using a toner pigment comprising fine powders of magnetic material. When the toner contains pigment powders charged with an unfavorable sign or quantity or pigment powders free from electrostatic charge, the magnetic brush picks up these powders and renders the resultant image clean when the magnetic force exceeds the Coulomb force. The operable magnetic materials in a fine powder form are (1) magnetic metal, such as iron, nickel, cobalt and their alloys, (2) magnetic oxide compound, such as magnetite, cobalt oxide (Co_3O_4) and ferrites, and (3) magnetic sulfide, such as FeS and CoS . In producing a toner pigment, it is desirable that the magnetic metal or alloy powder be coated with compound thereof such as oxide, hydroxide or sulfide for obtaining a high insulating coating by means of per se usual chemical techniques.

It is necessary that the pigment be in a finely divided powder form of 0.5μ to 5μ particle size. The preferable pigment consists of magnetite in 0.5μ to 2μ particle size in accordance with the present invention.

Of importance is that the amount of electrostatic charge of pigment powder be high and be uniformly distributed throughout the powder and that there exist no positively charged pigment powder during the brushing process. Addition of surface active agents such as stearic acid or palmitic acid are known to be useful for this purpose. According to the invention, preferable surface active agents are fatty acids containing more than 10 carbon atoms in the molecule. The more carbon atoms in the fatty acid, the more desirable the effect. The weight proportion of surface active agent to toner pigment is also required to be controlled. The preferable addition amount of stearic acid or palmitic acid is less than 5% by weight. An addition of more than 5% by weight of fatty acid results in an unhomogeneous mixture which produces undesirable images.

As described above, the "magnetic brush" comprises a permanent magnet and a mass of iron powder called a carrier. It is of importance that the carrier be negatively charged and the toner pigment positively charged during brushing. The electrostatic process relating to the toner and the carrier, however, has not yet been definitively clarified. It has been discovered according to the present invention that desirable amounts of negative charge of carrier are satisfactorily achieved by coating the surface of the carrier iron powder with fluorowax. The

preferable wax is poly trifluoro-chloro-ethylene wax having an average molecular weight of 1000 to 1300. Besides the preferable electrostatic properties, excellent lubricating properties between toner and carrier are also produced by applying the said wax in the developing process. From a consideration of fluidity, it is preferred that the carrier iron powder be in the form of spherical particles of 100 to 200μ in diameter. A preferable weight proportion of trifluorochloro-ethylene polymer wax to the iron powder is 2 to 4% by weight. An application of trifluoro-monochloro-ethylene polymer wax to the carrier powder is made in a per se well-known manner, for example, the iron powder is immersed in the molten fluorowax or in a solution thereof in an inert solvent and subsequently dried.

Further, according to the present invention, bonding of the fluorowax to the surface of the carrier iron powder is remarkably enhanced by treating the iron powder with a solution of free phosphoric acid, phosphate compound, such as ZnHPO_4 or Na_3PO_4 , and a promoter, prior to the application of the fluorowax. When the iron powder is immersed into a solution of, for example, zinc phosphate, the surface of the iron powder is firmly coated with a thin layer of $\text{Zn}_3(\text{PO}_4)_2$ which is not dissolved by any conventional solvents, such as water, alcohol or organic solvent, and is responsible for the strong adhesion of the fluorowax.

The following examples are given to illustrate presently preferred details of the invention, it being understood that the details of the examples are not to be taken as in any way limiting the invention thereto.

EXAMPLE 1.—TONER PREPARATION

Metallic cobalt powder in an average particle size of 1.4μ is heated at 800°C . in air to obtain a partly oxidized black powder. The black powder in an amount of 100 grams is immersed in 20 milliliters of benzene containing 0.5 gram of palmitic acid, and mixed sufficiently in a ball mill. The mixture in cream state is dried with hot air at 60°C ., and is then evacuated in a vacuum chamber at room temperature (about 20° to about 30°C .) for about five hours, producing a toner free from benzene.

EXAMPLE 2.—TONER PREPARATION

A solution of 20 milliliters of ethanol and various amounts of stearic acid are added to 100 grams of magnetite in an average particle size of 0.2μ and mixed in a ball mill. The magnetite is obtained by a per se well known chemical technique. The mixture in a cream state is dried with hot air at 60°C . and is then evacuated in a vacuum chamber at room temperature for about five hours, producing a toner free from ethanol.

