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ELECTROSTATIC PRINTING

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7 Claims. (Cl. 96—1)

This invention relates generally to electrostatic printing. More particularly, it relates to improved materials and methods for developing electrostatic images.

In the art of electrostatic printing, electrostatic images are produced on an insulating surface. Such images comprise a pattern of electrostatic charges on the surface. Visible images are commonly produced therefrom by cascading across the surface a dry mixture of finely-divided developer particles and substantially larger carrier particles. When the developer particles are triboelectrically charged in the opposite polarity to the electrostatic charges, they deposit in charged areas to produce a visible image in substantial configuration with the pattern of charges. When the developer particles have the same polarity as the electrostatic charges, a visible image is produced in reversed configuration with respect to the pattern of charges.

The foregoing method of developing electrostatic images is described in "Electrofax" Direct Electrophotographic Printing on Paper, by C. J. Young and H. G. Greig, RCA Review, December 1954, vol. XV, No. 4. Also described in that publication are other types of development such as: powder cloud, liquid mist and magnetic brush types.

Recently, a so called liquid process for developing electrostatic images has been proposed in which the solid developer particles are suspended in an insulating hydrocarbon carrier liquid. Deposition of the developer particles on the charge image is an example of the phenomenon known as electrophoresis or cataphoresis. A liquid developer process for charge images is described in greater detail by K. A Metcalfe and R. J. Wright in a paper entitled "Xerography," published in the Journal of the Oil and Colour Chemists' Association, November 1956, volume 39, No. 11, London, England.

Although the above-mentioned hydrocarbon liquid developer compositions are suitable for many purposes, their use in repetitive processes such as are employed in color printing present difficulties. One such difficulty is encountered when images are developed on a photoconductive coating such as is described in the Young and Greig publication, op. cit. Most hydrocarbons are solvents for the binder materials commonly used in such coatings and when a hydrocarbon dispersion is applied to the coating a portion thereof is removed or softened. Most hydrocarbon liquids are also solvents for developer powders which include resins, waxes, or organic pigments. When solvent action is severe, no useful result can be obtained. Even when the solvent action is less severe, or absent altogether, difficulties are encountered in producing an image having proper resolution, saturation of colors, and mixing of colors. Also, unless the image developed with such a hydrocarbon dispersion is fixed in some manner, the tacky developer particles will tend to smear during handling. Fixing may be accomplished with a fixative spray or, when thermoplastic developer particles are employed, by heating. When hydrocarbon carrier liquids are employed, heating can be extremely dangerous in view of the fire hazard involved. In addition to the fire hazard, whether heated or not, most hydrocarbon liquids have an objectionable odor and the vapors thereof are generally toxic.

Other developer dispersions are known which obviate

most of the disadvantages attendant the use of hydrocarbon dispersions. One is a dispersion of developer particles in trichlorotrifluoroethane. Another is a dispersion of developer particles in dimethylpolysiloxane. Both of the latter dispersions provide improved results and many advantages over hydrocarbon dispersions. However, with respect to the ethane liquid, development must be accomplished in a short time, under some circumstances. For example, when images are to be developed on electrophotographic paper having thereon a coating of photoconductive zinc oxide in a resinous silicone binder, the ethane fluid will tend to soften the binder when in contact therewith for more than about one second and will tend to remove portions of the binder when in contact therewith for more than above five seconds. While images can be readily produced within such times, there are, of course, applications wherein longer development times are desirable. Polysiloxane dispersions, while very advantageous for most applications, are not quick drying as are the ethane dispersions. Also, the polysiloxane liquid does not appear to be as electronegative as does the ethane liquid and, hence, requires somewhat longer development times particularly with electropositive developer particles.

Accordingly, it is a general object of this invention to provide improved compositions of matter for developing electrostatic images.

It is a further object of this invention to provide improved relatively non-toxic and non-inflammable developer compositions.

It is a further object of this invention to provide improved developer compositions for use with a photoconductive coating which includes an organic binder.

