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(54) **SOLVATION-BASED CHARGE DIRECTION OF LIQUID ELECTROPHOTOGRAPHIC DEVELOPER COMPOSITIONS**

EINE AUF SOLVATATION BASIERENDE LADUNGSSTEUERUNG VON
ELEKTRO-PHOTOGRAPISCHEN FLÜSSIGENTWICKLERZUSAMMENSETZUNGEN

DIRECTION DE CHARGE FONDEE SUR LA SOLVATATION DE COMPOSITIONS DE REVELATEUR
ELECTROPHOTOGRAPHIQUE LIQUIDES

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EP-A- 0 376 460 **JP-A- 1 211 711**
JP-A- 59 087 463 **US-A- 3 753 760**
US-A- 4 156 034 **US-A- 4 957 844**
US-A- 4 971 833

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Description

[0001] The present invention relates generally to the field of color electrophotography, and more particularly relates to an improved method for charge directing liquid electrophotographic developer compositions, and to novel toner and developer compositions produced thereby.

[0002] Preparation of printed images by electrophotographic, or "xerographic", processes involves coating a selected substrate, or xerographic plate (typically comprised of metal, glass or plastic), with a photoconductive insulating material such as selenium, and then providing an electrostatic charge on the photoconductive surface, e.g., by ionization from a corona discharge. A light image is then focused onto the charged surface, which discharges or lowers the potential of the irradiated areas, while leaving the remainder of the surface charged. The electrostatic image so formed is then made visible by application of a suitable developing composition, which may be in either dry or liquid form.

[0003] Conventional liquid developer compositions comprise a dispersion of pigment particles in an insulating carrier liquid. Application of such a composition to the substrate carrying the electrostatic image results in migration of charged pigment particles to the substrate surface and deposition thereon in conformance with the electrostatic image. The developed image is then transferred to another substrate such as paper. (In some cases, it is desirable to eliminate the intermediate step of image transfer, i.e., so that the developed image is directly produced upon the final surface; see, e.g., U.S. Patent No. 3,052,539 to Greig.)

[0004] Liquid developers for use in multicolor image development are relatively recent, and are comprised of colorant embedded in a thermoplastic resin core. These "toner" particles are then dispersed in an insulating carrier medium as above. Like compositions used in black-and-white electrophotography, these developer compositions additionally contain "charge directors", or "charge control agents", to control the charge acquired by the toner particles in the insulating liquid.

[0005] When a color image is to be produced electrophotographically, the above-described charging, exposure, and development steps are carried out separately in succession for each of the constituent colors of the image using a correspondingly colored toner. In some color printing processes, each of the color images is transferred from the electrophotographic member to a print substrate after development and prior to formation of the next color image. This process, however, requires extremely accurate registration of the successive color images on the substrate to which they are transferred in order to obtain a high-quality composite image.

[0006] Another color printing process, and the process currently in use commercially, is a four-color liquid electrophotographic process known as "consecutive color toning" or "consecutive multicolor image development". This process involves: (1) charging a photoconductive ("pc") surface; (2) impressing a first latent image on the surface by exposure through a colored transparency; (3) developing the image by contacting the pc with a liquid developer composition of a first color, typically yellow; and (4) discharging the pc surface. The steps are then repeated in sequence, typically using magenta, cyan, and black developer compositions, i.e., the cyclic process is repeated until the colored image is complete.

[0007] There are a number of problems which are frequently encountered in electrophotographic color processes. These include: toner instability; background staining, i.e., the appearance of toner in uncharged, non-image areas (a problem which is ubiquitous in zinc oxide and other positive toner systems); poor image resolution (i.e., poor edge acuity); poor image density resulting from insufficient deposition of toner particles in intended image regions; and "image" or "character" staining, where a second process color overtones the first image in regions where portions of the first image should have been discharged but were not. An additional problem with current electrophotographic color development processes is the need for multiple washing and drying steps during development, e.g., as described by Alexandrovich et al. in U.S. Patent No. 4,701,387.

The inventors therein propose a solution wherein the developed surface is rinsed with a polar liquid after each development step. It is suggested that application of a polar rinse liquid neutralizes and solvates residual counterions deriving from charge directors and stabilizers present in the liquid developer. The method is somewhat time-consuming and unwieldy (it is recommended in the '387 patent that "after each development step and before the next developer is applied, the developed image is rinsed..... After rinsing, the rinse liquid is removed from the photoconductive element by drying, wiping or other method...."; see column 2, lines 62-67).

[0008] JP-A-59 87463 describes developer compositions comprising a dispersion of toner particles in an electrically insulating liquid wherein the toner particles comprise a pigment and a polyolefin type resin having carbonyl groups. A charge director may be added to the electrically insulating liquid to promote the developing properties.

[0009] EP-A-0 376 460 describes liquid toners for developing photographic images containing dispersed toner particles which comprise a thermoplastic resinous core which is chemically anchored to an amphipathic copolymer steric stabiliser containing covalently attached groups of a co-ordinating compound. These groups are in turn capable of forming covalent links with organo-metallic charge directing compounds.

[0010] US-A-4156034 describes a liquid developer for electrophotography comprising a colouring agent, a resistivity controlling agent and a coating agent which is a copolymer containing a carboxyl or carboxylate group.