Referring to FIG. 2 wherein the charge intensity is represented in an arbitrary unit, it will be seen that the charge intensity increases with increase in the additive amount of stearic acid.

EXAMPLE 3.—CARRIER PREPARATION

An aqueous solution of 3% by weight of sodium phosphate is added to 1 kilogram of electrolyzed iron powder in an average particle size of 100 to 200μ . The mixture is heated at 95°C . for 30 minutes under stirring for cleaning the surface of the iron powder. After being washed with water, the cleaned powder is steeped in a hot aqueous solution of 3% by weight of monobasic zinc phosphate and 0.2% by weight of sodium nitrite.

The iron powder in the solution is stirred for 50 minutes in order to form an active phosphate layer on the surface of the iron powder, and then is thoroughly washed with water. In order to increase the durability of the bonding, the treated powder is steeped in an aqueous solution of 0.05% by weight of bichromic acid for 1 minute at room temperature and is quickly dried after being separated from the solution. Poly-trifluoro-monochloro-ethylene

having an average molecular weight of 1500 is added to 100 grams of the iron powder thus obtained. The mixture is heated at 80° C. with stirring. It is desirable for obtaining a homogeneous mixture to add 50 milliliters of methanol, which evaporates off completely during the mixing.

EXAMPLE 4.—COMPLETE EXEMPLARY PROCEDURE

Metallic copper is evaporated onto a sheet of commercial cellulose diacetate film of 150 μ in thickness. The white light transmittance of evaporated film is 63%. The copper evaporated film is placed immediately in a glass chamber containing a small amount of crystalline iodine powder. As the air of the chamber is evacuated, there is a diminishing of the copper color, and finally the film becomes transparent. The transmittance of the cuprous iodide laminated film is 90% with white light and the surface resistance is 10⁵ ohm-cm. A toluene solution of 15% by weight of polyvinyl acetate is coated onto said cuprous iodide film by a Baker type applicator and is dried thoroughly. The dried lacquering layer is 4 μ in thickness.

Coating of both the photoconductive layer and the top layer is carried out in a manner similar to that of the polyvinyl acetate adhesive layer. The compositions of both solutions are given in Tables 1 and 2, respectively. The thickness of the two dried layers are 18 μ and 10 μ , respectively.

Table 1.—Compositions of photosensitive layer

Material:	Parts by weight
Poly - N - vinylcarbazole ¹ (photoconductive matrix) -----	100
2-methyl-anthraquinone (sensitizer) -----	10
Rhodamine 6G ² (sensitizer) -----	0.04
Diphenyl chloride (plasticizer) -----	50
Toluene (solvent) -----	700

¹ Poly-n-vinylcarbazole is commercially available e.g. as Luvican M-170; BASF.

² See Schultz "Farbstofftabellen," 7th edition, 1st vol., 1931, p. 366, No. 866.

Table 2.—Compositions of top layer

Material:	Parts by weight
Polyvinylchloride acetate ¹ (top coating matrix) -----	100
Epoxy resin ² (plasticizer) -----	25
Chlorinated paraffin (plasticizer) -----	15
Methyl isobutyl ketone (solvent) -----	150
Toluene -----	350

¹ Commercially available e.g. under the trade name VAGH; U.C.C.

² Commercially available e.g. as Epikote 828; Shell.

The pale orange transparent electrophotographic film thus obtained is mounted on a 7 kv. corona generation apparatus and is charged up to 1000 negative volts in the dark, after which a static latent image of a subject to be reproduced is created by the conventional exposure method. The optimum exposure is 500 lux·sec.

The developer consisting of one part by weight of toner and ten parts by weight of carrier, obtained by the process according to Example 2 and Example 3 respectively, is mixed thoroughly with a permanent magnetic stick and a "magnetic brush" is formed. By sweeping the brush onto said latent image, an excellent visual image is developed.

Finally the visual imaged film is placed in a glass chamber containing dense vapors of carbon tetrachloride for a period of time less than 2 seconds. The image is fixed stably. The resolution of the resultant fixed image is 50 lines per mm., and its reproduction of half tone is 7 steps by the Eastman Kodak No. 2 grey scale; and no fog is observed.