It is another object of this invention to provide improved developer compositions which when used with a photoconductive coating which includes an organic binder, produces a slight controlled softening of the exposed surface of the coating resulting in enhanced picture quality.

It is a still further object of this invention to provide improved developer compositions which, in the development of electrostatic image, will provide visible color images of improved resolution, color saturation and color mixing.

It is yet another object of this invention to provide an improved developer composition which will produce a visible image when applied to a negative electrostatic image, said visible image being in reverse configuration with respect to the negative electrostatic image.

It is still a further object of this invention to provide improved methods for developing electrostatic images.

The foregoing objects and other advantages are accomplished in accordance with this invention which provides improved dispersion of developer particles in an electrically-insulating liquid. Appropriately colored electroscopic developer particles are dispersed in a carrier solution comprising about 48 to 58 volume percent trichlorotrifluoroethane and about 52 to 42 volume percent dimethyl polysiloxane. In the developer dispersion or composition the electroscopic developer particles may comprise, for example, up to 6% by weight. Very low concentrations of developer particles are best suited for use in automatic developing apparatus whereas higher concentrations are best suited for hand processing in developer trays. Also contemplated is a method wherein the ethane liquid and polyslioxane liquid are mixed together to provide a carrier solution. Appropriately colored electroscopic developer particles are mixed into the carrier solution to form a developer dispersion. The developer dispersion is then applied to an electrostatic image on an insulating surface to develop thereon a visible image.

An unusual feature of the developer compositions of this invention is that the improved results provided thereby are only obtained when the constituents of the carrier solution are mixed substantially in the narrow range of proportions specified. Maximum improvement is attained when the carrier solution is prepared with about 53 volume percent trichlorotrifluoroethane and about 47 volume percent dimethyl-polysiloxane. Improved results are particularly evident when images are developed on photoconductive coatings comprising photoconductive zinc oxide dispersed in a resinous binder such as, for example, resinous polysiloxane (silicone resin). When less than 48% ethane liquid is employed, image intensity is objectionably decreased and, when more than 58% is employed, resolution of the image is quite seriously impaired.

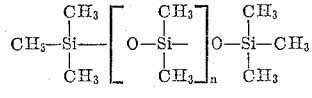
Results obtained with the developer dispersions of this invention indicate that the carrier solution set forth above embodies the best features of both of the ethane and polysiloxane liquids. Development time is equivalent to that required for an ethane dispersion. The solvent power of the ethane liquid appears to be considerably reduced resulting in substantially less softening of resin binders in a photoconductive coating. However, it is believed that some resin softening still occurs and, surprisingly enough, produces beneficial results. As mentioned heretofore, the developer compositions of this invention provide for enhanced color saturation, color mixing and improved resolution. It is believed that these advantages result from a slight, well controlled, softening of the surface of the binder-photoconductor coating whereby developer particles attracted thereto sink into that surface. When this result is achieved substantially no electrical masking is apparent when one color is overprinted on another. Also, color mixing is more easily and more intimately accomplished.

Specific examples and additional advantages of the developer compositions and of the improved methods of developing electrostatic images in accordance with this invention are included in the detailed description which follows.

CARRIER LIQUIDS

An important feature of this invention is the provision of a carrier solution obtained by mixing trichlorotrifluoroethane and dimethyl polysiloxane. In such a combination, the ethane liquid is a very selective solvent which will not dissolve most resins and waxes and which will only slowly dissolve binder materials such as, for example, resinous polysiloxanes. The ethane liquid has a viscosity of about 0.69 centipoise at room temperature and has an evaporation rate substantially in excess of that of toluene. It is far less toxic than materials such as gasoline or carbon tetrachloride, or almost any organic solvent. It has a flash point in excess of 650° C. Because of its low toxicity and high flash point, it can be handled in ordinary room atmosphere with practically no danger to health and without fire hazard.