[0011] The invention herein now provides a novel method for charge directing liquid electrophotographic developer compositions which addresses the aforementioned problems. The invention is premised on the generation of an extremely stable charge director/toner complex, which in turn provides a very stable developer composition of exceptionally high particle-mediated conductivity and charge. The present method and associated compositions provide for a streamlined development process and enable preparation of a final electrophotographic print of unexpectedly high quality.

Electrophotographic processing, generally:

[0012] R.M. Schaffert, Electrophotography (London: Focal Press, 1975), provides a comprehensive overview of electrophotographic processes and techniques. Representative references which relate to the field of color electrophotography, specifically, include U.S. Patent Nos. 3,060,021 to Greig, 3,253,913 to Smith et al., 3,285,837 to Neber, 3,337,340 to Matkan, 3,553,093 to Putnam et al., 3,672,887 to Matsumoto et al., 3,687,661 to Sato et al., and 3,849,165 to Stahly et al. References which describe electrophotographic toners and developers include U.S. Patent Nos. 4,659,640 to Santilli (which describes a developer composition containing dispersed wax), 2,986,521 to Wielicki, 3,345,293 to Bartoszewicz et al., 3,406,062 to Michalchik, 3,779,924 to Chechak, and 3,788,995 to Stahly et al.

[0013] Charge directors: References which relate to charge directors include U.S. Patent Nos. 3,012,969 to van der Minne et al. (polyvalent metal organic salts in combination with an oxygen-containing organic compound), 3,411,936 to Rotsman et al. (metallic soaps), 3,417,019 to Beyer (metallic soaps and organic surface active agents), 3,788,995 to Stahly et al. (various polymeric agents), 4,170,563 to Merrill et al. (phosphonates), 4,229,513 (quaternary ammonium polymers), 4,762,764 to Ng (polybutene succinimide, lecithin, basic barium petroleum sulfonates, and mixtures thereof), and Research Disclosure, May 1973, at page 66.

Image staining in consecutive color toning:

[0014] U.S. Patent No. 4,701,387 to Alexandrovich et al., discussed in the preceding section, and U.S. Patent No. 3,337,340 to Matkan, are relevant insofar as each of these references relates to the problem of image staining in consecutive color toning.

[0015] Toner resins: U.S. Patent No. 3,806,430 to Sato et al. describes the use of thermosetting binder resins such as polyisocyanate-cured alkyd resins, epoxy ester resins and copolymers of a vinyl monomer and styrene, acrylic and methacrylic esters or the like, alkyd resins cured with melamine formaldehyde, or benzoguanimine formaldehyde, drying oil modified alkyd resins, and epoxy ester resins cured with a catalyst. U.S. Patent No. 3,779,924 to Chechak describes alkyd and modified alkyd resins (e.g., soya oil-modified and linseed oil-modified alkyds) and phenolic and modified phenolic resins (phenol formaldehyde resins and derivatives thereof). U.S. Patent No. 4,845,003 to Kiriu et al. describes the use of acrylic, styrene-butadiene, epoxy, and polyester resins. U.S. Patent No. 3,345,293 to Bartoszewicz et al. describes a rosin-modified phenolformaldehyde resin, a polystyrene-based resin, and an epoxy resin. U.S. Patent No. 3,411,936 to Roteman et al. describe resinous binders that are preferably "substantially uncharged" (col. 2, line 70). U.S. Patent No. 3,788,995 to Stahly et al. describe toner resins containing polar moieties such as sulfoalkyl acrylate, sulfoalkyl methacrylate, and the like. U.S. Patent No. 4,229,513 to Merrill et al. describes halogenated polymers designed to serve as negatively charged binder resins. U.S. Patent No. 4,762,764 to Ng et al. describe thermoplastic toner resins such as poly(methyl methacrylate), poly(methyl acrylate), poly(ethyl methacrylate), and the like.

[0016] Surface-bound polymers: U.S. Patent No. 4,925,766 to Elmasry et al. describes a developer composition in which ion exchange polymers are bound to the surface of the dispersed toner particles, and wherein the chelation sites on the polymers are apparently designed to complex with a charge director present in the carrier liquid. U.S. Patent No. 4,946,753 to Elmasry et al. also describes such ion exchange resins used in conjunction with toner.

Disclosure of the Invention

[0017] Accordingly, it is a primary object of the invention to address the above-mentioned deficiencies of the prior art.

[0018] It is another object of the invention to provide a solvation-based method of providing charge on toner particles in a liquid electrophotographic developer composition.

[0019] It is still another object of the invention to provide a solvation-based method for charging toner particles in a liquid electrophotographic developer composition which involves incorporating into the resinous phase of the toner particle a polymer containing specific solvation sites effective to solvate a selected metal salt used as the charge director.

[0020] The invention makes use of a toner for incorporation into a liquid electrophotographic developer composition, wherein the toner is formulated with a resinous phase containing a polymer having such specific solvation sites.

[0021] It is still a further object of the invention to provide a liquid electrophotographic developer composition con-

taining such a toner and charge director dispersed in an insulating carrier liquid.

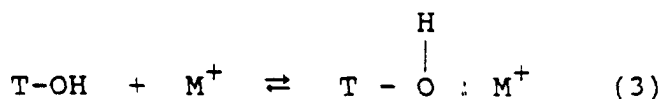
[0022] Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention.

[0023] The above objects are accomplished in accordance with the present invention by providing a solvation-based method for charging toner particles in a liquid electrophotographic developer composition. The method is premised on the importance of a highly stable, solvated toner particle/charge director complex. In contrast to prior art methods wherein toner particles are charged via simple adsorption of the charge director (see, e.g., Schaffert, supra, at pages 564-566), proton transfer, or ion exchange, the present method involves solvation, that is, charged toner particle complexes are formed by solvation. This is accomplished by incorporating a polymer having carboxyl groups as specific solvation sites into the resinous phase of the toner. The solvation sites and the metal salt which serves as the charge director are both selected so that very stable, charged toner complexes are formed, i.e., complexes of (i) the cationic, metal component of the charge director and (ii) the toner particle itself.

[0024] By way of background, solvation of cations such as metal ions is characterized by the formation of well-known aquo-complexes as



The exothermicity of complex formation and therefore the formation constant is related to the enthalpies of hydration (see Table 1, in Part (B) of the Detailed Description). Although precise thermodynamic values are not readily available for alcohols, carboxylic acids, and the like, a parallel correlation exists. As a consequence, when toner particles are interfaced with specific charge directors, the following equilibrium relationships are believed to be applicable:

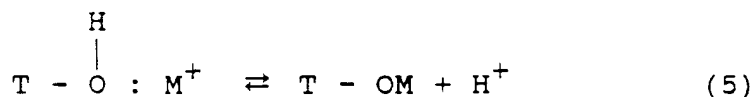


where X^- is the counterion and T the toner particle. This reaction is the equivalence of hydration of metal ions from the gas phase. That is, the complexation (i.e., charge direction) reaction is driven in solvents of low dielectric by solvation with sites on the toner particle surface. The most preferred solvation reactions should be quite exothermic and are characterized by large negative enthalpy. From inspection of the equation

$$\log K = \frac{T\Delta S - \Delta H}{2.3 RT} \quad (4)$$

as the enthalpy of solvation becomes increasingly negative, the equilibrium constant K for the solvation reaction becomes larger. In other words, the formation of the solvated complex becomes increasingly favorable.

[0025] As ionizable sites are employed on the toner particle, the reaction described in Equation (3) may indeed proceed according to the equation



↓

loss of particle charge

and result in a loss in developer conductivity and consequent instability. As will be described in further detail herein-

below, addition of the conjugate acid of the counterion suppresses this event and thus stabilizes the developer.

[0026] The resinous phase of the toner is formulated so that it contains a polymer having the aforementioned solvation sites, which are then present on the surface of the toner particle and thus exposed to and available to solvate charge director in the liquid developer. In an alternative embodiment, the resinous phase of the toner is formulated such that it contains monomeric and polymeric species with such solvation sites. It must be emphasized that preferred solvating materials are those which will exothermically solvate the cationic component of the charge director so as to maximize the stability of the resulting charged toner complex and minimize the presence of free, unassociated charge director in solution.

[0027] The invention provides a developer composition which contains such toner particles dispersed in an insulating carrier liquid together with a selected metal salt, the metal being selected from aluminium, magnesium, chromium or iron to serve as the charge director.

[0028] Other aspects of the invention include:

processes for manufacturing the above-described toner and developer compositions; and consecutive color toning processes making use of solvation-based charge direction.

A. Definitions:

[0029] "Toner" as used herein is intended to denote the resinous, colored particles (referred to sometimes herein as "toner particles") which ultimately form the electrophotographic image on the photoconductive (pc) surface.

[0030] By "developer composition" as used herein is meant a dispersion of toner and charge director in a selected insulating carrier liquid. The developer composition may contain a number of additional components as will be described below.

[0031] "Particle-mediated" conductivity and charge is intended to mean that virtually all of the conductivity and charge in a developer composition derive from the charged toner particles and not from free, unassociated salts which may be present in solution (i.e., from unassociated charge director or other ionizable species). The developer compositions of the invention display very high particle-mediated conductivity and charge and very low continuous phase conductivity.

[0032] "Consecutive color toning" as used herein is intended to mean an electrophotographic development process involving repetition of charging and development steps with more than one color (as outlined in the Background Section above) so as to provide a multicolor final image. The process is also sometimes referred to herein as "consecutive multicolor image development".

[0033] "Background staining" is a problem which can arise in any electrophotographic process. As used herein the term has its art-recognized meaning and refers to the problem wherein toner appears in unintended, uncharged, non-image areas.

[0034] "Image staining" is a problem which is specific to consecutive color toning, and similarly has its art-recognized meaning as used herein. The problem involves overtoning by a second or subsequent process color of an earlier color image in regions where portions of the earlier image should have been discharged but were not. "Image staining" is also sometimes referred to herein and in the art as "character staining".

[0035] By "specific solvation sites" is meant moieties present in a material contained within the toner resin and effective to solvate the metal salt or salts which will serve as the charge director. "Solvation" is used according to its conventional meaning, i.e., to indicate the association or combination of a solute unit (the charge director, in the present case) with a solvent species (the solvation sites on the toner surface herein). See, e.g., The McGraw-Hill Encyclopedia of Science and Technology, New York: McGraw-Hill, 1987. As discussed therein, solvation may involve chemical or physical interaction, or both, and may vary in degree from a loose complex to a distinct, tightly complexed structure. In the present invention, the solvation sites in the charge director are preferably selected such that solvation of the charge director is a highly exothermic process and gives rise to a very stable, charged toner particle.