What is claimed is:

1. An electrophotographic film, capable of being developed by a magnetic brush, comprising, in lamination

in the following order from the bottom up, a transparent polymer sheet, a transparent conductive layer, an organic photoconductive layer and a curable top coated resin layer which fixes a toner consisting of a pigment powder and a surface active agent and has a specific resistivity higher than 10¹⁰ ohm-cm., said transparent conductive layer and said organic photoconductive layer being joined together by a transparent adhesive polyvinylacetate.

2. An electrophotographic film according to claim 1, wherein said top coated resin layer is formed of vinylchloride/vinylacetate copolymer in a thickness of 5 to 10 μ .

3. An electrophotographic film according to claim 1, chloride vinylacetate copolymer in a thickness of 5 to 10 μ , cuprous iodide in a thickness of 200 m μ to 800 m μ .

4. An electrophotographic film according to claim 1, wherein said transparent adhesive is formed of polymer of vinyl acetate in a thickness of 3 to 7 μ .

5. An electrophotographic film according to claim 1, wherein said top coated resin layer is formed of vinylchloride/vinylacetate copolymer in a thickness of 7 μ , said transparent conductive layer is formed of cuprous iodide in a thickness of 400 m μ with a transmittance of 90 percent by incandescence, and said transparent adhesive layer is formed of polymer of vinyl acetate in a thickness of 5 μ .

6. A method for electrophotographic reproduction comprising (1) sweeping a toner consisting of 1 to 5% by weight of surface active agent selected from the group consisting of stearic acid and palmitic acid and 95 to 99% by weight of magnetite of particle size less than 5 μ by means of a magnetic brush consisting of a permanent magnet and iron powder in a diameter of 100 to 200 μ which is coated initially with zinc phosphate and finally with poly-trifluoro-mono-chloro-ethylene wax onto an electrophotographic film consisting, in lamination, of a transparent polymer sheet, a transparent conductive layer of cuprous iodide, an organic photoconductive material layer and a top coated vinylchloride/vinylacetate copolymer, and (2) heating a combination of said film and said magnetically brushed toner thereon for fixing said magnetite powder.

7. A method for electrophotographic reproduction according to claim 6, wherein said fixing of magnetite powder is effected by treating said combination of film and toner with vapors of an organic solvent for said copolymer.

8. An transparent electrophotographic film comprising, in lamination in the following order from the bottom up, a transparent polymer backing sheet, a transparent electrically conductive layer and a transparent layer of organic photoconductive material, said transparent conductive layer and said organic photoconductive layer being joined together by a transparent layer of polyvinyl acetate adhesive.

9. A transparent electrophotographic film comprising, in lamination in the following order from the bottom up, a transparent polymer backing sheet, a transparent electrically conductive layer, a transparent layer of organic photoconductive material and a curable top coated resin layer which fixes a visible-imaged fine powder without binder material and which is formed of vinylchloride/vinylacetate copolymer in a thickness of 5 to 10 μ , said transparent conductive layer and said organic photoconductive insulating layer being joined together by a transparent layer of polyvinyl acetate adhesive.

10. An electrophotographic film according to claim 8 wherein the polyvinyl acetate adhesive layer is from 3 to 7 μ in thickness.

11. An electrophotographic film according to claim 9 wherein the polyvinyl acetate adhesive layer is from 3 to 7 μ in thickness.

12. A method for electrophotographic reproduction comprising (1) sweeping a toner which contains no binder material by means of a magnetic brush consisting of a

magnetic magnet and iron powder onto a top coated surface of an electrophotographic film according to claim 9, and (2) heating a combination of said top coated surface and said magnetically brushed toner thereon for fixing said toner.

13. A method for electrophotographic image reproduction according to claim 12, wherein said fixing of toner is effected by treating said combination of film and toner with vapors of organic solvent which can soften said top coated surface.

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J. TRAVIS BROWN, *Primary Examiner*.

J. C. COPPER, *Assistant Examiner*.

U.S. Cl. X.R.

96—1; 117—17.5

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,438,773 Dated April 15, 1969

Inventor(s) YOSHIKI HAYASHI and HIKOFUMI OIDO

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

Claim 3, line 2, rewrite as follows:

-- wherein said transparent conductive layer is formed
of cuprous --

Signed and sealed this 6th day of July 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents