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ELECTRO-PHOTOGRAPHIC PROCESS USING A LIQUID DEVELOPER CONTAINING A POLYMERIC DYE

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ABSTRACT OF THE DISCLOSURE

Liquid developer compositions for use in developing electrostatic charge patterns are formed of an electrically insulating organic carrier liquid having dispersed therein marking particles comprised of a polymeric dye having a linear backbone chain to which are attached pendant side chains containing a chromophoric moiety.

This invention relates to electrophotography and more particularly, to the development of electrostatic images using liquid development techniques and compositions.

In electrophotography, it is known to use an element comprised of a support having on it a layer of a photoconductive composition comprising a resinous binder and a photoconductor, either organic or inorganic, which in the dark will accept and retain an electrostatic charge After charging, such an element is then exposed in any suitable manner so as to vary the charge thereon in accordance with the relative energy received by the element during the exposure. After exposure the element is usually developed by applying thereto a charge powder which is drawn to the element in conformity with the charge pattern produced by exposure. The powder is then fixed or fused in some manner thus producing a powder image.

One of the difficulties with this type of development has been the inability to uniformly distribute the powder over the element. If the powder is unevenly applied, the image will similarly be formed in an uneven manner thus resulting in copy which is not a true representation of the original. Another difficulty is fixing the powder on the element in a permanent manner which is normally accomplished by including a resin in the powder and subjecting the deposited powder to heat. Also it is difficult to obtain high resolution with powder developers.

Many of the disadvantages of dry powder developers, such as dust, poor resolution, uneven distribution, etc., can be avoided by the use of a liquid developer. Liquid developers, such as those disclosed previously in U.S. Pat. No. 2,907,674, are usually composed of an insulating carrier liquid, a pigment such as carbon black and a resin to bind the pigment. However, when the pigment is deposited in an imagewise fashion, it scatters unabsorbed light rather than transmitting it. Such scattering of light makes pigment-containing developers of this type unsuitable for possible application in a multicolor subtractive process.

A further difficulty with pigment-containing liquid developers of this type is that the pigment and the resin binder do not necessarily have the same electrostatic charge polarity. Such bicharging can result in unwanted background density in images prepared from these developers. Still another problem encountered is that the pigment and the binder are not always depleted at the same rate. This latter problem results in a continually changing developer concentration with use. Such a condition is highly undesirable in that each of a series of images developed in one developer solution will not be uniform in quality. Still another problem that is sometimes encountered is that of the color leaching out of developed images.

It is, therefore an object of this invention to provide new liquid developers for electrostatic charge patterns.

It is another object of this invention to provide novel liquid developers for forming colored images which absorb most incident light.

It is a further object of this invention to provide novel liquid developers in which the binder and colorant are depleted during use at the same rate.

Still another object of this invention is to provide methods for preparing novel liquid developers containing substantially transparent, non-leachable colored dyes.

These and other objects of the invention are accomplished by preparing a liquid developer composition comprised of a carrier liquid containing a polymeric dye. In general, the polymeric dyes used in this invention are comprised of a linear backbone chain having attached thereto pendant side chains containing a chromophoric moiety. The polymeric dyes of this invention are typically prepared by forming a polymeric coupler which is then reacted with a suitable material to form the polymeric dye.

By polymeric couplers are meant polymers having nuclei which are capable of coupling with, for example, the oxidation products of color coupling aromatic primary amino developing agents such as formed on development of silver salt images to form an azomethine dye. Such polymeric couplers also include polymers having nuclei which are capable of coupling with diazotized aromatic amines to form azo dyes. Nuclei of the above type are well known in the dye art and color photography art. They are sometimes called color-forming couplers, color-formers, coupling components, etc. These dye intermediate nuclei or coupling nuclei generally have as the active coupling group one of the following: (a) an active open-chain methylene group; (b) an active cyclic methylene group; and (c) a phenolic nucleus bearing an active methine group. Of course, the hydrogen atom at the coupling position of the coupler can be replaced by a moiety which is readily eliminated in the coupling reaction, e.g., halogen, sulfonic acid, carboxylic acid, etc. Yellow couplers usually contain group (a) above, magenta couplers generally contain group (a) or (b) while cyan couplers typically contain group (c).

In a typical method of preparing a polymeric coupler, a suitable first vinyl monomer and a vinyl-containing dye intermediate or color-former are polymerized together to form a hydrophobic polymeric coupler having a linear backbone chain with pendant side chains attached thereto containing a color-forming nucleus. In general, the first vinyl monomer, which contains no color-former can be selected from a wide variety of materials depending upon the physical properties desired in the final polymer. Useful monomers would include styrene, including substituted styrene having such substituents as an amino radical and alkyl radicals preferably having about 4 to 18 carbon atoms; alkyl acrylates having from about 4 to 18 carbon atoms in the alkyl moiety such as isobutyl, pentyl, hexyl, decyl, dodecyl, pentadecyl, octadecyl acrylates, etc.; vinyl acetate; vinyl chloride; vinyl alkyl ethers having from about 4 to 18 carbon atoms in the alkyl moiety such as isobutyl, pentyl, hexyl, decyl, dodecyl, pentadecyl, octadecyl, etc.; alkyl methacrylates having from about 4 to 18 carbon atoms in the alkyl moiety such as isobutyl, pentyl, hexyl, decyl, dodecyl, pentadecyl, octadecyl methacrylates, etc.; and similar vinyl monomers. Mixtures of these materials as well as mixtures of the above monomers with alkyl acrylates, alkyl methacrylates and vinyl alkyl ethers having from 1 to 3 carbon atoms in the alkyl moiety and with vinyl chloride, vinyl acetate, etc., are also useful. Preferred monomers contain alkyl moieties containing from about 4 to 18 carbon atoms.

Monomers containing these longer alkyl radicals produce polymeric dyes having an enhanced compatibility with the hydrocarbon carrier liquids used in forming the liquid developers of the present invention. Of course, mixtures of a predominant amount of the preferred monomers with monomers which do not contain the longer alkyl radicals are also useful.

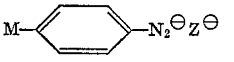
The second vinyl monomer used in forming the polymeric couplers is, in general, similar to the first vinyl monomer, only attached thereto is a substituent which contains a color-forming nucleus. This color-forming nucleus can be (a) an active open chain methylene group, (b) an active cyclic methylene group or (c) a phenolic nucleus having an active methine group attached. The first and second monomers are then copolymerized by typical vinyl polymerization techniques to form a suitable polymeric coupler. Of course, useful polymeric couplers can be prepared by forming a linear polymer having reaction sites where color-forming substituents can subsequently be attached. By whatever means formed, the resultant polymeric couplers are comprised of a linear backbone chain having pendant side chains containing as the coupling unit one of the following: (a) an open chain methylene coupling moiety, (b) a cyclic methylene coupling moiety and (c) an active methine-substituted phenolic coupling moiety.

The polymeric couplers described above can be readily converted to polymeric dyes useful in developers of the present invention. Typically, the polymeric couplers are reacted with oxidation products of color coupling aromatic primary amine developing agents such as p-phenylenediamines and p-aminophenol. Typical aromatic primary amine developing agents include:

N,N-diethyl-p-phenylenediamine,
2-amino-5-diethylamino toluene,
N-ethyl-β-methanesulfonamido-ethyl-3-methyl-4-amino aniline,
4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline,
4-amino-N-ethyl-3-methoxy-N-(-β-sulfoethyl)aniline,
4-amino-N-ethyl-N-(β-hydroxyethyl)aniline,
4-amino-N,N-diethyl-3-hydroxymethyl aniline,
4-amino-N-methyl-N-(β-carboxyethyl)aniline,
4-amino-N,N-bis(β-hydroxyethyl)aniline,
4-amino-N,N-bis(β-hydroxyethyl)-3-methyl aniline,
3-acetamido-4-amino-N,N-bis(β-hydroxyethyl)aniline,
4-amino-N-ethyl-N-(2,3-dihydroxypropyl)-3-methyl aniline sulfate salt,
4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline, and the like.

The resultant polymeric dyes are azomethine dyes.

Similarly, the polymeric couplers above can be reacted with diazotized aromatic amines (diazonium salts) to form azo dyes. Advantageous diazonium salts include benzene diazonium salts such as those having the formula:

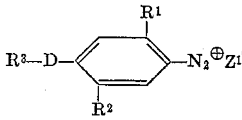


wherein M is either:

(1) a hydrogen atom,
(2) a halogen atom,
(3) an aryl radical,
(4) an amino radical including substituted amino radicals which can be cyclic radicals including the amino nitrogen atom and other hetero atoms such as oxygen, sulfur, nitrogen, etc.,
(5) a mercapto radical, or
(6) an alkyl or aryl thioether radical, and

$Z^{\ominus}$ is an acid anion. These compounds can also be substituted on one or more of the nuclear benzene carbons with, for example, at least one of either a halogen atom, an aliphatic alkyl radical, an alkoxy radical, an acyl radical, a carbamyl radical, a carboxyl radical or a nitro radical. Aliphatic alkyl radicals are defined herein to include straight and branched chain alkyl radicals having from 1 to 8 carbon atoms such as methyl, ethyl, isopropyl, tert-vutyl, n-amyl, octyl and the like.

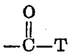
Other useful diazonium salts include p-aminobenzene-diazonium salts having the formula as described above wherein M is either an amino radical including substituted amino radicals or a thioether radical such as described above, and wherein the benzene nucleus is unsubstituted or substituted in at least one of the 2-position and the 5-position with either an aliphatic alkyl radical or an alkoxy radical. This class of useful diazonium salts can be represented by the formula:



wherein:

(1) D is either a sulfur atom or a radical having the formula NR^4,

(2) R^3, when taken alone, is either a hydrogen atom when D is NR^4, or a lower aliphatic alkyl radical, a lower alkoxy radical, an acyl radical having the formula:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-T$$

wherein T is either an aryl radical or an alkyl radical as described elsewhere herein, or a phenyl radical when D is either a sulfur atom or NR^4,

(3) R^4, when taken alone, is either a hydrogen atom, a lower alkyl radical or a lower alkoxy radical,

(4) R^3 and R^4, when taken together, complete a divalent radical having the formula:

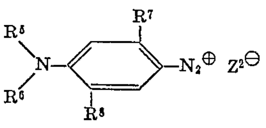
$$-(CH_2)_a-O_b-(CH_2)_c-$$

wherein *b* is an integer having a value of 0 or 1, each of *a* and *c* is a positive integer, and the sum of *a*, *b* and *c* has a value of 5,

(5) R^1 and R^2 are each either a hyrrogen atom, a lower aliphatic alkyl radical (preferably methyl or ethyl) or a lower alkoxy radical (preferably methoxy or ethoxy), and

(6) $Z^{1\ominus}$ is an acid anion.

Additional p-aminobenzene diazonium salts include substituted aminobenzene diazonium salts having the formula:



wherein:

(1) Each of R^5 and R^6, when taken alone, is a lower alkyl radical,

(2) R^5 and R^6, when taken together, are the number of carbon and hetero oxygen atoms necessary to complete a morpholino radical,

(3) Each of R^7 and R^8 is a hydrogen atom, a lower alkyl radical or a lower alkoxy radical, and

(4) $Z^{2\ominus}$ is either a chlorozincate anion, a fluoroborate anion, a sulfate anion, a phosphate anion, or a chlorostannate anion.

Other well suited benzene diazonium salts are the fluoroborate salts wherein:

(1) R^7 and R^8 are alkoxy radicals when R^5 and R^6 complete a morpholino radical, and

(2) R^7 and R^8 are each a hydrogen atom when R^5 and R^6 are each a lower alkyl radical.

Illustrative of the suitable diazonium salts are such compounds as the salts of

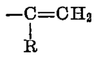
1-diazo-2,5-dimethoxybenzene;
1-diazo-2,5-diethoxybenzene;
1-diazo-4-chloro-2,5-diethoxybenzene;
4-diazo-2,5-dimethoxybiphenyl;
4-diazo-2,5,4′-triethoxybiphenyl;
1-diazo-4-dimethylaminobenzene;
1-diazo-4-(diethoxyamino)benzene;
1-diazo-4-[bis(hydroxypropyl)amino]benzene;
1-diazo-4-(N-methyl-N-allylamino)benzene;
1-diazo-4-(diamylamino)benzene;
1-diazo-4-(oxazolidino)benzene;
1-diazo-4-(cyclohexylamino)benzene;
1-diazo-4-(9-carbazolyl)benzene;
1-diazo-4-(dihydroxyethylamino)-3-methylbenzene;
1-diazo-4-dimethylamino-3-methylbenzene;
1-diazo-2-methyl-4-(N-methyl-N-hydroxypropylamino)benzene;
1-diazo-4-dimethylamino-3-ethoxybenzene;
1-diazo-4-diethylamino-3-chlorobenzene;
1-diazo-2-carboxy-4-dimethylaminobenzene;
1-diazo-3-(2-hydroxyethoxy)-4-pyrrolidinobenzene;
1-diazo-2,5-diethoxy-4-acetoxyaminobenzene;
1-diazo-4-methylamino-3-ethoxy-6-chlorobenzene;
1-diazo-2,5-dichloro-4-benzylaminobenzene;
1-diazo-4-phenylaminobenzene;
1-diazo-4-morpholinobenzene;
1-diazo-4-morpholino-3-methoxybenzene;
1-diazo-4-morpholino-2,5-dimethoxybenzene;
1-diazo-4-morpholino-2-ethoxy-5-methoxybenzene;
1-diazo-4-morpholino-2,5-dibutoxybenzene;
1-diazo-2,5-diethoxy-4-benzoylaminobenzene;
1-diazo-2,5-dibutoxy-4-benzoylaminobenzene;
1-diazo-4-ethylmercapto-2,5-diethoxybenzene;
1-diazo-4-tolylmercapto-2,5-diethoxybenzene

and the like, as well as mixtures thereof.

In addition to the above-mentioned p-aminobenzene diazonium salts, similar substituted diazonium salts are also useful. Any or all of the remaining carbon atoms can be substituted with a variety of substituents such as a lower alkyl radical of 1 to 5 carbon atoms, a lower alkoxy radical having 1 to 5 carbon atoms, an aryl radical such as phenyl, tolyl, etc., a halogen atom such as chlorine, etc., a heterocyclic radical such as morpholino, etc., a nitro radical, an amino radical, including substituted amino radicals, and the like.

Azo and azomethine type polymeric dyes are representative of a wide variety of polymeric dyes which are suitable for use in the formation of liquid developer compositions in accordance with this invention. Thiazone type polymeric dyes can be formed using N-acrylamidomethylthionine prepared as described in J. Polymer Sci., A–6, 2967 (1968) and copolymerizing with styrene or other suitable monomer to produce a blue polymeric dye. Triphenylmethane type dyes can be prepared using the polymerizable triphenylmethane base, bis(p-aminophenyl)-p-vinylphenyl carbinol, Ber. 93, 1899 (1960), and copolymerizing with styrene or some other monomer. Anthraquinone type polymeric dyes can be prepared by copolymerizing glycidyl methacrylate with styrene or acrylic esters and treating the resultant polymer with 1,4-diaminoanthraquinone to give a blue dye (C.A. 65 13853). Polymeric styryl dyes are prepared, for example, by copolymerizing vinyl phthalic anhydride with styrene or other suitable monomers and treating the product with 2-(4-hydroxyethoxystyryl)pyridinium chloride to form a yellow dye.

In addition to the various coupling procedures described above, suitable polymeric dyes can be formed by copolymerizing a dye containing a polymerizable group with a suitable monomer. For example, suitable materials can be prepared by copolymerizing azo and anthraquinone dyes containing a polymerizable group, said polymerizable group having the general formula:



$$-\underset{R}{\underset{|}{C}}=CH_2$$

wherein R represents a hydrogen atom or a lower alkyl radical having from 1 to 3 carbon atoms such as methyl, ethyl, isopropyl, etc. Suitable materials for copolymerizing with the above dyes would include the following: vinyl chloride, vinyl sulfonic acid, styrene and derivatives substituted on the benzene nucleus, acrylic acid, α-chloroacrylic acid, acrylic acid esters, methacrylic acid esters of methacrylic acid, α-chloroacrylic acid esters, esters of maleic acid, fumaric acid, crotonic acid, maleic anhydride, acrylamide or acrylonitrile, esters of vinyl alcohol and of allyl alcohol with organic acids, vinyl ethers, N-vinylcarbazole, N-vinylpyrrolidone, vinylidene chloride or vinylidene cyanide. Mixtures of the above dyes can be used as can mixtures of the above polymerizable groups.

As seen above, useful polymeric dyes can be prepared in several different ways; however, the resultant materials have features in common. The final polymeric dyes typically have a linear backbone to which are attached pendant side chains containing a chromophore. The number of side chains attached to the linear backbone can be very large, but the number of side chains containing a chromophoric moiety canbe quite small in comparison. The chromophoric moieties which are functional in the useful polymeric dyes can include azo, azomethine (including indoaniline), thiazine, triphenylmethane, styryl, anthraquinone, oxazine and the like dye moieties, with azo and azomethine dye moieties being among the preferred. The chromophoric moiety typically comprises only a minor portion of the polymeric dye. In general, the polymeric dyes used in this invention contain from about 5 to about 50% by weight of the chromophoric moiety.

Where desired, the electrostatic charge polarity of the marking particles of the present invention can be enhanced or altered by the addition of suitable charge control agents. A variety of materials can be used as charge control agents. Illustrative of suitable materials would be polyoxyethylated alkyl surfactants such as polyoxyethylated alkylamine, polyoxyethylene palmitate, polyoxyethylene stearate, etc. Other useful materials are magnesium and heavier soaps of fatty and aromatic acids as described in Beyer U.S. Pat. No. 3,417,019. Useful metal soaps include cobalt naphthenate, magnesium naphthenate, manganese naphthenate, zinc resinate, calcium naphthenate, zinc linoleate, aluminum resinate, isopropyl titanium stearate, aluminum stearate, and others many of which are also described in U.S. Pat. No. 3,259,581.

The polymeric dyes of the present invention can be used alone or in conjunction with a colorless resin. Suitable colorless resins can be used if desired to facilitate binding of the colorant to the surface to be developed. Suitable resinous materials for this purpose can be selected from a wide variety of substances. The following are illustrative of suitable materials: rosins, including hydrogenated rosins and esters of hydrogenated rosins; alkyl methacrylate copolymers having from 1 to 18 carbon atoms in each alkyl moiety, such as isobutyl methacrylate, n-butyl methacrylate copolymers, etc.; phenolic resins, including modified phenolic resins such as phenol formaldehyde resins; pentaearythritol phthalate, coumarone-indene resins; ester gum resins; vegetable oil polyamides; alkyd resins, including modified alkyd resins such as soya-oil-modified and linseed-oil-modified alkyds, phthalic, maleic and styrenated alkyds, etc., and the like. Suitable colorless resins are typically used in amounts between about 25 to 75% by weight based on the total toner composition.

Developers according to the present invention are typically prepared by forming suitable size particles of the polymeric dye and any other desired addenda and dispersing these particles in an insulating liquid. The marking particles can be prepared by various methods. Two convenient techniques for producing these particles are spray-drying or melt-blending followed by grinding. The spray-drying technique involves dissolving the polymeric dye typically in a volatile organic solvent such as dichloromethane. This solution is then sprayed through an atomizing nozzle using a substantially nonreactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent evaporates from the airborne droplets, producing particles of polymeric dye. The ultimate particle size is determined by varying the size of the atomizing nozzle and the pressure of the gasous atomizing agent. Conventionally, particles of a diameter between about ¼ and about 25 microns are used, with particles between about 1 and 15 microns being preferred, although both larger and smaller particles can be used where desired for particular developer conditions or developer compositions.

As mentioned above, suitable toner particles can also be prepared by melt-blending. This technique involves melting a polymeric dye and any of the other desired additives. The materials can be readily melted on heated compounding rolls which are also useful to stir or otherwise blend the various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant mass is then broken into small pieces and finely ground to form a free-flowing powder of toner particles. The resultant particles usually range in size from about ¼ to about 25 microns as above.

After formation of the toner particles utilizing the polymeric dyes of the instant invention, the particles are dispersed in a suitable carrier vehicle. Carrier liquids which may be used to form the present developers can be selected from a wide variety of materials. Preferably, this liquid has a low dielectric constant and a very high electrical resistance such that it will not disturb or destroy the electrostatic latent image being developed. In general, useful carrier liquids should have a dielectric constant of less than about 3, should have a volume resistivity of greater than about 10^{10} 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 typical boiling range of from about 2 to about 55° C. Other hydrocarbon solvents are also useful such as isoparaffin hydrocarbons having a boiling range of from about 150 to about 185° C. such as Isopar G (Humble Oil and Refining Co.). Additional useful carrier liquids include polysiloxanes, odorless mineral spirits, octane, cyclohexane, etc. Another property of the carrier liquid is that it cannot be a complete solvent for the polymeric dye. When colorless resins are also used, a small degree of solubility of the resin in the carrier can be tolerated.

Developer compositions can also be prepared by dissolving the present polymeric dyes in a small amount of solvent followed by dispersing this solution in a nonsolvent for the polymeric dye. Useful developer compositions prepared by suitable means typically have from about 0.1 to about 10 g. of toner material per liter of carrier liquid, with a preferred concentration of about ½ to 5 g./l.

The following examples are included for a further understanding of the invention.

EXAMPLE 1—Yellow polymeric dye

A mixture of 56 g. of styrene, 14 g. of p-aminostyrene and 2 g. of azobisisobutyronitrile is flushed with nitrogen and heated to 100° C. for 16 hours. This gives solid poly (styrene-co-p-aminostyrene) with an amine equivalent weight of 595. Next, 9 g. (.015 mole of amine) of the above copolymer are dissolved in 40 ml. of pyridine to which is added 6.5 g. (.020 mole) of α-pivalyl-4-chlorosulfonylacetanilide. The mixture is stirred for 2 hours at 65° C. and then stirred overnight at 45° C. After dilution with 50 ml. of acetone, the solution is poured slowly into water to precipitate the polymer. Reprecipitation from an acetone solution into isopropyl alcohol gives the coupler polymer, poly{α-pivalyl - 4 - [N - (4 - vinylphenyl) sulfamyl]acetanilide-co-styrene}. To a solution of 2.6 g. (0.0030 mole) of the polymeric coupler in 40 ml. of peroxide-free tetrahydrofuran is added, with stirring, 30 ml. of a sodium carbonate-sodium bicarbonate (0.5 molar each) aqueous buffer solution. To this mixture is added 0.96 g. (0.0045 mole) of 4-diethylamino-2-methylaniline hydrochloride in 5 ml. of water followed by the addition of 1.6 g. (0.006 mole) of potassium persulfate in 15 ml. of water. The mixture is stirred for one-half hour. The product is precipitated by pouring the mixture into vigorously stirred water. The polymeric dye is collected, partially dried, and redissolved in 40 ml. of tetrahydrofuran. The solution is filtered and the polymer again precipitated in water. The yield of poly{α(4-diethylamino-2-methylphenylimino) - α - pivalyl - 4 - [N-(4-vinylphenyl)sulfamyl]acetanilide-co-styrene} is 2.8 g. The absorption maximum of a chloroform solution of this yellow dye is 450 nm.

EXAMPLE 2—Magenta polymeric dye

A mixture of 126 g. of styrene and 14 g. of p-aminostyrene are copolymerized as in Example 1. To 20 g. (0.017 mole) of the poly(styrene-co-p-aminostyrene) in 100 ml. of tetrahydrofuran and 3 ml. of pyridine is added 6.2 g. (0.018 mole) of 1-phenyl-3-(2-chlorocarbonylbenzamido)-5-pyrazolone in 60 ml. of tetrahydrofuran at 10° C. The mixture is stirred at 40 to 50° C. for 2 hours and poured into water to precipitate the product. Reprecipitation from methylene chloride solution gives 15 g. of the coupler, poly[N-(4-vinylphenyl)-N'-(1-phenyl-5-pyrazolon-3-yl)phthalamic acid-co-styrene]. This polymeric coupler is converted to a magenta dye, poly{N-(4-vinylphenyl)-N'-[4 - (4 - diethylamino-2-methylphenylimino) - 1 - phenyl-5-pyrazolon-3-yl]phthalamic acid-co-styrene}, in the same manner as described for the yellow dye of Example 1. The absorption maximum of a chloroform solution of this polymeric dye is 540 nm.

EXAMPLE 3—Cyan polymeric dye

A solution of 45 g. of styrene, 5 g. of N-(3,5-dichloro-2-hydroxy-4-methylphenyl)acrylamide and 2.5 g. of azobisisobutyronitrile in 20 ml. dimethylformamide is flushed with nitrogen and heated at 60° C. for 20 hours. The resultant copolymer, poly[N-(3,5-dichloro-2-hydroxy - 4-methylphenyl)acrylamide-co-styrene], is recovered by precipitation in methanol. The polymeric coupler is converted to a cyan dye, poly{6-acrylamido-2-chloro-N-[(4-diethylamino-2-methyl)phenyl] - 3 - methyl - p - benzoquinone imine-co-styrene}, in accordance with the coupling procedure of Example 1. The polymeric dye in a chloroform solution has an absorption maximum at 665 nm.

EXAMPLES 4–6

Each of the dyes produced according to Examples 1 through 3 is dissolved in a separate portion of dichloromethane using 1 g. of dye in about 84 g. of solvent. The solution is then spray-dried through a pneumatic atomizing nozzle using nitrogen gas at 10 p.s.i.g. as the atomizing gas. The solvent is dried off at room temperature to produce toner particles having an average particle size of about 2 microns. Developer compositions A, B and C are prepared using the toner particles containing the polymeric dyes of Examples 1, 2 and 3, respectively. A 0.5 g. portion of the spray-dried toner particles is dispersed in 250 ml. of an Isopar G (supra). Each of the three developers is then used to develop an electrostatic charge pattern on an electrophotographic element. This element is comprised of a conductive support having thereon a photoconductive layer containing an organic photoconductor dispersed in a polycarbonate binder. This element is uniformly charged by subjecting it to a negative polarity corona discharge in the dark. The element is given an imagewise exposure which causes dissipation of the charge in the exposed areas thus forming an electrostatic charge pattern. The element is then placed into contact with one of the above developers. This procedure is repeated for all three developers using a different element each time. The resultant positive images are not fixed; however, exposure to dichloromethane vapor for a brief period causes the images to be fixed. All three images are of good quality. The above procedure is repeated with the yellow developer A after reducing the concentration of 0.5 g. of dye per liter of Isopar G. The diluted developer still produces images of acceptable density. Developer C remains stable for over a month with only a slight amount of a sediment appearing. This settling does not appear to be the result of agglomeration, as the settled particles are readily redispersed by shaking.

EXAMPLE 7—Azo polymeric dyes

The polymeric coupler, poly{α - pivalyl-4-[N-(4-vinylphenyl)-sulfamyl]acetanilide-co-styrene}, of Example 1 is added to a molar excess of an alkaline aqueous solution of 4-diethylaminobenzene-diazonium zinc chloride double salt. The mixture is stirred for about 30 minutes at room temperature and a yellow polymeric dye (No. 4), poly{α-(4-diethylaminophenylazo) - α - pivalyl-4-[N-(4-vinylphenyl)sulfamyl]acetanilide-co-styrene}, is precipitated. This same procedure is repeated using the polymeric coupler of Example 2 to produce a magenta dye (No. 5), poly{N-4 - vinylphenyl) - N′ - [4-(4-diethylaminophenylazo) - 1 - phenyl - 5 - pyrazolon - 3 -yl]phthalamic acid-co-styrene}. Similarly, the polymeric coupler, poly[N-(3, 5-dichloro-2-hydroxy-4-methylphenyl) - acrylamide - co-styrene], of Example 3 is treated with a molar excess of the above diazonium salt under alkaline conditions to form a cyan dye (No. 6), poly[6-acrylamido - 2 - chloro-4 - (4 - diethylaminophenylazo) - 3 - methylphenol - co-styrene]. Polymeric dyes Nos. 4, 5 and 6 are each dissolved in dichloromethane and spray-dried as in Examples 4–6 to produce dye particles. About ½ g. of dye is dispersed in 250 ml. of Isopar G to form three developer compositions D, E and F, respectively. Each of these developers is then used to develop an electrostatic charge pattern as described in Examples 4–6. The resultant images are all of good quality.

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 an electrophotographic process wherein an electrostatic charge pattern is formed and liquid developed, the improvement comprising using a liquid developer comprised of an electrically insulating hydrocarbon carrier liquid having a dielectric constant of less than about 3 and a volume resistivity of greater than 10^{10} ohm-cm., said liquid having dispersed therein marking particles comprising at least one polymeric dye, said polymeric dye consisting essentially of the reaction product of (1) a polymeric coupler having a linear backbone chain to which are attached pendant side chains containing a coupling unit selected from the group consisting of an open chain active methylene coupling moiety, a cyclic active methylene coupling moiety, and a phenolic nucleus bearing an active methine group, and (2) a member selected from the group consisting of diazonium salts and oxidation products of color coupling aromatic primary amine developing agents, said marking particles having a particle size within the range of from about 0.25 to about 25 microns and wherein said marking particles are present in said liquid developer in a concentration of about 0.1 to 10 grams per liter of developer.

2. The invention as described in claim **1** wherein said oxidation product developing agents are selected from the group consisting of oxidized p-phenylene diamines and oxidized p-aminophenols.

3. The invention as described in claim **1** wherein said diazonium salt is a benzene diazonium salt.

4. The invention of claim **1** wherein said diazonium salt is a p-amino-benzene diazonium salt.

5. The invention of claim **1** wherein said polymeric dye is comprised of a linear backbone chain formed of a vinyl polymer.

6. The invention of claim **1** wherein said linear backbone chain contains polymerized monomers selected from the group consisting of styrene, alkyl acrylates having from about 4 to 18 carbon atoms in the alkyl moiety, vinyl acetate, vinyl chloride, vinyl alkyl ether having from about 4 to 18 carbon atoms in the alkyl moiety, alkyl methacrylate having from about 4 to 18 carbon atoms in the alkyl moiety and mixtures thereof.

7. The invention of claim **1** wherein said marking particles contain from about 25 to 75% by weight of a colorless resin.

8. The invention of claim **1** wherein said polymeric dye is selected from the group consisting of

poly{6-acrylamido-2-chloro-N-[(4-diethylamino-2-methly)phenyl]-3-methyl-p-benzoquinone imine-co-styrene},
poly{N-(4-vinylphenyl)-N′-[4-(4-diethylamino-2-methylphenylimino)-1-phenyl-5-pyrazolon-3-yl]-phthalamic acid-co-styrene},
poly{α-(4-diethylamino-2-methylphenylimino)-α-pivalyl-4-[N-(4-vinylphenyl)sulfamyl]-acetanilide-co-styrene},
poly{α-(4-diethylaminophenylazo)-α-pivalyl-4-[N-(4-vinylphenyl)sulfamyl]acetanilide-co-styrene},
poly{N-(4-vinylphenyl)-N′-[4-(4-diethylaminophenylazo)-1-phenyl-5-pyrazolon-3-yl]-phthalamic acid-co-styrene},
poly[6-acrylamido-2-chloro-4-(4-diethylaminophenylazo)-3-methylphenol-co-styrene].

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