[0036] By "carboxyl" as used herein is meant the carboxylic acid moiety -COOH.

B. Overview of the Novel Method:

[0037] As noted above, the focus of the present invention is on a solvation-based mechanism for providing charge on toner particles contained in a liquid electrophotographic developer composition.

[0038] The present invention thus involves a novel method of creating very stable charge director/toner complexes. As explained in co-pending, commonly assigned U.S. Patent Application Serial No. 07/464,896, incorporated by reference above, the stability of the charge director/toner complex has been found to be of the utmost importance in liquid electrophotography. In the '896 application, the focus was on the use of toners containing surface ion exchange sites effective to form extremely stable, ionic complexes with the metal salts that serve as the charge director. In the present application, the focus is on a solvation interaction, i.e., the cationic, metal component of the charge director is complexed via solvation to the surface of the toner particle. As explained in the '896 application, if the toner and the cationic

component of the charge director are such that complexation between the two components is heavily favored, as here, virtually all of the charge director will be present in complexed form, and there will be substantially no unassociated charge director in solution. In the present case, the solvation sites and the charge director are selected such that solvation is a highly exothermic process, giving rise to an extremely stable complex. Examples of particular toner materials and charge directors which may be used in this manner, to provide an extremely stable charged toner particle, are set out in Part (C) of this section.

[0039] In general, the solvation sites may derive from one or more polymers and optionally one or more monomeric species incorporated into the toner resin. Indeed, the toner resin itself may be a polymer containing the desired solvation sites. It is preferred that the charge director be either a pH-neutral salt (i.e., a metal salt of a strong acid) or a salt that contains a self-stabilized counterion, as will be described in the next section. Also, an amount of acid, preferably the acid form of the charge director's counterion, is added into the developer composition to force equilibrium towards the non-ionized form of the species (the added acid will thus give rise to COOH groups as opposed to the ionized COO⁻ species).

[0040] The charge director should also be selected with a view towards maximizing the stability of the "solvated" charged toner particle complex. More specifically, the charge director is a metal salt containing a metal ion selected from aluminium, magnesium, chromium and iron, which will give rise to a highly exothermic solvation interaction with the aforementioned solvation sites. These metals have large negative enthalpies of hydration. The following table illustrates the enthalpies of hydration of some ions:

Enthalpies of Hydration* of Some Ions (kJ mol ⁻¹)					
H ⁺	-1091	Ca ²⁺	-1577	Cd ²⁺	-1807
Li ⁺	-519	Sr ²⁺	-1443	Hg ²⁺	-1824
Na ⁺	-406	Ba ²⁺	-1305	Sn ²⁺	-1552
K ⁺	-322	Cr ²⁺	-1904	Pb ²⁺	-1481
Rb ⁺	-203	Mn ²⁺	-1841	Al ²⁺	-4665
Cs ⁺	-264	Fe ²⁺	-1946	Fe ³⁺	-4430
Ag ⁺	-473	Co ²⁺	-1996	F ⁻	-515
Tl ⁺	-326	Ni ²⁺	-2105	Cl ⁻	-381
Be ²⁺	-2494	Cu ²⁺	-2100	Br ⁻	-347
Mg ²⁺	-1921	Zn ²⁺	-2046	I ⁻	-305

*Absolute values are based on the assignment of $-1091 \pm 10 \text{ kJ mol}^{-1}$ to H⁺ (cf. H.F. Halliwell and S.C. Nyburg, *Trans. Faraday Soc.*, 1963, 59: 1126). Each value probably has an uncertainty of at least $10n \text{ kJ mol}^{-1}$, where n is the charge of the ion.

[0041] (F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, New York: John Wiley & Sons, 1972.)

[0042] The present invention involves solvation by materials other than water, and thus does not involve hydration as such. Enthalpies of solvation will, however, typically correlate with these enthalpies of hydration. The enthalpy of solvation here (i.e., of the cationic, metal component of the charge director by the solvation sites) is generally a large negative value (i.e., the solvation reaction involves an enthalpy of solvation that is more negative than about -50 kJ/mole, preferably more negative than about -100 kJ/mole, most preferably more negative than about -500 J/mole). As may be deduced from the above table, small, highly charged metal ions give rise to the most exothermic hydration or solvation reactions. (See the CRC Handbook of Chemistry and Physics, 67th Ed., at page F-157.) Such metals are, accordingly, preferred charge directors for use in conjunction with the present invention.

[0043] Selection of toner solvation sites and a charge director that will give rise to a very stable toner/ charge director complex in turn enables preparation of a liquid developer composition in which (1) virtually all of the solution's conductivity and charge derives from the toner particles, (2) the toner is highly charge-stabilized, i.e., will retain charge over a prolonged period of time, and (3) the toner particles are themselves highly charged. As emphasized throughout this application, these features yield a final image of exceptionally high quality, i.e., with respect to image density, edge acuity, and the like, and also enable use of the toner in a consecutive color process without need for intermediate processing steps which have heretofore been necessary to remove residual toner in unwanted, "non-image" areas.

C. Novel Developer Compositions:

[0044] In addition to the aforementioned method, the present invention encompasses novel developer compositions comprising a toner. The toner is useful for formulating a liquid developer composition in which conductivity and charge are both substantially particle-mediated, as explained above. As with currently available toner compositions, the toner of the invention includes two basic components: (a) resin; and (b) colorant.

[0045] However, the present invention involves, as noted above, the incorporation of a polymer containing specific solvation sites into the resinous phase of the toner particle.

[0046] Materials which may be incorporated into the resinous phase of the toner particle, as discussed in the preceding section, may be either monomeric or polymeric or polymeric and monomeric, and have carboxyl sites as specific solvation sites. Examples of particularly preferred polymers for use herein are ethylene-acrylic acid copolymers, ionomers and mixtures thereof. It will be appreciated by those skilled in the art, however, that a wide range of polymeric materials may be used herein, so long as the selected material contains carboxyl groups and enables solvation of the charge director to give a highly stable toner/charge director complex, and does not interact in a deleterious manner with any of the other components of the developer composition.

[0047] It is generally preferred that the materials containing specific solvation sites be non-ionized under the conditions used in electrophotographic development, i.e., such that at least about 80%, more preferably at least about 90%, and most preferably at least about 95%, of the solvation sites are not ionized during ordinary conditions of storage and use. As the carboxyl group solvation sites are readily ionizable species, acid is included in the developer composition so that the ionization of the carboxyl groups is suppressed. Typically, this will involve adding the acid form of the charge director counterion. For example, where the charge director counterion is diisopropylsalicylate (DIPS), one would add a sufficient quantity of diisopropylsalicylic acid to force the equilibrium to the point where the carboxylic acid groups are in substantially un-ionized form.

[0048] As will be pointed out below, it is also desirable, to ensure the formation of a stable toner/charge director complex, that the metal ion which serves as the cationic component of the charge director is one that will be solvated exothermically by aforementioned material. Aluminum, magnesium, chromium and iron have very negative enthalpies of hydration and thus, herein, give rise to an enthalpy of solvation that is more negative than about -500 kJ/mol, more preferably more negative than about -1000 kJ/mol. Such values will give rise to a charged toner complex which is extremely stable, in turn enabling preparation of a liquid developer composition having a virtually indefinite shelf-life. This aspect of the invention represents a tremendous advantage relative to currently available developer compositions, which can be relatively unstable and have a finite shelf-life.

[0049] The colorants which may be used in the toner can include virtually any pigments, dyes or stains which may be incorporated in the toner resin and which are effective to make visible the electrostatic latent image. Examples of suitable colorants include: Phthalocyanine blue (C.I. 74160), Dine blue (C.I. 21180), Milori blue (an inorganic pigment equivalent to ultramarine) as cyan colorants; Brilliant carmine 6B (C.I. 15850), Quinacridone magenta (C.I. Pigment Red 122) and Thio indigo magenta (C.I. 73310) as magenta colorants; benzidine yellow (C.I. 21090 and C.I. 21100) and Hansa Yellow (C.I. 11680) as yellow colorants; organic dyes; and black materials such as carbon black, charcoal and other forms of finely divided carbon, iron oxide, zinc oxide, titanium dioxide, and the like. It should also be noted that the polymers for use in conjunction with the present invention tend to dissolve the aforementioned pigments and dyes readily and are thus quite advantageous in that regard.

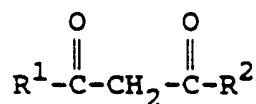
[0050] The developer compositions of the invention contain the aforementioned toner, together with a selected charge director, as described above, dispersed in an insulating carrier liquid.

[0051] One class of metal salts useful as charge directors herein is described in parent U.S. Patent Application Serial No. 07/464,896, filed 16 January 1990, incorporated by reference above. Those charge directors include as a counterion the intramolecularly stabilized anion of an ortho-hydroxy aromatic acid, e.g., salicylic acid or a derivative thereof. By a salicylic acid "derivative" applicant intends to include salicylic acid substituted with one to four, typically one to two, substituents independently selected from the group consisting of lower alkyl (1-6C), lower alkoxy (1-6C), halogen, amino, hydroxy, nitro and sulfonate.

[0052] These charge directors may typically be represented by the formula $(RO^-)_x M^{+n} (AA^-)_y$ in which M is a metal atom, AA^- represents the anion of the ortho-hydroxy aromatic acid, and R is selected from the group consisting of $R'CO-$, C_1-C_{15} alkyl, n is 2, 3 or 4, and x and y are integers the sum of which, clearly, is n. The metal atom "M" may be divalent, trivalent or tetravalent, and is selected from aluminium, magnesium, chromium and iron. (In one particularly exemplary embodiment, AA^- is diisopropyl salicylate (DIPS), R is $C_{10}H_{21}CO-$ (i.e., R' is $C_{10}H_{21}$), n is 3, x is 1 or 2, and y is 1 or 2.)

[0053] A second class of charge directors useful herein is described in detail in parent U.S. Patent Application Serial No. 07/546,044, also incorporated by reference. These charge directors are of the formula $(X^-)_a M^{+n} (AA^-)_b$ in which M is a metal atom as described above, AA^- represents the anion of an ortho-hydroxy aromatic acid as described with regard to the charge directors of Serial No. 07/464,906, X^- represents the anion of an α,β -diketone, n is 2, 3 or 4, and a and b are integers the sum of which is equal to n, with the proviso that neither a nor b is 0.

[0054] As described in U.S. Serial No. 07/546,044, the anion X^- represents the anion of an α,β -diketone, one which preferably has the formula:



wherein R¹ and R² are independently selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, haloalkyl, aryl, alkaryl, and haloaryl. If alkyl, alkenyl, alkynyl, cycloalkyl, or haloalkyl, the substituent preferably contains from about 1 to about 12 carbon atoms, more preferably from about 1 to about 6 carbon atoms (wherein the latter type of moiety is sometimes referred to herein as "lower" alkyl, alkenyl, alkynyl, etc.). If aryl, alkaryl, or haloaryl, the substituent preferably contains one to about three rings, more preferably, one to two rings, and most preferably is monocyclic. An example of a particularly preferred α,β -diketone is acetyl acetone, i.e., wherein R¹ and R² are both methyl.

[0055] The developer compositions of the invention contain toner and developer dispersed in an electrically insulating carrier liquid as well-known in the art. The liquid is typically oleophilic, stable under a variety of conditions, and electrically insulating. That is, the liquid has a low dielectric constant and a high electrical resistivity so as not to interfere with development of the electrostatic charge pattern. Preferably, the carrier liquid has a dielectric constant of less than about 3.5, more preferably less than about 3, and a volume resistivity greater than about 10⁹ ohm-cm, more preferably greater than about 10¹⁰ ohm-cm. Examples of suitable carrier liquids include halogenated hydrocarbon solvents such as carbon tetrachloride, trichloroethylene, and the fluorinated alkanes, e.g., trichloromonofluoromethane and trichlorotrifluoroethane (sold under the trade name "Freon" by the DuPont Company); acyclic or cyclic hydrocarbons such as cyclohexane, n-pentane, isooctane, hexane, heptane, decane, dodecane, tetradecane, and the like; aromatic hydrocarbons such as benzene, toluene, xylene, and the like; silicone oils; molten paraffin; and the paraffinic hydrocarbon solvents sold under the names Isopar G, Isopar H, Isopar K and Isopar L (trademarks of Exxon Corporation). The foregoing list is intended as merely illustrative of the carrier liquids which may be used in conjunction with the present invention, and is not in any way intended to be limiting.

C. Toner and Developer Manufacture:

[0056] Toner is prepared by admixing resin and colorant at an elevated temperature, followed by dry comminution. The intermediate particles so provided are then subjected to liquid attrition to give the final toner particles. The following exemplifies such a process:

Resin and colorant are admixed at a temperature in the range of about 70°C to 200°C. A two-roll mill, an extruder, an intensive mixer or the like, is used to ensure complete mixing. The admixture is then comminuted dry, i.e., without addition of liquid, to give intermediate particles typically averaging 30 mills in diameter or less. This dry comminution step is carried out in a jet mill, a hammer mill, or the like. The intermediate particles so obtained are then subjected to liquid attrition in a selected attrition liquid to give the final toner particles. The liquid used for attrition is typically selected from the same class of liquids useful as the carrier liquid for the developer composition, as will be described below.

The developer compositions of the invention -- prepared by dispersion of toner and charge director in the insulating carrier liquid -- can contain additional materials, e.g., an incompatible phase such as a wax, which is preferably incorporated into the toner at the initial stage of manufacture, i.e., admixed with the colorant, resin, etc., in step (a) (see related application Serial No. 07/464,896). The developer can also contain an antistain agent to reduce the problem of background staining, as discussed in the parent application hereto; again, the antistain agent is preferably incorporated into the composition at the stage of toner manufacture. The developer composition can also contain other materials as known in the art, e.g., dispersants, stabilizers and the like.

D. Consecutive Multicolor Image Development:

[0057] Briefly, a consecutive multicolor image development process (or a "consecutive color toning" process) using the materials of the invention may be carried out as follows.

[0058] The surface of a photoconductive insulating layer on a relatively conductive substrate is charged, and an initial electrostatic charge pattern (or "latent image") is formed on that surface by exposure through a colored transparency. This latent image is then developed with a liquid developer composition of a first color, i.e., comprising toner formulated with a first colorant, typically yellow. The photoconductive layer is then discharged, either optically or non-optically, i.e., via a corona. These steps are then repeated in sequence with developer compositions of different colors, typically (in order) magenta, cyan and black, at which point the developed image may, if desired, be transferred to another substrate, e.g., paper. Using the toner and developer compositions of the invention, i.e., compositions which involve a solvation interaction between the surface of the toner particles and the incorporated charge director, it is possible to carry out the aforementioned sequence of steps without any intermediate processing steps, i.e., rinsing,

drying or the like. These steps have typically been necessary in the prior art, as exemplified by the Alexandrovich et al. patent, cited supra, to address the problem of image staining.

[0059] As illustrated by the above disclosure and the examples which follow, the compositions and processes of the invention address and overcome a number of significant obstacles heretofore present in color electrophotographic image development.

[0060] The following examples illustrate preparation and use of materials in conjunction with the compositions and processes of the invention.

Reference Example 1

[0061] Two hundred and twenty-five g of RJ-100 (a styrene-allyl alcohol copolymer obtained from Allied Chemical Corp., Morristown, New Jersey) were melted at 95°C on a two-roll mill. To the polymer melt was added 32 g of Heliogen Blue, 3 g of Pigment Green 7 and 0.9 g of Sicofast Yellow D-1155. Mixing was done in 30 minutes, at which time 10 g of carnauba wax was added. After an additional 15 minutes of mixing the mill was cooled and the resultant product was removed. This mixture was cryogenically comminuted on a hammer mill. Thirty g of this powder were charged into an attritor with 130 g of Isopar G (Exxon). After 45 minutes, the attrition was terminated, discharged from the attritor and diluted with 130 g of Isopar to give a 10% concentrate.

[0062] Forty g of the above concentrate was diluted to 400 g with Isopar G to give 1% working developer. To the latter was added 0.4 g of a 1% solution of aluminum diisopropyl salicylate. The developer thus prepared exhibited a stable conductivity of 4.1 pmhos, and also exhibited an excellent shelf-life. This positively charged developer produced sharp, dense images on ZnO photoconductors.

Reference Example 2

[0063] The procedure of Example 1 was repeated, except that the charge director used, instead of aluminum diisopropyl salicylate, was chromium octoate. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Reference Example 3

[0064] The procedure of Example 1 was repeated, except that the charge director used, instead of aluminum diisopropyl salicylate, was aluminum tri-neodecanoate (Mooney Chemical). Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Reference Example 4

[0065] The procedure of Example 1 was repeated, except that the charge director used, instead of aluminum diisopropyl salicylate, was ferric octoate (Mooney Chemical). Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Reference Example 5

[0066] The procedure of Example 1 was repeated, except that the charge director used, instead of aluminum tri-neodecanoate, was aluminum dinonylnaphthalene sulfonate. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Reference Example 6

[0067] The procedure of Example 1 was repeated, except that the charge director used, instead of aluminum diisopropyl salicylate, was $\text{Al}(\text{AcAc})(\text{DIPS})_2$, wherein "AcAc" represents acetyl acetate, and "DIPS" represents diisopropyl salicylate.

[0068] This charge director was prepared as follows. Aluminum acetyl acetate (Aldrich Chemical Co., 6.4 g; 0.2 mL) and 8.88 g of diisopropyl salicylic acid (Aldrich Chemical Co.) were dissolved in 100 g of toluene. The resultant solution was heated at 95-100°C for 2 hours. The solvent was removed at 95°C (steambath) in vacuo, leaving 11.3 g of a viscous glass. The latter was dissolved in 25 mL of hot acetone. Upon removal of the acetone in vacuo, a brittle foam resulted which was dried at 70°C for 24 hours. For the product $\text{C}_{31}\text{H}_{41}\text{O}_8\text{Al}$, $[\text{Al}(\text{AcAc})(\text{DIPS})_2]$, the theoretical percentage of Al is 4.75, while 4.73 was found. The product was readily soluble in Isopar and conferred a positive charge to toners at the rate of 10^{-7} - 10^{-5} mole/g toner.

[0069] When used in the process described in Example 1, substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Reference Example 7

[0070] One hundred seventy-five g of ACX 251 (an ethylene-vinyl alcohol polymer obtained from Allied Chemical) was melted at 90°C on a two-roll mill. To the polymer melt was added 31.4 g of Heliogen Blue L 7080, 2.9 g of Heliogen Green (Pigment Green 7), 0.8 g of Sicofast D-1155, and 6.6 g of WB-11, a cationic wax dispersant (Petrolite). Mixing was continued for 30 minutes. The mill was cooled and the product removed and processed to a 10% concentrate as described in Example 1.

[0071] To 400 g of 1% working developer was added 0.6 g of a 1% solution of ferric trinaphthenate (Nuodex). The conductivity was 7.8 pmhos. As in Example 1, the shelf-life of the developer was quite superior. This positively charged developer yielded excellent, dense, high resolution images on ZnO photoconductors. "DIPS" are defined above. The charge director was prepared as described in Example 8.

[0072] When used in the process described in Example 8, substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Example 1

[0073] One hundred twenty g of AC 201 resin® (Allied Chemical) were placed onto a two-roll mill at 100°C. To the polymer melt was added 52 g of Sicofast D-1155®. After 30 minutes of mixing, 60 g of AC 540 resin (Allied) and 60 g of AC 7® (Allied) were added. After 15 minutes of mixing, 10 g of Ethomid HT 60 dispersant (obtained from Akzo) and 13 g of WB-17 dispersant (Petrolite) were added. Mixing was continued for 20 minutes and the product was discharged and processed to give a 10% developer as described in Reference Example 1.

[0074] To 400 g of 1% developer was added 1 g of 0.05% aluminum diisopropyl salicylate and 2 g of a 1% solution of diisopropyl salicylic acid. The conductivity was 3.7 pmhos. This developer -- which, like the developer compositions of the reference examples, exhibited a superior shelf-life -- produced sharp, dense images on ZnO photoconductors.

Example 2

[0075] The procedure of Example 14 was repeated, except that the charge director used, instead of aluminum diisopropyl salicylate, was $\text{Al}(\text{AcAc})(\text{DIPS})_2$, wherein "AcAc" and "DIPS" are defined above. The charge director was prepared as described in Reference Example 6.

[0076] When used in the process described in Reference Example 1, substantially the same results. With respect to stable conductivity, shelf-life and image quality were obtained.

