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[54] ELECTROGRAPHIC FORMATION OF DYE IMAGES

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[51] Int. Cl. G03g 13/22, G03g 13/10

[58] Field of Search 96/1 LY, 1.2; 117/37 LE; 101/464; 252/62.1

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[57]

ABSTRACT

The present invention relates to an electrographic method for the formation of water-soluble dye images. An electrostatic charge pattern is developed using a liquid developer having toner particles containing a polymeric material which is normally hydrophobic, but which is readily convertible to a hydrophilic form when contacted by an activating solution of appropriate pH. The toner particle image is formed on a hydrophobic surface and is contacted with the activating solution to convert the toner particle image to hydrophilic form. The hydrophilic toner particle image is then contacted with a water-soluble dye solution to preferentially deposit dye on the hydrophilic toner image. If desired, the dye image thus formed may be transferred to a suitable receiver element.

21 Claims, No Drawings

ELECTROGRAPHIC FORMATION OF DYE IMAGES

This invention relates to the field of electrography and to methods of forming and transferring dye images using electrographic materials and techniques.

Electrographic imaging processes and techniques, especially electrophotographic processes, are well known in the art. These processes generally have in common the steps of forming an electrostatic latent charge image on an insulating surface and the development of this charge pattern to form the visible image by the selective deposition thereon of finely-divided electrostatically attractive toner or marking particles. Typically these toner or marking particles contain a resinous binder and, in addition, there may be associated with the resin a colorant material such as a pigment or dye. The visible image thus formed may be transferred to another support, such as a sheet of paper, or the visible images formed by the marking particles may be fixed to the insulating layer on which it is deposited to form a permanent image.

According to one form of electrography, the electrostatic charge pattern is made visible by the use of water soluble dyes. The use of various water-soluble dyes to form visible electrographic images has been found particularly useful in the formation of multiple color electrographic prints and transparencies. Various methods have been developed in the art for formation of dye images and the transfer of these images to various receiving sheets. In this regard, reference may be made to U.S. Pat. Nos. 3,003,891 issued Oct. 10, 1961; U.S. Pat. No. 3,060,052 issued Oct. 23, 1962; U.S. Pat. No. 2,843,499 issued July 15, 1958; U.S. Pat. No. 3,253,913 issued May 31, 1966; and various foreign patent publications such as French Patent 1,369,344 published July 6, 1964; French Patent 1,245,790 published Oct. 3, 1960; French Patent 83,756 (first addition to French 1,323,519) published Aug. 31, 1964, and British patents 1,255,445 and 1,255,762, both published Dec. 1, 1971.

In much of the work relating to the use of water-soluble dye image formation, a liquid development system is used for the formation of an image corresponding to the latent electrostatic charge pattern carried on an insulating substrate such as a photoconductive composition. However, various problems have been associated with the use of such liquid developers. Typically, these developers contain a synthetic resin having associated therewith the water-soluble dye as a colorant material. One problem relating to this type of liquid developer has been the fact that it is difficult to find a colorant-binder combination having the proper hue and possessing the proper electrical charge characteristics for use in a liquid development system. Problems of this type are discussed, for example, in British Patent 1,016,581. In addition, although the colorant material may have the proper electrical charge characteristics and/or hue it may be difficult to find a binder material suitable for use with such a colorant. For example, it has been found that various hydrophilic binder materials useful with water-soluble dyes such as poly(vinyl alcohol), poly(vinylpyrrolidone), etc. such as is described in Chechak, U.S. application Ser. No. 58,191, filed July 24, 1970, tend to become unstable.

In addition to the above-described problems related to many known liquid development systems used in the

formation of water-soluble dye images, it would be desirable to have available a means for controlling dye image density independent of and in addition to the electrostatic charge differential associated with conventional electrographic imaging processes such as the electrophotographic process. For example, if such independent means of color control were available, various color correction problems could be handled more easily.

In addition, it would be advantageous to utilize a liquid development system for the formation and transfer of water-soluble dye images wherein the colorants used to form the dye images need not necessarily be present in the marking or toner particles of the liquid developer material. Such a system would permit the use of various water-soluble colorants which are presently not easily dispersible in conventional liquid developers or are not compatible with the binder which may be contained in the developer. Moreover, such a system, would, of course, greatly simplify the formation of multiple color prints and transparencies since one would require essentially only one developer composition rather than a separate developer composition for each primary color as many conventional multiple color systems now require.

In accordance with the present invention there is provided a method for the formation of water-soluble dye images and the transfer of such images, if desired, to various receiving elements. According to the method of the invention, an electrostatic charge pattern carried on an electrically insulating surface is developed utilizing a liquid developer composed of a liquid carrier having admixed therein toner particles containing a polymeric material which is normally hydrophobic, but which is readily convertible to a hydrophilic form when contacted by an activating solution of appropriate acidity or basicity as described hereinafter. In accordance with the invention, the developed toner particle image is formed directly on a hydrophobic surface or transferred to a receiving element having a hydrophobic surface. Subsequently the developed image carried on the hydrophobic surface is contacted with the aforementioned activating solution to form the hydrophilic form of the polymeric toner particle image. As a result, upon contact of the liquid developed image (formed by the above-described polymeric toner particles) with an aqueous water-soluble dye solution, the dye contained in said solution is preferentially deposited on said hydrophilic form of the polymer. Subsequently, if desired, the dye image corresponding to said toner particle image may be transferred to a suitable receiver element.

As will be apparent, the aqueous water-soluble dye solution and activation solution may comprise separate solutions or a single treatment vehicle having a suitable pH and containing dissolved therein a water-soluble dye. In the latter case, the hydrophobic polymeric toner particle image is converted to its hydrophilic form, and, substantially simultaneously therewith, the image, now in its hydrophilic form, is colored with the water-soluble dye contained in the activating solution. If desired, the dye image may then be transferred to a suitable receiver element.

In any of the embodiments of the invention, it will be appreciated that, if desired, the hydrophobic toner particle image may itself be transferred to a suitable receiving element prior to use of the aforementioned ac-

tivating solution and water-soluble dye solution. Such a mode of operation may be particularly advantageous where the electrostatic charge pattern to be developed is formed on a reusable electrographic element, e.g. a reusable electrophotographic element containing a radiation sensitive photoconductive layer.

As suggested hereinbefore the process of the present invention offers several significant advantages over many of the known techniques used to form water-soluble dye images corresponding to an electrostatic charge pattern. For example, the color-forming operation becomes primarily a matter of chemical and physical processing independent of electrographic development, thereby providing an additional colorimetric control. Moreover, the process uses only a single electrographic developer composition for reproducing multiple color images whereas many conventional processes require a separate electrographic developer for each separate color to be reproduced. Thus, apparatus and machine requirements are less complex than those of many conventional multi-color electrographic systems which require separate electrographic developer application mechanisms, etc. for each separate developer. In addition, the liquid developer used in the process of the present invention contains toner particles composed of hydrophobic resins, rather than hydrophilic resins. Thus, the toner particles are compatible with conventional hydrocarbon carrier liquids, exhibiting greater stability and less tendency to agglomerate than hydrophilic resin marking particles employed in some liquid developers used with water soluble dye colorants.

An important element of the present invention is the use of toner particles containing a polymeric material which is normally hydrophobic in its free base or free acid form, but which, when contacted by an activating solution of the appropriate pH, is readily convertible to a hydrophilic form of the polymer. In accordance with the invention, it has been discovered that polymers useful in the present invention are polymers containing as a repeating unit thereof a group derived from an ethylenically unsaturated polymerizable monomer, said repeating unit having attached thereto a moiety capable of forming a salt when contacted with an activating solution of appropriate pH. Typical of such moieties are acidic moieties, such as carboxylic acids, sulfonic acids, etc., and basic moieties such as nitrogen-containing moieties, e.g., amino styrene, vinyl pyridine, etc.

Polymers such as those described above may be formed by a number of well-known methods. For example, in accord with a first embodiment of the invention, a polymer formed from one or more ethylenically unsaturated monomers such as the "soluble" and "insoluble" monomers described hereinafter may be prepared. Subsequently, substituents containing an acidic moiety or a basic moiety may be attached to the repeating units forming the backbone chain of the polymer. Useful acidic and basic moieties are described in greater detail hereinafter in connection with a preferred embodiment of the invention wherein the polymeric materials are formed from polymerizable monomers which initially contain an acidic or basic moiety. In accord with this first embodiment of the invention, the amount of acidic or basic moieties which should be incorporated in the resultant polymer to form a polymeric material capable of being converted to hydrophilic form when contacted by an activating solution of

appropriate pH may vary. Typically, if the resultant polymer contains repeating units having basic moieties attached thereto, from about 10 to about 50 percent by weight of the polymer should be composed of repeating units having a basic moiety attached thereto. If the resultant polymer contains repeating units having acidic moieties attached thereto, from about 1 to about 30 percent by weight of the polymer should be composed of repeating units having an acidic moiety attached thereto.

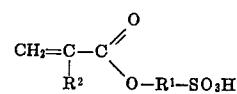
In accord with a preferred embodiment of the invention, the polymeric material comprising the toner particles is a polymerized blend of ethylenically unsaturated monomers, at least a portion of said monomers containing a moiety capable of forming a salt when contacted with an activating solution of appropriate pH. Typical of such monomers are polymerizable monomers containing acidic moieties, such as carboxylic acids, sulfonic acids, etc., or basic moieties, such as amino styrene, vinyl pyridine, etc.

More particularly, useful polymerizable acidic organic monomers generally are materials containing (a) 3 to 15 carbon atoms, (b) polymerizable ethylenically unsaturated moiety (ie.



), and (c) an acidic moiety including preferably carboxylic acid moieties (ie. $-\text{COOH}$) and the anhydrides and partial alkyl esters thereof; however, sulfonic acid moieties (ie. $-\text{SO}_3\text{H}$) may also be useful. Representative carboxylic acids include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, vinyl benzoic acid, maleic acid, etc. The anhydrides include, for example, maleic anhydride. The term "partial ester" has reference to the half acid, half ester of an ethylenically unsaturated dicarboxylic acid, for example ethyl hydrogen maleate.

Representative of such polymerizable acidic organic materials containing sulfonic acid groups include materials such as sulfoalkyl acrylates and methacrylates having the formula:

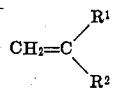


wherein R^2 is hydrogen or alkyl typically containing 1 to about 2 carbon atoms and R^1 is an alkylene or alkylidene group typically containing 2 to about 6 carbon atoms. The carboxylic acids, and the anhydrides and partial alkyl esters thereof are generally preferred for use as the above-described acidic organic materials, rather than the sulfonic acid materials, because of the relatively higher degree of hydrophilicity exhibited by copolymers having a substantial number of repeating units containing a sulfonic acid moiety. Thus, if sulfonic acid-containing materials are used as the monomeric acidic constituent of the copolymeric toners used in the present invention, smaller amounts of the acidic component should be employed than would otherwise be the case if a carboxylic acid, or anhydride or partial alkyl ester thereof, etc. were used as the acidic constituent.

The amount of the polymerizable acidic organic monomeric material useful in making the copolymeric toner materials employed in the present invention gen-

erally constitutes from about 1 to about 30 percent by weight of the monomeric blend (based on the dry weight of the blend absent any solvent or dispersion media) which is copolymerized to form the resultant copolymeric toner materials.

Typical polymerizable basic monomers useful in forming the copolymer toner particles employed in the present invention are basic monomers preferably comprising 2 to about 19 carbon atoms and having the following formula:



wherein R^1 represents hydrogen; a halogen such as fluorine, bromine, chlorine, or iodine; or an aliphatic alicyclic radical comprising 1-8 carbon atoms; and where R^2 is a basic moiety typically comprising 0 to about 15 carbon atoms. Particularly good results are obtained where R^2 represents a nitrogen-containing moiety, including aliphatic, carbocyclic, and heterocyclic moieties, comprising 0 to about 12 carbon atoms. Various useful such monomers include amino styrene, vinyl amine, vinyl pyridine, amino substituted alkyl methacrylates and acrylates, vinyl imidazole, etc. In a preferred embodiment of the present invention it has been found that vinyl pyridine provides an especially suitable such monomer because copolymers formed from such a monomer have been found to provide toner particles for a liquid developer which are extremely stable and resistant to agglomeration and settling. The amount of basic monomer useful in forming the copolymers employed in the toner particles of the present invention typically constitutes from about 10 to about 50 percent by weight of the monomeric blend (based on the dry weight of the blend absent any solvent or dispersion media) which is copolymerized to form the resultant copolymeric toner material.

It will be apparent to those skilled in the art that other polymerizable basic and acidic monomers may be utilized in accordance with the present invention in addition to the various monomers noted specifically hereinabove. That is, by routine laboratory procedures one need only determine (1) whether a particular monomer under consideration is capable of polymerizing to form a suitable polymer as described in detail hereinafter and (2) whether the monomer contains a moiety, such as a nitrogen-containing moiety, capable of being converted to hydrophilic form when contacted with an activating solution of suitable pH.

The remaining monomers used to form the polymers employed in the toner particles of the present invention may be selected from a wide variety of well-known polymerizable monomers useful in forming hydrophobic polymeric toner particles for liquid developers. Representative of said monomers are polymerizable ethylenically unsaturated materials such as styrene e.g. halogenated, alkyl, and alkoxy styrenes, alkyl acrylates and methacrylates, vinyl alkyl ethers, vinyl esters of aliphatic acids, etc.

Although the remaining monomers used to form the copolymers employed in the toner particles used in the invention may, as noted above, be selected from a variety of monomers, it has been found particularly useful, in accordance with a preferred embodiment of the in-

vention, to utilize in the toner particles at least one copolymer prepared from a blend of monomers as described in detail hereinafter. These preferred copolymers have been found to provide toner particles which are extremely stable and exhibit good replenishment properties.

Such preferred polymers are prepared from a monomeric blend and are generally characterized by a dispersibility ratio in the liquid carrier greater than about 0.825. As used in the present specification the dispersibility ratio of a particular copolymer in a particular developer carrier liquid is defined by the following test. A 4.0 gram quantity of copolymer to be tested is admixed into one liter of a particular developer carrier liquid using a Waring or Polytron Blender operating within the range of 10,000 to 18,000 rpm. The mixture is then centrifuged at 34,000 G forces for about 60 minutes. At the end of this time, the mixture is analyzed to determine the amount of polymer which has precipitated. To form the stable developers of the present invention, it has been determined that useful polymers should be dispersible to the extent that at least about 3.3 grams of the original 4.0 gram quantity of polymer remain suspended or dissolved in the carrier liquid after centrifuging. The dispersibility ratio is then calculated as the amount of polymer which remains suspended in the carrier liquid divided by the 4.0 grams of polymer originally mixed into the carrier liquid. A dispersibility ratio of 0.825 is equivalent to 3.3 divided by 4.0.

Exemplary of various additional monomers which may be utilized together with the acidic or basic monomers described hereinabove to form the above-noted preferred copolymeric toner particles for use in the present invention are "soluble" monomers, and "insoluble" monomers as set forth in Stahly and Merrill, U.S. application Ser. No. 149,851, filed June 3, 1971, incorporated herein by reference thereto.

As used in the present specification, "soluble" monomeric moieties which can be copolymerized to form the polymer used in the liquid developer of the invention are generally those moieties which, when polymerized, are capable of forming a homopolymer having an inherent viscosity as hereinafter defined of from about 0.4 about 0.5 in chloroform at room temperature (about 25°C.) and a solubility (at 25°C) in the carrier liquid to the extent that at least 5 parts by weight of polymer are soluble in 95 parts by weight of carrier liquid. In contrast, the term "insoluble" has reference to a monomeric moiety, a homopolymer of which, under the aforementioned viscosity conditions, is soluble in the carrier liquid to the extent of less than about 1 part by weight of polymer per 99 parts by weight of carrier liquid.

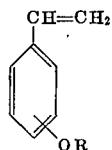
Representative soluble moieties which generally can be copolymerized to form the polymer used in the liquid developers of the invention may be selected from the following group:

A. alkyl styrenes such as compounds having the formula



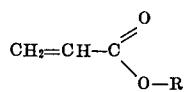
where R is an alkyl having from about 3 to about 10 carbon atoms in the alkyl moiety;

B. alkoxy styrenes such as compounds having the formula



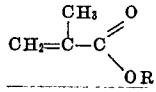
where R is an alkyl having from about 3 to about 10 carbon atoms in the alkyl moiety, for example, p-amyloxy styrene;

C. alkyl acrylates such as compounds having the formula



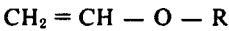
where R is an alkyl having from about 8 to about 22 carbon atoms in the alkyl moiety;

D. alkyl methacrylates such as compounds having the formula



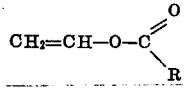
where R is an alkyl having from about 8 to about 22 carbon atoms in the alkyl moiety;

E. vinyl alkyl ethers such as compounds having the formula



where R is an alkyl having from about 8 to about 22 carbon atoms in the alkyl moiety; and

F. vinyl esters of aliphatic acids such as compounds having the formula:



where R is an alkyl having from about 6 to about 22 carbon atoms in the alkyl moiety; and mixtures thereof. Other soluble moieties may also be used.

Preferred soluble moieties which may be used in preparing the polymers contained in the liquid developers used in the invention generally include the following:

A. alkyl styrene having from about 5 to about 10 carbon atoms in the alkyl moiety;

B. alkyl acrylates and methacrylates having from about 12 to about 22 carbon atoms in the alkyl moiety; and

C. vinyl esters of aliphatic acids having from about 10 to about 22 carbon atoms in the alkyl moiety; and mixtures thereof. Typical moieties or groups which can be so used include the following:

4-pentyl styrene

4-hexyl styrene

4-octyl styrene

lauryl acrylate

hexadecyl methacrylate

octadecyl methacrylate
eicosyl acrylate
docosyl methacrylate
vinyl caprate
vinyl laurate
vinyl palmitate
vinyl stearate
vinyl eicosate
vinyl docosate

10 and mixtures thereof.

The term "inherent viscosity" as used herein, is defined by the following formula: $\eta_I = 1/n [\eta \text{ solution}/\eta \text{ solvent}] / C$

wherein η solution is the viscosity of the solution, η solvent is the viscosity of the solvent and C is the concentration in grams per 100 ml. of the polymer solvent. The determination is made at a concentration of 0.25 grams of polymer in 100 ml. of chloroform at a temperature of 25°C.

20 As noted, polymers used in the preparation of the liquid developers of the invention may also contain, if desired, at least one insoluble monomer copolymerized with the aforementioned soluble monomers. Representative insoluble monomers which may be suitable for being so copolymerized include the following:

- A. styrene selected from the group of styrene, methylstyrene, methoxystyrene and a halogenated styrene;
- B. alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety;
- C. alkyl methacrylates having from 1 to 4 carbon atoms in the alkyl moiety;
- D. vinyl alkyl ethers having from 1 to about 4 carbon atoms in the alkyl moiety; and
- E. vinyl esters of aliphatic acids having from about 1 to about 4 carbon atoms in the alkyl moiety; and mixtures thereof.

Preferred insoluble monomers which may be used in preparing the polymers contained in the developers used in the present invention generally include the following:

- A. styrene and methylstyrene;
- B. alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety;
- C. alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety; and
- D. vinyl esters of aliphatic acids having from 1 to about 4 carbon atoms in the alkyl moiety; and mixtures thereof. Typical insoluble moieties or groups which can be so used include the following:

styrene

α -methyl styrene

ethyl acrylate

methyl acrylate

butyl acrylate

ethyl methacrylate

propyl methacrylate

butyl methacrylate

vinyl acetate

vinyl propionate

vinyl butyrate

and mixtures thereof.

It will be apparent that the choice of particular soluble or insoluble monomeric moieties is determined by a number of factors. The degree of solubility in the carrier liquid may be controlled by proper adjustment of the ratio of soluble moiety to insoluble moiety. In addi-

tion, the nature of the particular soluble monomeric moiety, such as the degree of solubility of a homopolymer comprising it, will influence the particular insoluble monomeric moiety chosen to copolymerize with it to give the final copolymer. For example, if the soluble monomer is one having a relatively long alkyl group attached to it, rendering a polymer containing it relatively soluble, the insoluble monomer is desirably one having a relatively short alkyl group attached to it, to balance the properties. On the other hand, a relatively short alkyl group on the soluble monomer in general requires a somewhat longer alkyl group on the insoluble monomer. Generally, as indicated above, useful polymers of the present invention are dispersible in the carrier liquid to the extent that if a 4.0 gram quantity of polymer is added to one liter of carrier, at least about 3.3 grams will remain dispersed therein after centrifuging the mixture at 34,000 G forces for about 60 minutes.

In general, the polymers comprising the liquid developers of the invention may be prepared by an addition polymerization reaction wherein all of the component monomers are combined in a reaction vessel in a reaction medium, such as dioxane, and a suitable free radical initiator. The vessel containing the solution is then flushed with an inert gas, such as nitrogen, and heated to a temperature sufficient for the polymerization reaction to proceed at a reasonable rate. The temperature, in general, is above room temperature and preferably about 40° to 100° C. After the polymer has formed, it is removed from the reaction mixture and purified as necessary. Polymers produced according to this procedure typically have an inherent viscosity, as hereinbefore defined and measured, in the range of from about 0.1 to about 0.8. The resultant polymers typically contain (a) one or more different recurring units derived from soluble monomers, said units containing no acidic or basic side chain moiety and (b) one or more different recurring units containing as a side chain an acidic or basic moiety. If desired, the polymers may also contain as a recurring unit thereof one or more different units derived from insoluble monomers. In general, a typical polymer used in the liquid developers of the invention may contain from about 10 to about 70 weight percent of recurring units derived from soluble monomers, said units containing no acidic or basic side chain moiety and from about 0 to about 65 weight percent of recurring units derived from insoluble monomers. The dispersibility of the polymer can be adjusted as desired by proper balancing of the relative abundance of the soluble and insoluble monomers. Mechanical properties such as abrasion resistance, and fixability of the resultant toner image can also be adjusted by properly balancing the ratio of the components in the polymer.

It should be noted that the relative abundance of the various starting monomers in the polymerization medium is not always indicative of the percentage composition to be expected in the resultant polymer. When acrylic monomers are used as starting materials, for example, it is found that the composition of the polymer bears a very close correlation to the relative abundance in the starting solution, whereas when styrenes are used as starting materials, the correlation is not so close. Such deviations are well known to the polymer chemist, and one skilled in the art should readily be able to produce such variations in composition as may be desired to meet particular requirements.

Liquid developers containing the polymers described herein typically comprise a dispersion of the polymer in a suitable carrier liquid. A common method of preparing such a dispersion is solvent milling. A quantity of the polymer is dissolved in a suitable solvent and the solution placed in a ball mill. Other additives such as charge control agents which may be desirable are added to the mix and the whole milled for a suitable time, typically up to a week. Alternatively, a viscous solution of the polymer is placed on compounding rolls having chilled (5° to 10°C.) water passing through the cooling system. Other additives are then placed on the rolls and thoroughly mixed and blended with the polymer. After passing the complete mix through the mill several times to completely blend the ingredients, the mix is removed.

Liquid developers are made from the toner concentrate formed as above by dispersing the concentrate in a suitable electrically insulating carrier liquid. Carrier liquids which may be used to form such developers can be selected from a wide variety of materials. Preferably, the liquid has a low dielectric constant and a very high electrical resistance such that it will not disturb or destroy the electrostatic charge pattern being developed. In general, useful carrier liquids should have a dielectric constant of less than about 3, should have a volume resistivity greater than about 10⁸ ohm-cm, preferably greater than about 10¹⁰ ohm-cm, and should be stable under a variety of conditions. Suitable carrier liquids include halogenated hydrocarbon solvents, for example, fluorinated lower alkanes, such as trichloromonofluoromethane, trichlorotrifluoroethane, etc., having a boiling range typically from about 2°C. to about 55°C. Other hydrocarbon solvents are useful, such as isoparaffinic hydrocarbons having a boiling range of from about 145°C. to about 185°C., such as Isopar G (Humble Oil and Refining Co.) or cyclohydrocarbons such as cyclohexane. Additional carrier liquids which may be useful in certain situations include polysiloxanes, odorless mineral spirits, octane, etc.

As described hereinabove, the activating solutions utilized in the process of the present invention are selected to have a pH appropriate to convert the acidic or basic organic moieties contained in the copolymeric toner particles described hereinabove to a hydrophilic salt form. That is, if the toner powder particles selected contain an acidic organic moiety capable of being converted to its hydrophilic salt form, the activating solutions selected should have a basic pH, i.e. a pH greater than 7.0, in order to convert the acidic organic moiety to its hydrophilic form. On the other hand, if the toner powder particles utilized in the present invention contain a basic organic moiety capable of being converted to its hydrophilic form, then the activating solution selected should have an acidic pH, i.e. a pH less than 7.0. Typically, the activating solution comprises a mixture of an acid or base in a suitable polar solvent such as an aqueous media, e.g. water, water-alcohol mixtures, etc. Typically, the activating solution comprises a mixture of an acid or base in a suitable polar solvent such as an aqueous media, e.g. water, water-alcohol mixtures, etc.

Concerning an acid activating solution, the relative proportion of acid and solvent may vary within a relatively wide range. Typically, the acid activating solutions have a pH less than about 6.5, preferably below about 5.0. The particular acid utilized to acidify the activating solution is not critical. The particular acid se-

lected typically is chosen on the basis of its compatibility with other addenda which may be present in the activating solution, for example, water soluble dyes which advantageously are incorporated in an aqueous activating solution according to a preferred embodiment of the invention. Naturally, the acid selected should not have a deleterious effect on the toner particle image contacted by the activating solution. Typical acids which may be employed include the following: acetic acid, chloroacetic acid, formic acid, acrylic acid, glycolic acid, fumaric acid, oxalic acid, phosphoric acid, hydrochloric acid, sulfuric acid, potassium bisulfate, propionic acid, and mixtures thereof. An activating solution which has been found to work well and is compatible with the components utilized in a typical electrostatic toner particle image bearing element and conventional water soluble dyes is an aqueous acetic acid solution.

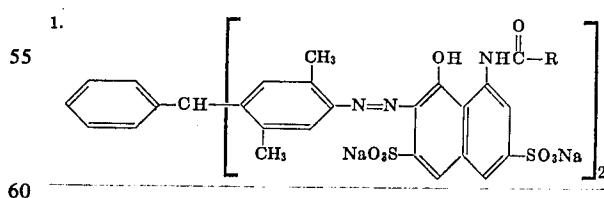
As discussed hereinabove with respect to the acid activating solutions, the basic activating solutions may also have a quite varied composition. So long as the basic activating solution has a suitable basic character to convert the acidic organic moiety of the polymeric toner image to its hydrophilic salt form, the particular composition thereof is not critical. Typical basic activating solutions utilized in the present invention have 1 pH greater than about 7.5, preferably from about 8.0 to about 13.0. Generally, a particular base selected for use in the activating solution is chosen primarily on the basis of its compatibility with other system components. Typical solvents useful in the basic activating solution are polar solvents such as an aqueous media, e.g. water, water-alcohol mixtures, etc. It will be apparent, therefore, that the selection of a particular basic material for a particular basic activating solution will depend upon the other materials utilized in the process such as the composition of the toner image-bearing substrate, any water soluble dyes which may be incorporated together with the basic component in an aqueous basic activating solution utilized according to a preferred embodiment of the incorporated etc. Among various bases which may be employed are the following: ammonia, hydroxylamine, methylamine, quanidine, hydrazine, trimethylamine, acetamidine, imidazole, N-methylpyrrolidine, sodium carbonate, sodium bicarbonate, sodium hydroxide, trisodium phosphate, tetramethylammonium hydroxide.

As stated hereinabove, the water-soluble dyes utilized in the present invention may be applied to the toner particle image which has been converted to its hydrophilic form as a separate aqueous dye solution or, in accordance with a preferred embodiment of the invention, the water-soluble dye may be incorporated in an aqueous activating solution and applied to the polymeric toner particle image simultaneously with the activating solution. In the latter case, the toner particle image is substantially simultaneously converted to a hydrophilic form and colored by the water-soluble dye contained in the aqueous treatment solution. Since the toner particle image is formed on a substrate which is hydrophobic relative to the polymeric toner particle image which has been converted to its hydrophilic form by the activating solution, the water soluble dye contacting the image-bearing surface is preferentially attracted to the hydrophilic toner particle image. The

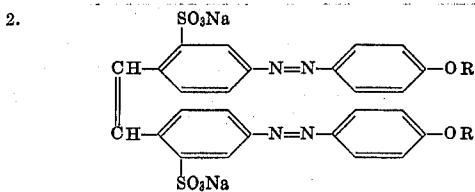
precise mechanism whereby the water soluble dye is attracted to the hydrophilic form of the polymeric toner particle image is not fully understood. The mechanism may be an absorption, imbibition, adsorption, a type of mordanting phenomena, or a combination of the above.

An acidic water-soluble dye, as used herein, is a water-soluble dye having as substituents at least one acid radical selected from sulfonic acid or carboxy acid radicals which are capable of forming salts with alkaline metals commonly used in the dye trade, such as sodium, potassium, lithium, etc. This term also includes the salts of such dyes, for example, the sodium, potassium, lithium, ammonium, triphenylguanidine, diphenylguanidine, di-o-tolylguanidine, aminoguanidine, cobalt, zinc, cadmium, copper, calcium, and barium salts. Other salts in addition to those noted above could also be used. A basic water-soluble dye, as the term is used herein, is a water-soluble dye having as substituents at least one amino or substituted amino radical and which is typically used as the hydrohalide (for example, hydrochloride, etc.), sulfate, nitrate, etc. Substituents for the amino group can be an alkyl group having from 1 to about 8 carbon atoms, and may be a straight or branched chain alkyl group, e.g., methyl, ethyl, isopropyl, hexyl, octyl, 2,2,4-trimethylpentyl, etc.; and aryl groups, for example, phenyl, naphthyl, etc., including substituted aryl groups bearing such substituents as alkyl as defined above, amino, including substituted amino, nitro, halogen and the like.

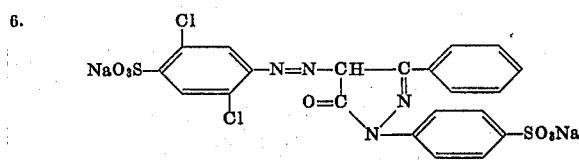
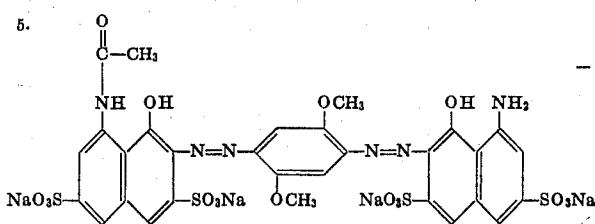
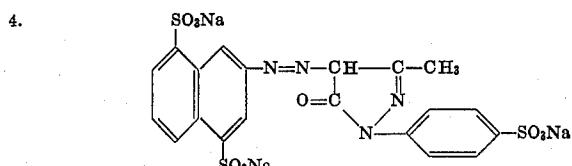
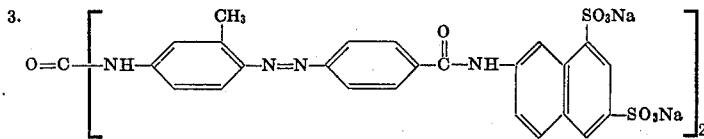
The choice of useful dyes to be employed in the process of the present invention is generally determined by their solubility and spectral absorption characteristics. As will be apparent, the dyes utilized may be chosen from a wide variety of known dye classes. For example, dyes selected from the following classes are useful: nitro, azo, including disazo, etc., arylmethane including di- and tri-arylmethane, methine, anthrapyrindones, indigo type dyes, azines, thiazines, oxazines, acridines, etc. These and other useful classes of dyes can be found in the preamble to the *Colour Index*, Volume 3, Second Edition, 1956. From the standpoint of color, solubility, and ease of transfer, the following are among the preferred water soluble acid dyes: Brilliant Alizarine Light Red B, Erio Fast Cyanine S, Tartrazine (C. I. 19140), Alizarine Astrol B (C.I. 61530), Alizarine Rubinol R (C. I. 68215), Alizarine Viridine FF (C. I. 62555), Fast Light Yellow 3G (C. I. 19120), copper phthalocyanine tetrasulfonic acid sodium salt (C. I. 74220), and the dyes exemplified by the following structures:



wherein R is an alkyl radical of from 1 to 12 carbon atoms with 1 to 7 carbon atoms being preferred or a phenyl radical, including substituted phenyl such as tolyl, xylyl, etc.



wherein R is an alkyl group of from 1 to 7 carbon atoms with 1 to 4 carbon atoms being preferred.



Compounds having the structural formulas 1 through 6 can be named as follows:

1. 4,4'-bis(1-acylamino-3,6-disodiumsulfo-8-hydroxynaphthalene-7-azo)-2,2',5,5'-tetramethyltriphenylmethane

2. 4,4'-bis(p-alkoxyphenylazo)-2,2'-disodiumsulfotilbene;

3. 4,4'-(6,8-disodiumsulfo-2-naphthylaminocarbonyl-p-phenylazo)-3,3'-dimethylurea;

4. 1-(p-sulfophenyl-3-methyl-4-(4,8-disulfonaphthyl-2-azo)-5-pyrazolone trisodium salt;

5. (1-hydroxy-3,6-disodiumsulfo-8-acetylaminonaphthyl-2-azo)-4-(1-hydroxy-3,6-disodiumsulfo-8-aminonaphthyl-2-azo)-2,5-dimethoxybenzene

6. 1-(p-sulfophenyl-3-phenyl-4-(2,5-dichloro-4-sulfophenyl-1-azo)-5-pyrazolone disodium salt.

Other acidic dyes which are illustrative of the many dyes include the following:

7. 1-carboethoxy-3-methyl-6-(4'-chloro-2'-fulfoanilino)-2-oxo-2,3-dihydrobenzanthrone, sodium salt;

8. 5,5'ureylenebis[2-(2-amino-6-sulfo-8-hydroxy-1-

naphthylazo)benzenesulfonic acid], tetrasodium salt, C.I. 25380;

9. 3,3'-[4,4'-ureylenebis(2-methylphenylazo)]bis(1,5-benzenedisulfonic acid), tetrasodium salt, C.I. 29025;

10. 5-[2-anilino-4-[4-(3-carboxy-4-hydroxyphenylazo)-s-triazin-2-ylamino]-4-hydroxy-3-[4-(8-hydroxy-3,6-disulfo-1-naphthylazo)-2-methoxy-3-

10 methylphenylazo]-2,7-naphthalenedisulfonic acid,

pentasodium salt, C.I. 34045;

20 11. 6,6'-ureylenebis{2-[4-(2,4-dichloro-6-sulfophenylazo)-3-methylphenylazo]-1-naphthol-3-sulfonic acid}, tetrasodium salt, C.I. 35785; and

12. anhydro-3,6-bis(diethylamino)-9-(2,4-disulfo-phenyl)-xanthium hydroxide, sodium salt, C.I. 45100.

25 Dyes such as 7-12 are sold under various names, including the following:

Solantine Pink 4BL, C.I. 25380

Solantine Yellow RL, C.I. 29025

Pontamine Fast Green G, C.I. 34045

Sirius Rubine 6B, C.I. 35785

Xylene Red B, C.I. 45100

Solophenyl Fast Blue Green BL, C.I. Direct Green 27

Similarly, many basic dyes can be used, including the following illustrative materials:

35 13. 9-o-carboxyphenyl-3,6-bis(diethylamino)xanthium chloride, C.I. 45170;

14. 1,1',3,3,3',3'-hexamethylindocarbocyanine chloride, C.I. 48070;

15. bis[3,7-

40 bis(dimethylamino)phenazathionium]tetrachlorozincate, C.I. 52015; and

16. bis(3-amino-7-dimethylamino-2-methylphenazathionium)tetrachlorozincate, C.I. 52040.

45 Dyes such as 13-16 above are sold under various names, including the following:

Rhodamine B, C.I. 45170

Astaphloxine FF, C.I. 48070

Methylene Blue BX, C.I. 52015 Toluidine Blue, C.I. 52040

Genacryl Yellow 5GF, C.I. Basic Yellow 13

Genacryl Yellow 2RL, C.I. Basic Yellow 25

Whether the above-described water-soluble dyes are contacted with the image formed by the copolymeric toner materials described hereinabove in an aqueous vehicle separate from the above-described activating solution, or whether these dyes are present in an aqueous activating solution so that only one treatment vehicle need be employed, the concentration of the dyes employed in the aqueous vehicle remains substantially the same. Typically satisfactory results are obtained using a concentration of dye in an aqueous vehicle varying from about 1 to about 10 grams of dye per liter of aqueous vehicle. Although, as noted hereinabove, a wide range of water soluble dyes may be employed in the process of the present invention, best results have typically been obtained utilizing acidic or basic dyes.

The mordantable acid dyes especially have been found highly useful because of their mordantability which permits dye images formed from these dyes to be easily superimposed one on top of the other to form sharp, multiple dye images on a single dye receiving sheet. The mordantability of these dyes is especially useful in such a multiple image superimposition process as it prevents the tendency of a previously formed dye image from deteriorating due to diffusion or wandering of the dyes which tends to occur during a subsequent dye transfer operation. Suitable mordantable dyes include those dyes often referred to in the dye trade as "dye-transfer dyes".

The electrostatic charge image utilized in the process of the present invention may be formed by a variety of well-known techniques. For example, a typical electrographic electrostatic image may be formed employing any of a number of well-known photoconductive materials including inorganic photoconductors, organic photoconductors and organo-metallic photoconductors. A typical electrophotographic process, as is well-known, involves uniform charging of the photoconductive element followed by subsequent image-wise exposure, thereby forming an electrostatic charge pattern corresponding to the image-wise exposure. Such a process can be developed to form either positive or negative images of the original exposed image. This may be done simply by the appropriate use of development electrodes in the development process, all of which is well-known in the electrographic art. Various other techniques for forming the electrostatic latent image may be also used, such as persistent conductivity image formation wherein a photoconductive surface is exposed to an optical image to form a latent conductivity image which is then subjected to an electrical charge using, for example, a corona charge device. In such a process the latent conductivity areas, being conductive, will dissipate the surface charge in the previously exposed areas, whereas in the unexposed areas the surface charge will remain to form an electrostatic image which is a reversal of the latent conductivity image. Other electrostatic imaging techniques which may be used include electrostatic printing or recording by the use of imagewise charging electrodes. Further detail concerning persistent conductivity imaging process and electrographic printing processes may be found, for example, in the book entitled "Electrophotography" by R.M. Schaffert, chapters IV and IX, respectively, published by The Focal Press in 1965. A variety of other particularized methods for forming electrostatic patterns using electrographic techniques may also be found in the Schaffert text noted above.

Having formed the electrostatic charge pattern, the next step utilized in the present invention involves the development of that charge pattern using the liquid developer containing the polymeric toner materials described, in detail, hereinabove. Following the application of the liquid developer to the electrostatic charge-bearing element, there is formed a toner particle image corresponding to the electrostatic charge pattern. As explained hereinabove, depending upon whether a development electrode or other reversal technique is utilized, the toner particle pattern thus formed may be either a positive or a negative image of the original image. The electrostatic charge pattern which is carried on an electrically insulating substrate may be liquid de-

veloped by contacting the charge pattern with the liquid developers described hereinabove. This may be accomplished by a variety of techniques such as rolling the liquid developer over the charge pattern-bearing element, dipping the charge pattern-bearing element into a tank or trough containing the liquid developer, spraying the liquid developer onto the electrostatic charge pattern bearing element, etc.

Upon development of the electrostatic charge pattern to form a polymeric toner particle image corresponding thereto, the toner particle image pattern may be subjected to the above-described activating solution and dye solutions. Or, in accordance with the other embodiments of the invention, the polymeric toner particle image pattern may first be transferred to a receiver element and then subjected to the activating solution and dye solutions. This latter embodiment is especially advantageous where, for example, one is utilizing a reusable charge bearing element for the formation of the electrostatic image pattern. In such case, it may be desirable to transfer the toner particle image as soon as possible so that the charge bearing element may be recycled for use in a subsequent electrostatic imaging operation. In addition, it may be desirable to avoid subjecting the element used for formation of the electrostatic charge pattern to the subsequent activating and dyeing operations to avoid contaminating this element with these materials.

Methods of transferring liquid developed toner particle images from the surface of one element, e.g. electrophotographic elements having a photoconductive layer, to a receiving element are well known in the electrographic art. The use of a particular method or methods does not constitute a critical element of the present invention. Accordingly, an extended discussion thereof is deemed unnecessary in the present specification. Generally, transfer of liquid developed images can be accomplished by impression in much the same manner as ink images are transferred from a printing plate. Electrostatic transfer may also be used. In general, except as noted herein or as required by a particular transfer operation, no special coatings are required on the surface of the receiving element.

Regardless of whether the toner particle image is subjected to the activating solution and dye solutions on the original electrographic element utilized for formation of the electrostatic charge pattern or whether the toner particle image is transferred from such an element to a subsequent receiver element, it is important that the toner particle image be carried on a substantially hydrophobic surface when contacted with the activating solution and dye solutions. This is to insure that good dye image differential is ultimately obtained. Moreover, it will be apparent that the particular hydrophobic surface chosen should further be characterized as a hydrophobic material which is chemically inert with respect to the activating solution. That is, the hydrophobic surface should be composed of a material or materials which are not converted to a hydrophilic substance when contacted with the activating solutions.

The terms hydrophilic and hydrophobic as used throughout the present specification and claims are used in accordance with their conventional meaning. Thus, a hydrophobic material is a material lacking an affinity for water whereas a hydrophilic material is a material having a strong affinity for water, i.e., water is readily absorbed or adsorbed thereto. As is apparent,

therefore, the hydrophobic surface on which the polymeric toner particles of the present invention are carried may be composed of a variety of various substances including a large number of organic materials including synthetic and natural organic materials such as various polymers, rosins, waxes, etc., to impart hydrophobicity to the surface. A partial listing of suitable hydrophobic materials includes polyacrylamides, polyamides, cellulose acetate butyrate, poly(vinylacetate), poly(vinyl chloride), polyethylene, poly(ethylene terephthalate), polystyrene, poly(vinylbutral), bisphenol A polycarbonate, unhydrolyzed cellulose acetate, cellulose nitrate, cumar resin, shellac, poly(methyl methacrylate), alkydo, silicone resins.

Having contacted the toner particle image carried on a hydrophobic receiving surface with the activating solution and dye solutions, the resultant image may then be dried and fixed to form a useable dye toner particle image. Alternatively, the dye image may be transferred to another receiving sheet, for example, a mordant-containing receiving sheet, to form a more permanent dye image.

This latter embodiment is especially useful where one wishes to obtain a more stable permanent dye image. In such case, it is desirable, as suggested above, to transfer the activated dye image to a receiving surface containing a mordant for the dye. Transfer is typically accomplished by intimately contacting the activated dye toner particle image with the receiving surface. The mordant, of course, reacts with the dye of the toner particle image to form a stable, fixed dyemordant image on the receiving surface. A variety of well-known mordanting compounds may be used in this embodiment of the invention. Such mordants are thoroughly familiar to those acquainted with the use of water-soluble acid and basic dyes.

The particular mordants selected are not critical and generally are selected on the basis of their utility with the particular acid or basic water soluble dyes used in the process of the present invention. For example, if acid dyes are to be mordanted, the image-receiving surface used in this embodiment of the invention can contain basic mordants such as polymeric aminoquandine derivatives of vinyl methyl ketone such as described in the Minsk, U. S. Pat. No. 2,882,156 granted Apr. 14, 1959, and basic polymeric mordants such as described in copending U.S. Application Ser. No. 100,491 of Cohen et al. filed Dec. 21, 1970, now U.S. Pat. No. 3,709,690. Other mordants useful in the invention include poly(4-vinylpyridine), poly(2-vinyl-N-methylpyridinium p-toluenesulfonate), and similar compounds described in Sprague et al. U. S. Pat. No. 2,484,430 granted Oct. 11, 1949, and cetyltrimethylammonium bromide, etc. Effective mordanting compositions are also described in Whitmore U. S. Pat. No. 3,271,148 and Bush U. S. Pat. No. 3,271,147. The mordanting compositions described in the Whitmore patent comprise at least one hydrophilic organic colloid containing a finely-divided, uniform dispersion of droplets or globules of a high-boiling, water-immiscible organic solvent in which is dissolved a high concentration of a cationic, nonpolymeric, organic dyemordanting compound for acid dyes. The mordanting compositions described in the Bush patent comprise at least one hydrophilic organic colloid containing a finely divided, uniform dispersion of particles of a salt of an organic acidic composition containing free acid moi-

ties and a cationic, nonpolymeric, organic dyemordanting compound for acid dyes. Useful cationic or basic organic dye-mordanting compounds for dyes include quaternary ammonium and phosphonium, and 5 ternary sulfonium compounds in which there is linked to the N, P or S onium atom at least one hydrophobic ballast group such as long-chain alkyl or substituted alkyl groups.

Typically, the dye-image receiving surface contains a 10 hydrophilic, organic colloid layer such as N-methoxymethyl poly(hexamethylene adipamide); partially hydrolyzed poly(vinyl acetate); poly(vinyl alcohol) with or without plasticizers; cellulose acetate; gelatin; and other materials of a similar nature. Furthermore, depending on the particular dye, the dye-image receiving surface may be sufficient by itself to 15 mordant the dye as in the case with the aforementioned colloids which are alkaline solution-permeable layers. Generally good results are obtained when the image-receiving layer is about 0.25 to about 0.04 mil in thickness. This thickness, of course, can be modified depending upon the result desired. The image-receiving layer can also contain ultraviolet-absorbing materials 20 to protect the mordanted dye images from fading due to ultraviolet light and/or brightening agents such as the stilbenes, coumarins, triazines, oxazoles, etc.

As suggested hereinbefore, the present invention is especially useful in providing multiple color copies of an original image pattern. It will be understood, of course, that the invention has application in any embodiment wherein it is desired to form a water-soluble dye image of an original image pattern using an electrographic imaging system. However, as will be apparent to those skilled in the art, the invention has particular applicability to multiple color electrographic systems wherein it is desired to form color copies of an original image pattern composed of multiple colors. As an example of a typical color system, a multiple-colored composite dye image copy of an original image pattern 30 may be prepared in accord with the present invention as follows: a series of color separation positive images corresponding to the original image pattern are prepared. Preparation of such color separation images are well-known in the photographic and electrographic arts and extended discussion thereof is deemed unnecessary. In general such color separation images are formed by preparing a separate color copy of the original image pattern corresponding to each of the primary colors, i.e. red, blue, and green. If desired, a separate color separation image may also be made corresponding to the black color of the original image pattern. The resultant color separation images may then be used to form individual electrostatic charge images, one charge 40 image corresponding to each color separation image, on electrographic elements, e.g. organic photoconductor-containing elements. The resultant charge images, as set forth hereinabove, are formed on hydrophobic surface. Liquid development of these charge images 45 may then be performed. Each electrostatic charge separation image is developed with a liquid developer containing hydrophobic toner particles which are convertible to hydrophilic form, as described hereinabove to form a series of toner particle images corresponding to the color separation images. Each toner particle image 50 is then contacted with an activating solution of appropriate pH and a suitably colored dye solution. In a typical subtractive multiple color processing system in ac-

cord with the present invention, each toner particle separation image is treated with a dye solution having a color complementary to the original color separation image. Thus, the toner particle image corresponding to the red color separation image is contacted with a dye solution containing a cyan dye as colorant; the electrographic element containing a toner particle image corresponding to the blue separation image is contacted with a dye solution containing a yellow dye as colorant; and the electrographic element containing the toner particle image corresponding to the green color separation image is contacted with a dye solution containing a magenta dye as colorant. Subsequently, if desired, each of the resultant dye-toner-particle images may be contacted one at a time in register to a receiving element having a suitable receiving surface such as a hydrophilic organic colloid as described hereinabove. Accordingly, the dye images from each of the individual toner particle images are transferred in register and superimposed one on top of the other on the surface of the receiving element to form the final multiple color copy of the original image pattern. Preferably, as described hereinabove, the surface of the receiving element contains a mordant for the dye images to reduce any tendency for the individual dye images to migrate as they are transferred and superimposed one on top of the other. Also, as discussed hereinabove, the process may be simplified by combining the activating solution with the dye solution so that the conversion of the hydrophobic toner particles to hydrophilic form may occur substantially simultaneously with the formation of the dye image on the toner particle image.

Of course, as those skilled in the art will recognize, many possible variations of the above-described color processing technique may be employed in accordance with the present invention. Certain of these variations are illustrated in the subsequent working examples. However, the aforementioned color processing technique as well as those set forth in the examples are merely illustrative of possible techniques and are not intended as exhaustive of all known color processing systems useful in accordance with the invention.

The following examples are presented to further illustrate, not limit, the present invention, especially the use of the present invention to form multiple color images.

An electrographic liquid developer is prepared for use in Exs. 1-3 as follows: A developer concentrate is admixed having the following composition:

1. poly(2-methyl-5-vinylpyridine-co-methyl-methacrylate-co-lauryl methacrylate) [this polymer has a monomer weight ratio of 30/45/24, respectively] — 0.5 g.

2. Solvesso 100 (trademark of Humble Oil and Refining Co. used to identify an aromatic petroleum hydrocarbon having a flash point of 100°F., boiling range of 315°-350°F., and a composition, expressed in weight percent as follows: 96% aromatics including 9% xylenes, 16% monoalkyl benzenes, 36% dialkyl benzenes, 39% trialkyl benzenes; 4% aliphatics) — 10 ml.

3. 50 percent by weight solution of Uversol Cobalt Liquid purchased from Harshaw Chemical Co. (Uversol Cobalt Liquid is a trademark used to identify a cobalt naphthenate-containing liquid containing 6 percent by weight cobalt.) — 2 ml.

A working developer is prepared from the above-described concentrate by slowly pouring the concentrate into a Polytron-Waring Blender containing 500

ml. of Isopar G (Isopar G is a trademark of Humble Oil and Refining Co., used to identify a liquid mixture of isoparaffinic hydrocarbons having a boiling point in the range of 145°C to 185°C). During the addition of the concentrate the blender is run at a relatively low speed. After the addition of the concentrate, the blender is run at a higher speed.

Example 1 — Formation of the dye-colored images on three separate recording layers containing the transferred polymer images

A sheet of organic photoconductive element is uniformly charged to a negative surface potential of 600 volts with a corona charging device. An electrostatic, halftone image is produced by contact exposing the charged photoconductive element with a separation positive transparency (a record of the red information of the original scene) illuminated with tungsten radiation.

The electrostatic image is then developed in the liquid developer described above comprising finely divided particles of poly(2-methyl-5-vinylpyridine-co-methyl methacrylate-co-lauryl methacrylate), having a monomer weight ratio 30/45/25, suspended in Isopar G. These polymer toner particles, when suspended in the Isopar G, assume a positive polarity with respect to the carrier liquid and are therefore attracted to the negative electrostatic charge on the photoconductive surface.

The polymer toner particle image is then electrostatically transferred to a separate receiving element comprising a poly(ethylene terephthalate) support bearing a thin electrically conductive hydrophobic surface layer of cellulose nitrate containing cuprous iodide.

After rinsing the surface of the receiving element containing the transferred toner particles briefly with Isopar G, the surface is dried with warm air.

The toner particle image is then dyed by immersing the layer for 30 seconds in a combined activating and dye solution. The combined solution is an acidic, aqueous solution of 2 grams of 13660 Erio Fast Cyanine S (cyan dye marketed by Sandoz Color and Chemical Corporation, C.I. 63010) in 400 ml distilled water, plus 10 ml glacial acetic acid. After rinsing the surface briefly with distilled water, the surface is blotted dry with a photographic blotter and the image permanently fused to the poly(ethylene terephthalate) element by heating in a oven at 105°C for several seconds.

Polymer images corresponding to the blue and green information in the original scene are made in the same manner using yellow and magenta dye baths, respectively, on separate receiving elements. The dye used to form the magenta dye solution is Brilliant Alizarine Light Red B (C.I. Acid Red 58 marketed by Sandoz Color and Chemical Corp.). The dye used to form the yellow dye solution is 1-(p-sulfophenyl-3-methyl-4-(4,8-disulfonaphthyl-2-aso)-5-pyrazolone trisodium salt.

Superposition and registration of the three separate recording layers bearing the cyan, magenta, and yellow dye images results in a full color halftone transparency.

Example 2 — Formation of the colored images on a single, separate recording layer

This color transparency is made in essentially the same way as described in Example 1, except that all three colored images are formed on a single sheet of

the electrically conducting surfaces receiving element. Polymer images corresponding to the red, green, and blue records are formed and dyed in the cyan, magenta, and yellow acidic dye baths described in Example 1. To reduce interimage effects (the absorption of dye on a previously dyed image) each of the dyed polymer images is fused on a hot plate at 300°F for several seconds before subsequent transfers thereto.

A full color transparency results.

Example 3 — Formation of multiple colored image on a mordant-containing receiving element.

Three separate sheets of organic photoconductive element are charged to an initial surface potential of 500 volts (negative polarity). The charged layers are exposed, respectively, to the red, green, and blue component of a 35-mm Ektachrome (trademark of the Eastman Kodak CO.) transparency with filtered light from a Kodak A Enlarger, thereby forming electrostatic images on each of the layers.

The charged layers are then developed for 30 seconds in an aluminum tray containing the above-described liquid developer.

The charged surface of the photoconductive element is faced toward the aluminum bottom of the tray and during development a direct current bias potential of 50 volts is applied between the aluminum tray and the conducting layer of the photoconductive element to reduce spurious deposits of the polymer particles in the non-image areas. After development, the surface of the photoconductive layer is rinsed briefly with Isopar G and the image is fixed by warm air from a hair dryer.

Each of the matrices is then dyed in its respective cyan, magenta, and yellow aqueous activating-dye baths. The activating-dye baths are prepared as follows: a dye solution containing dilutions of dye-transfer dye concentrates in a 1:16 weight ratio of dye concentrate aqueous media is prepared. The glacial acetic acid is added to each of the dye baths in the proportion of 20 ml of acid per 710 ml of dye solution (working concentration).

After dyeing and a brief rinse of the materials with distilled water, the dyes in the polymer image material are transferred sequentially and in register to a receiving element comprising a paper base having a gelatin overcoat containing a basic mordant (this element is commercially available under the trademark of Kodak Dye Transfer paper), previously conditioned for one-half hour in an aqueous solution containing acetic acid. This results in a full-color print. Duplicate prints are made by re-dyeing the matrices and transferring the dyes to another sheet of dye transfer paper.

EXAMPLE 4

An electrographic liquid developer is prepared for Example 4 utilizing a developer concentrate having the following composition: a first mixture is prepared containing 1 gram of a hydrophobic polymer, i.e., poly(ethyl acrylate-co-ethyl methacrylate-lauryl methacrylate-co-sulfoethyl methacrylate) admixed in 20 ml. of Isopar G (trademark of Humble Oil); a second mixture is prepared containing 2 grams of a hydrophobic polymer of poly(styrene-co-lauryl methacrylate-co-sulfoethyl methacrylate) admixed in 15 ml. of Isopar G; the resultant first and second polymer mixtures are blended together and Isopar G is slowly added with stirring to obtain one liter of result-

tant mixture which is used as the liquid developer of Example 4.

Next, a sheet of organic photoconductive element is uniformly charged with a corona charger to a negative polarity potential of 500 volts and then contact exposed to a high contrast positive image transparency using tungsten illumination. After exposure, the charge-image bearing organic photoconductive element is developed by immersing the photoconductive element in the above-described liquid developer, rinsed with a substantially pure Isopar G rinse, and dried with warm air. As a result, a hydrophobic polymeric toner particle image corresponding to the original positive transparency is deposited on the surface of the photoconductive element.

The hydrophobic toner particle image-bearing photoconductive element is then immersed in a basic aqueous dye-containing activating solution composed of 0.5 gram of a basic dye Colour Index Basic Violet 15 having the trademark "Sevron" Brilliant Red 3B purchased from E.I. duPont Nemours and Co., 2 cc. of ammonium hydroxide, and 200 cc. of distilled water. As a result, the basic dye is absorbed to the polymeric toner particle image to form a hydrophilic dyed toner particle image. If desired, the resultant dyed image may be briefly rinsed using distilled water.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In a method of liquid developing an electrostatic charge pattern carried on an electrically insulating substrate to obtain a water-soluble dye image corresponding to the charge pattern, the improvement which comprises:

- 35 A. forming on a hydrophobic surface an image of substantially colorless electrostatically attractive toner particles corresponding to such charge pattern utilizing a liquid developer comprising said toner particles admixed in a liquid carrier vehicle having a dielectric constant less than about 3.0 and a resistivity greater than about 10^8 ohm-cm, said toner particles comprising a hydrophobic polymer having as a repeating unit thereof a group derived from an ethylenically unsaturated polymerizable monomer, said unit having attached thereto a substituent selected from the group consisting of (1) sulfonic acid moieties and carboxylic acid moieties or the anhydrides and partial alkyl esters thereof, or (2) basic nitrogen-containing moieties;
- B. contacting said toner particle image carried on said hydrophobic surface with an activating solution selected from the group consisting of
 - a. acidic aqueous solutions having a pH less than about 7.0 when said hydrophobic polymer contains units having substituents selected from group (2) above, or
 - b. basic aqueous solutions having a pH greater than about 7.0 when said hydrophobic polymer contains units having substituents selected from group (1) above to convert said hydrophobic polymer contained in said toner particles to the hydrophilic form thereof; and

C. contacting said hydrophilic toner particle image with an aqueous dye solution comprising a water-soluble dye selected from the group consisting of

- acid water-soluble dyes when said copolymer contains units having substituents selected from group (2) above, or
- basic water-soluble dyes when said copolymer contains units having substituents selected from group (1) above

to form a visible water-soluble dye image corresponding to said toner particle image.

2. The invention of claim 1 wherein following (C), the hydrophobic surface bearing said dye image and a receiving element for said dye image are contacted together to transfer said dye image to said receiving element.

3. The invention of claim 1 wherein following (C), the hydrophobic surface bearing said dye image and a receiving element comprising a hydrophilic colloid layer containing a mordant for the dye are contacted together to transfer and mordant said dye image to the colloid layer of the receiving element.

4. The invention of claim 1 wherein following (C), the toner particle-dye image is fixed to said hydrophobic surface.

5. The invention of claim 1 wherein (B) and (C) are performed substantially simultaneously by admixing said aqueous dye solution of (C) together with said activating solution of (B) and contacting such admixture with the toner particle image carried on said hydrophobic surface.

6. The invention of claim 1 wherein a multiple-color image is obtained by successively repeating (A) to (C) to form a series of individual dye-containing toner particle images, each of said images representing an individual color separation image of an original image, and superimposing said dye-containing toner particle images in register on a single receiving element to form a resultant multiple-color image.

7. The invention of claim 1 wherein a multiple-color water-soluble dye image is obtained by successively repeating (A) to (C) to form a series of individual dye-containing toner particle images, each of said images representing an individual color separation image of an original image, and successively contacting each of said dye-containing toner particle images with a single receiving element to transfer and superimpose, in register, the dye images of said dye-containing toner particle images to the receiving element, said receiving element having a hydrophilic colloid layer comprising a mordant for each of said dye images.

8. In a method of liquid developing an electrostatic charge pattern carried on an electrically insulating substrate to obtain a water-soluble dye image corresponding to the charge pattern, the improvement which comprises

- forming on a hydrophobic surface an image of substantially colorless electrostatically attractive toner particles corresponding to such charge pattern by using a liquid developer comprising said toner particles admixed in a liquid carrier vehicle having a dielectric constant less than about 3.0 and a resistivity greater than about 10^8 ohm-cm, said toner particles comprising a hydrophobic copolymer which contains as a repeating unit thereof a group derived from an ethylenically unsaturated polymerizable monomer comprising 2 to about 19

carbon atoms and a basic nitrogen-containing moiety;

B. contacting said toner particle image carried on said hydrophobic surface with an activating solution comprising an acidic aqueous solution having a pH less than about 6.5 to convert said hydrophobic copolymer contained in said toner particles to the hydrophilic form thereof;

C. contacting said hydrophilic toner particle image with an aqueous dye solution comprising an acid water-soluble dye to form a visible water-soluble dye image corresponding to said toner particle image;

D. contacting said dye image together with a receiving element comprising a hydrophilic colloid layer containing a mordant for the dye to transfer and mordant said dye image to the colloid layer of the receiving element.

9. A method of liquid developing an electrostatic charge pattern carried on a hydrophobic surface of a photoconductive element to obtain a water-soluble dye image corresponding to the charge pattern, said method comprising:

A. contacting the charge pattern carried on said hydrophobic surface with a liquid developer comprising substantially colorless electrostatically attractive toner particles admixed in a liquid carrier vehicle having a dielectric constant less than about 3.0 and a resistivity greater than about 10^{10} ohm-cm to form a toner particle image, said toner particles comprising a hydrophobic copolymer which contains as a repeating unit thereof a group derived from an ethylenically unsaturated polymerizable monomer, said monomer selected from the group consisting of (1) acidic organic monomers comprising 3 to about 15 carbon atoms and a moiety selected from the group consisting of sulfonic acid moieties and carboxylic acid moieties or the anhydrides and partial alkyl esters thereof, or (2) basic organic monomers comprising 2 to about 19 carbon atoms and a basic nitrogen-containing moiety;

B. contacting said toner particle image carried on said hydrophobic surface with an activating solution selected from the group consisting of

- acidic aqueous solutions having a pH less than about 7.0 when said hydrophobic copolymer contains units selected from group (2) above, or
- basic aqueous solutions having a pH greater than about 7.0 when said hydrophobic copolymer contains units selected from group (1) above

to convert said hydrophobic copolymer contained in said toner particles to the hydrophilic form thereof; and

C. contacting said hydrophilic toner particle image with an aqueous dye solution comprising a water-soluble dye selected from the group consisting of

- acid water-soluble dyes when said copolymer contains units selected from group (2) above, or
- basic water-soluble dyes when said copolymer contains units selected from group (1) above to form a visible water-soluble dye image corresponding to said toner particle image.

10. The invention of claim 9 wherein a multiple-color image is obtained by successively repeating (A) to (C) to form a series of individual dye-containing toner particle images, each of said images representing an individual color separation image of an original image, and superimposing said dye-containing toner particle im-

ages in register on a single receiving element to form a resultant multiple-color image.

11. The invention of claim 9 wherein a multiple-color water-soluble dye image is obtained by successively repeating (A) to (C) to form a series of individual dye-containing toner particle images, each of said image representing an individual color separation image of an original image, and successively contacting each of said dye-containing toner particle images with a single receiving element to transfer and superimpose, in register, the dye images of said dye-containing toner particle images to the receiving element, said receiving element having a hydrophilic colloid layer comprising a mordant for each of said dye images.

12. A method of developing an electrostatic charge pattern carried on a hydrophobic surface of a photoconductive element to obtain a water-soluble dye image corresponding to the charge pattern, the method comprising:

A. contacting the hydrophobic surface of said photoconductive element with a liquid developer comprising substantially colorless electrostatically attractive toner particles admixed in a liquid carrier vehicle having a dielectric constant less than about 3.0 and a resistivity greater than about 10¹⁰ ohm-cm to form a toner particle image, said toner particles comprising a hydrophobic copolymer which contains as a repeating unit thereof a group derived from an ethylenically unsaturated polymerizable monomer comprising 2 to about 19 carbon atoms and a basic nitrogen-containing moiety;

B. contacting said toner particle image carried on said hydrophobic surface with an activating solution comprising an acidic aqueous solution having a pH less than about 6.5 to convert said hydrophobic copolymer contained in said toner particles to the hydrophilic form thereof; and

C. contacting said hydrophilic toner particle image with an aqueous dye solution comprising an acid water-soluble dye to form a visible water-soluble dye image corresponding to said toner particle image.

13. The invention as described in claim 12 wherein said basic nitrogen-containing moiety comprises 0 to about 12 carbon atoms.

14. The invention as described in claim 12 wherein said basic nitrogen-containing moiety is selected from the group consisting of aminostyrene, vinyl amine, vinylpyridine, amino-substituted alkyl methacrylates, amino-substituted alkyl acrylates, and vinyl-imidazole.

15. The invention as described in claim 12 wherein following (C) the hydrophobic surface bearing said dye image and a receiving element for said dye image are contacted together to transfer said dye image to said receiving element.

16. The invention of claim 12 wherein following (C), the hydrophobic surface bearing said dye image and a receiving element comprising a hydrophilic colloid layer containing a mordant for the dye are contacted together to transfer and mordant said dye image to the colloid layer of the receiving element.

17. The invention of claim 12 wherein (B) and (C) are performed substantially simultaneously by admixing said aqueous dye solution of (C) together with said activating solution of (B) and contacting such admixture with a toner particle image carried on said hydrophobic surface.

18. The invention of claim 12 wherein a multiple-color image is obtained by successively repeating (A) to (C) to form a series of individual dye-containing toner particle images, each of said images representing an individual color separation image of an original image, and superimposing said dye-containing toner particle images in register on a single receiving element to form a resultant multiple-color image.

19. The invention of claim 13 wherein a multiple-color water-soluble dye image is obtained by successively repeating (A) to (C) to form a series of individual dye-containing toner particle images, each of said images representing an individual color separation image of an original image, and successively contacting each of said dye-containing toner particle images with a single receiving element to transfer and superimpose, in register, the dye images of said dye-containing toner particle images to the receiving element, said receiving element having a hydrophilic colloid layer comprising a mordant for each of said dye images.

20. A method of liquid developing an electrostatic charge pattern carried on the surface of a photoconductive element to subsequently obtain an imaged element having a water-soluble dye image corresponding to the charge pattern, said method comprising:

A. contacting the charge pattern carried on said photoconductive element with a liquid developer comprising substantially colorless electrostatically attractive toner particles admixed in a liquid carrier vehicle having a dielectric constant of less than about 3.0 and a resistivity greater than about 10¹⁰ ohm-cm to develop said charge pattern, said toner particles comprising a hydrophobic copolymer which contains as a repeating unit thereof a group derived from an ethylenically unsaturated polymerizable monomer, said monomer selected from the group consisting of (1) acidic organic monomers comprising 3 to about 15 carbon atoms and a moiety selected from the group consisting of sulfonic acid moieties and carboxylic acid moieties or the anhydrides and partial alkyl ester thereof, or (2) basic organic monomers comprising 2 to about 19 carbon atoms and a basic nitrogen-containing moiety;

B. transferring said developed toner particle image to a receiving element having a hydrophobic surface;

C. contacting said toner particle image carried on said hydrophobic surface with an activating solution selected from the group consisting of

a. acidic aqueous solutions having a pH less than about 7.0 when said hydrophobic copolymer contains units selected from group (2) above, or
b. basic aqueous solutions having a pH greater than about 7.0 when said hydrophobic copolymer contains units selected from group (1) above to convert said hydrophobic copolymer contained in said toner particles to the hydrophilic form thereof; and

D. contacting said hydrophilic toner particle image with an aqueous dye solution comprising a water-soluble dye selected from the group consisting of
a. acid water-soluble dyes when said copolymer contains units selected from group (2) above, or
b. basic water-soluble dyes when said copolymer contains units selected from group (1) above to form a visible water-soluble dye image corresponding to said toner particle image.

21. The invention of claim 15 wherein (B) and (C) are performed substantially simultaneously by admixing said aqueous dye solution of (C) together with said activating solution of (B) and contacting such admixture with the toner particle image carried on said hydrophobic surface.

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