Dimethyl polysiloxanes have the following structural formula:



where n may vary from 0 to 2000 and even higher. The higher the value of n, the higher the viscosity of the liquid at a given temperature. At room temperature, viscosity may vary from as low as 0.65 centistoke to as high as 1,000,000 centistokes, but for the purpose of the present invention, it is preferred to use only those members of the family of mixtures thereof having a viscosity up to about 3 centistokes at room temperature. This family of liquids comprise poor solvents for organic plastics. They also have relatively high flash points, for example: a dimethyl polysiloxane having a viscosity of 2 centistokes, has a flash point of 175° F. and one of 3 centistokes a flash point of 215° F. The solution of ethane liquid and polysiloxane will of course have a considerably higher flash point. In addition to the foregoing, the polysiloxanes like the ethane liquid are practically odorless, non-toxic, hydrophobic, and have excellent dielectric properties.

DEVELOPER COMPOSITIONS

In the preparation of developer compositions, it is useful to first formulate concentrates containing the electroscopic developer particles. These generally comprise 5 to 40 parts by weight of developer particles in about 200 parts by weight of dimethyl polysiloxane having a viscosity of about 0.6 to about 3 centistokes. This ratio is a convenient one for preparing a concentrate which is to be stored for an extended period or which is to be provided to the ultimate user. An important advantageous property of dimethyl polysiloxane evidences itself when developer concentrates are stored for extended periods. Developer particles comprising thermoplastic material, examples of which are provided hereinafter, may be dispersed in such liquids and stored practically indefinitely without agglomerating.

Prior to use, the concentrate is mixed into the trichlorotrifluoroethane-dimethyl polysiloxane solution in an amount to provide a concentration of developer particles in the composition of up to about 6% by weight. For a developer composition which is to be employed in automatic developing apparatus, developer particles are included therein in an amount such as, for example, 0.005 or less parts by weight. In the production of color maps it has been found that with only about .005 part of developer particles in 10 ounces of composition, sufficient composition is provided for developing images in one color on over 126 square feet of electrophotographic surface. For tray development it is preferred to employ a composition such as, for example, one having therein about 0.2 to 6 parts by weight of developer particles.

DEVELOPER PARTICLES

Specific examples of developer material suitable for dispersion in dimethyl polysiloxane to form a concentrate or for dispersing in the trichlorotrifluoroethane polysiloxane carrier solution to form developer compositions are as follows:

Example I

BLACK DEVELOPER PARTICLES

A black pigment is prepared by making two solutions. Solution one comprises:

6 grams Iosol Black (C.I. Solvent Black 13)
400 grams methanol

Solution two comprises:

9 grams Spirit Nigrosine (C.I. 50415)
400 to 600 grams methanol

Solution one is poured into solution two with continuous stirring. Once the solutions have been thoroughly mixed, and a black relatively insoluble pigment is precipitated, the mixture is filtered and the filter cake allowed to dry. The dried filter cake is broken up and dispersed in dimethyl polysiloxane liquid having a viscosity of about 2 centistokes to provide a concentrate. The proportions by weight in this concentrate are about 1 to 8 parts black pigment to about 40 parts of liquid. It is preferred that the liquid content be kept as low as possible but sufficient to provide a uniform dispersion. After ball milling to produce fine particles, the black pigment is classified as to particle size. Particles having a diameter of 74 microns or less are preferred.

Example II

BLACK DEVELOPER PARTICLES

200 parts by weight of Piccolastic Resin 4358A (an elastic thermoplastic resin composed of polymers of

styrene, substituted styrene and its homologs of the Pennsylvania Industrial Chemical Corp., Clairton, Pennsylvania)
12 parts by weight carbon black
12 parts by weight Nigrosine SSB, Color Index No. 50415
8 parts by weight Iosol Black, Color Index Solvent Black 13

This developer material is prepared by melting the resin and mixing in the other materials. When a uniform mix is obtained, it is cooled, ground to a fine powder and classified to obtain a desired particle size. A convenient particle size is one obtained by screening through a 200 mesh which provides a maximum particle diameter of about 74 microns. This developer material may be dispersed in dimethyl polysiloxane by any of the commonly known techniques to provide a concentrate.

Example III

BLACK DEVELOPER PARTICLES

A low-melting point (120° C.) developer material suitable for dispersion in a dimethyl polysiloxane may be prepared as follows:

60 parts by weight Piccolastic D 100
40 parts by weight Piccolastic C 125
9 parts by weight carbon black

These materials are mixed together in powder form, then melted and mixed again to obtain a homogeneous dispersion. The melt is then cooled, ground and classified to obtain the desired particle size. It has been found that even with a low-melting toner of this character, which has a tendency to cake with storage, a stable non-caking dispersion is obtained in a dimethyl polysiloxane having a viscosity of about 2 centistokes.

OTHER THERMOPLASTIC MATERIALS

In the foregoing examples many organic resins and waxes may be substituted for those described. Some of these are the following:

Acrawax C (a synthetic wax, octadecenamide), The Glycol Products Co., Brooklyn, N.Y., melting point between 133 and 140° C.
Carnauba wax, melting point about 80° C.
Polymekon Wax (a commercially modified microcrystalline wax of the Warwick Wax Co., N.Y.), melting point about 93 to 127° C.
Ultracera Amber Wax, a microcrystalline petroleum wax of the Bareco Wax Co., Barnsdall, Oklahoma, melting point between about 108 and 112° C.
Be Square Wax White, a microcrystalline petroleum wax of the Bareco Wax Co., Barnsdall Oklahoma, melting point between about 105 and 109° C.
Petronauba D Wax, a microcrystalline petroleum wax of the Bareco Wax Co., melting point about 103° C.
Piccolyte S–135, a thermoplastic hydrocarbon of the Pennsylvania Industrial Chemical Co., Clairton, Pa., melting point about 135° C.

Various coloring agents may be employed, singly or in combination, in the foregoing compositions in place of the black pigments or dyes specifically set forth in Examples I and II. Colored developer particles will generally include from 0.2 to 12 parts by weight of a coloring agent for each 100 parts by weight of developer particles. Suitable coloring agents include the following:

(1) Cyan Blue Toner GT (described in U.S. Patent 2,486,351 to R. H. Wiswall, Jr.)
(2) Benzidine Yellow
(3) Brilliant Oil Blue BMA, Color Index No. 61555
(4) Sudan III Red, Color Index No. 26100
(5) Oil Yellow 2G, Color Index No. 11020
(6) Hansa Yellow G, Color Index No. 11680

COATED ZINC OXIDE PARTICLES

Various thermoplastic developer materials which comprise coated particles may also be conveniently employed in color printing in accordance with this invention. It is preferred in such cases to incorporate in the particles a core material made up of zinc oxide. The zinc oxide comprises one having a value of surface photoconductivity of at least 10^{-9} ohm^{-1}/square/watt/cm.^{2} when subjected to light of a wavelength of about 3900 A. These coated zinc oxide developer materials are convenient for use in color processes wherein one color is overprinted over another to provide for color mixing. When particles of too large a diameter and which are insulating in character are deposited on an electrostatic image to produce a first color, such particles will inhibit overprinting thereon with another color. By providing a photoconductive zinc oxide core coated with a low-melting thermoplastic coating, developer particles are produced which, when fused to a surface, permit overprinting of a color with another and therefore provide for color mixing.

The process by which coated zinc oxide particles provide for overprinting is unique. When the particles are fused to a surface, the coating material melts to form a continuous layer adhering to the surface. After fusing, at least the topmost particles of zinc oxide are left protruding above the layer. When photoconductive zinc oxide particles are employed, an image surface is produced which can be charged, exposed and overprinted as easily as an original photoconductive surface. Thus, in some applications such as those wherein fusing between steps is not objectionable, the use of photoconductive developer particles can be very advantageous.

Examples of suitable material for color printing include the following:

Example IV

WHITE DEVELOPER PARTICLES

1 part by weight carnauba wax
2 parts by weight photoconductive zinc oxide

The wax is melted and particles of zinc oxide having a particle size from 0.25 to .5 micron mean diameter are added to the melt. Particle size and shape of the zinc oxide determine to some extent the ratio of the zinc oxide to the coating material. Continuous stirring of the melt from 15 to 20 minutes is sufficient to disperse the zinc oxide in the wax if the batch weighs about 100 grams. The mixture is allowed to cool, after which it is reduced to a fine powder and classified as to particle size. A concentrate is then prepared or the powder dispersed in a carrier solution and used directly.

Example V

BLUE DEVELOPER PARTICLES

20 parts by weight Acrawax C (a synthetic wax-octadecenamide, of the Glyco Products Co., Brooklyn, New York)
30 parts by weight photoconductive zinc oxide
0.3 part by weight calcium stearate (pigment wetting agent)
1.5 parts by weight Cyan Blue Toner GT

This composition is prepared the same as in Example IV except that the calcium stearate is added to the melt before the zinc oxide and the coloring agent is added to the melt after the zinc oxide.

Example VI

RED DEVELOPER PARTICLES

36 parts by weight Acrawax C
5 parts by weight of a solid silicone resin (such as Dow Corning R–5071)
80 parts by weight photoconductive zinc oxide
4 parts by weight Sudan 3 red, Color Index No 26100
2 parts by weight Oil Yellow 2G, Color Index No. 11020

The wax and silicone resin are melted together. First the zinc oxide and then the coloring agents are stirred into the melt. After a uniform dispersion is obtained,

the mixture is cooled, ball milled, and classified as to particle size.

PIGMENTS

It is also possible to provide concentrates which consist of organic pigments dispersed in dimethyl polysiloxane liquid or developer compositions of the organic pigments in the trichlorotrifluoroethane-polysiloxane solutions. Preferably the concentrates comprise up to about 20 parts by weight of pigment the remainder being liquid and compositions up to 6 parts by weight of pigment. The term pigment as employed herein is intended to include coloring agents which are sometimes referred to as dyes but which nevertheless are insoluble in the ethane liquid or the polysiloxane. When used as taught herein these so-called dyes have all the properties and attributes of pigments. Suitable pigments for such purposes include the following:

(1) Cyan Blue Toner GT (described in U.S. Patent 2,486,-351 to Richard H. Wiswall, Jr.)
(2) Benzidine Yellow (Color Index No. 21090)
(3) Brilliant Oil Blue BMA (Color Index No. 61555)
(4) Sudan 3 red (Color Index No. 26100)
(5) Oil Yellow 2G (Color Index No. 11020)
(6) Pyrazalone pigment (such as C.I. 21080 C. I. Pigment Red 39)
(7) Hansa Yellow G (Color Index No. 11680)

In many of the foregoing dispersions it is convenient to provide a surfactant (surface active agent) to enhance the electrical properties of a selected pigment. A surfactant solution may be prepared by dispersing 10 grams of Nalcamine G–14 in 20 grams of toluene and, while mixing, heating the dispersion to dissolve the Nalcamine G–14 in the toluene. Nalcamine G–14 is a chemical of the type 1-(2-hydroxyethyl)-2-hydrogenated tallow-2-imidazoline (National Aluminate Corp., Chicago, Illinois). The Nalcamine G–14 solution is added to pigment dipersions before they are ball milled in the polysiloxane to form concentrates. Such a surfactant when applied, for example, to a red pyrazolone pigment substantially enhances the electropositive nature thereof.

Any of the foregoing developer compositions may be applied to an electrostatic image consisting of a pattern of negative electrostatic charges. Particles suspended in the carrier liquid are attracted by the negative charges and deposited on the pattern of such charges. In such a process, these compositions therefore constitute direct developer compositions.

When the compositions are employed to develop electrostatic images consisting of patterns of positive electrostatic charges they will be repelled by the charges and will deposit in non-charged areas of the electrostatic image to produce a reverse visible image and hence can be called reverse developer compositions in such processes.

REVERSAL TYPE POWDERS

This invention also provides a developer composition which is capable of producing reverse images. By this is meant that when the composition is applied to an electrostatic image consisting of a pattern of negative electrostatic charges, the developer material will adhere in non-charged areas of the image rather than in the charged areas thereof. Such a developer composition may be prepared by dispersing a pigment in a binder material such as one which is predominantly comprised of polyvinyl chloride.

Example VII

BLACK REVERSAL PARTICLES

4 grams carbon black
30 grams dimethyl polysiloxane, viscosity about 2 centistokes

The carbon black is dispersed in the polysiloxane and the dispersion ball milled in a 2 ounce glass jar with steel balls for about 40 hours. The reversal type developer composition is then made up as follows:

3 grams carbon black dispersion in polysiloxane
5 grams of "Vinylite VYNV" (96% polyvinyl chloride, 4% polyvinyl acetate)
30 grams dimethyl polysiloxane

This mixture is again ball milled for about 16 to 40 hours to provide a concentrate.

Color dispersions may be prepared in a like manner employing most of the pigments discussed heretofore. Some of these are set forth below along with the proportions of the constituents therein:

Example VIII

RED REVERSAL PARTICLES

11 grams "Vinylite VYNV"
2 grams red pyrazolone pigment
30 grams dimethyl polysiloxane, viscosity about 2 centistokes

This mixture is ball milled for about 32 hours.

Example IX

YELLOW REVERSAL PARTICLES

14 grams "Vinylite VYNV"
2 grams Hansa Yellow G
40 grams dimethyl polysiloxane, viscosity about 2 centistokes

Preparation the same as for Example VIII.

Example X

BLUE REVERSAL PARTICLES

12 grams "Vinylite VYNV"
2 grams Patent Blue
30 grams dimethyl polysiloxane, viscosity about 2 centistokes

Preparation the same as in Example VIII.

IMAGE DEVELOPMENT

Use of any of the above-described developer compositions in electrostatic printing processes as contemplated in this invention provides for new and substantially improved results. In accordance with this invention, the methods comprise applying the developer composition to the electrostatic image by such means as, for example, flowing across the image, spraying, application with a roller or by immersing the image in a tray containing the liquid composition, by electrophotographically producing a plurality of successive electrostatic images and developing with different colored particle compositions a composite color image is produced.

If desired, the permanence of the final print may be enhanced by a fixing procedure. Thermoplastic developer particles can be fused to the surface of the photoconductive material by heat. Alternatively, a fixative may be applied to the print. A convenient fixative comprises polyisobutyl methacrylate dissolved in trichlorotrifluoroethane. The fixative can be applied in any known manner.

This application is a division of my copending application Serial No. 6,633, filed February 4, 1960.

What is claimed is:

1. A method of developing an electrostatic charge pattern comprising the steps of preparing a liquid carrier solution by mixing together about 48 to 58% by volume trichlorotrifluoroethane and about 52 to 42% by volume dimethyl polysiloxane having a viscosity of from about 0.6 to about 3.0 centistokes, preparing a developer composition by dispersing in said carrier solution up to about 6.0% by weight of a finely-divided electroscopic developer material, and applying said composition to the surface of a recording member carrying said electrostatic charge pattern.

2. The method of claim 1 wherein said liquid carrier

dispersion is prepared by mixing together about 53% by volume of trichlorotrifluoroethane and about 47% by volume of dimethyl polysiloxane.

3. A method of electrostatic printing comprising the steps of electrophotographically producing in succession a plurality of electrostatic images on a photoconductive surface, developing each electrostatic image so produced with a separate developer composition each separate composition comprising different colored developer particles dispersed in a carrier solution consisting essentially of about 48 to 58% by volume trichlorotrifluoroethane and about 52 to 42% by volume of dimethyl polysiloxane having a viscosity of from about 0.6 to about 3.0 centistokes, and after developing all of said electrostatic images, fixing said developer particles to said photoconductive surface.

4. The method of claim 3 wherein said developer particles comprise pigmented thermoplastic material and said fixing is accomplished by fusing said particles to said surface with heat.

5. The method of claim 3 wherein said fixing is accomplished by applying fixative material to said photoconductive surface.

6. The method of claim 5 wherein said fixing is accomplished by applying to said surface a resinous material dissolved in trichlorotrifluoroethane.

7. The method of claim 6 wherein said resinous material comprises polyisobutyl methacrylate.

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