Example 3

[0077] The procedure of Example 1 is repeated, except that Sicofast D-1155 is replaced with Hostaperm Red E5B-02. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Example 4

[0078] The procedure of Example 1 is repeated, except that Sicofast D-1155 is replaced with Heliogen Blue L-7080. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Example 5

[0079] The procedure of Example 1 is repeated, except that Sicofast D-1155 is replaced with Novaperm Yellow FGL. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Example 6

[0080] The procedure of Example 1 is repeated, except that Sicofast D-1155 is replaced with Indofast Brilliant Scarlet R-6335. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Example 7

[0081] The procedure of Example 1 is repeated, except that Sicofast D-1155 is replaced with Quindo Magenta RV6832. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Example 8

[0082] The procedure of Example 1 is repeated, except that Sicofast D-1155 is replaced with Quindo Red 6713. Substantially the same results -- with respect to stable conductivity, shelf-life, and image quality -- were obtained.

Claims

1. An electrophotographic liquid developer composition comprising, dispersed in an electrically insulating carrier liquid, (a) a charge director comprising a metal ion selected from aluminum, magnesium, chromium and iron and a counterion; (b) toner particles comprising resinous phase which contains colorant and which comprises a polymer having carboxyl groups as specific solvation sites effective to solvate the metal ion; and (c) an acid to suppress ionization of the solvation sites.
2. A composition according to claim 1, wherein the polymer is selected from ethylene-acrylic acid copolymers and ionomers and mixtures thereof.
3. A composition according to any one of claims 1 to 2, wherein the charge director is selected such that solvation thereof by the polymer is an exothermic reaction with a ΔH that is more negative than about -50 kJ/mole.
4. A composition according to any one of claims 1 to 3, wherein the acid is the acid form of the counterion of the charge director.
5. A process for providing surface charge on toner particles for use in a liquid electrophotographic developer composition, comprising preparing, in an electrically insulating carrier liquid, a dispersion of: (a) a charge director comprising a metal ion selected from aluminum, magnesium, chromium and iron and a counterion; (b) toner particles comprising a resinous phase which contains colorant and which comprises a polymer having carboxyl groups as specific solvation sites effective to solvate the metal ion; and (c) an acid to suppress ionization of the solvation sites.
6. A process according to claim 5, wherein the polymer is as defined in claim 2.
7. A process according to claim 5 or 6, wherein the charge director is as defined in claim 3.
8. A process according to any one of claims 5 to 7, wherein the acid is the acid form of the counterion of the charge director.
9. A process for developing an electrostatic charge pattern using a consecutive color toning system, comprising:
 - (a) forming an initial electrostatic charge pattern on a substrate and developing the initial pattern with a first liquid developer composition as claimed in any one of claims 1 to 4, and then
 - (b) forming a second electrostatic charge pattern on the substrate and developing the second pattern with a second liquid developer composition as claimed in any one of claims 1 to 4;
 wherein steps (a) and (b) are conducted in immediate succession without any additional processing steps therebetween.

Patentansprüche

1. Elektrophotographische Flüssigentwicklerzusammensetzung, die dispergiert in einer elektrisch isolierenden Trägerflüssigkeit folgendes umfaßt: (a) eine die Ladung leitende Substanz mit einem aus Aluminium, Magnesium,

Chrom und Eisen ausgewählten Metallion und einem Gegenion; (b) Tonerteilchen mit einer Harzphase, die einen farbgebenden Stoff enthält und ein Polymer mit Carboxylgruppen als spezifische Solvatationsstellen umfaßt, die wirksam sind, um das Metallion zu solvatisieren; und (c) eine Säure zur Unterdrückung der Ionisierung der Solvatationsstellen.

2. Zusammensetzung nach Anspruch 1, bei der das Polymer ausgewählt ist aus Ethylen-Acrylsäure-Copolymeren und - Ionomeren und Mischungen derselben.

3. Zusammensetzung nach einem der Ansprüche 1 bis 2, bei der die die Ladung leitende Substanz so gewählt ist, daß ihre Solvation durch das Polymer eine exotherme Reaktion mit einem ΔH ist, das negativer ist als etwa -50 kJ/mol.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, bei der die Säure die saure Form des Gegenions der die Ladung leitenden Substanz ist.

5. Verfahren zur Bereitstellung von Oberflächenladung auf Tonerteilchen zur Verwendung in einer elektrophotographischen Flüssigentwicklerzusammensetzung, bei dem in einer elektrisch isolierenden Trägerflüssigkeit eine Dispersion hergestellt wird aus: (a) einer die Ladung leitenden Substanz mit einem aus Aluminium, Magnesium, Chrom und Eisen ausgewählten Metallion und einem Gegenion; (b) Tonerteilchen mit einer Harzphase, die einen farbgebenden Stoff enthält und ein Polymer mit Carboxylgruppen als spezifische Solvatationsstellen umfaßt, die wirksam sind, um das Metallion zu solvatisieren; und (c) eine Säure zur Unterdrückung der Ionisierung der Solvatationsstellen.

6. Verfahren nach Anspruch 5, bei dem das Polymer der Definition von Anspruch 2 entspricht.

7. Verfahren nach Anspruch 5 oder 6, bei dem die die Ladung leitende Substanz der Definition von Anspruch 3 entspricht.

8. Verfahren nach einem der Ansprüche 5 bis 7, bei dem die Säure die saure Form des Gegenions der die Ladung leitenden Substanz ist.

9. Verfahren zur Entwicklung eines elektrostatischen Ladungsmusters unter Verwendung eines Systems zur fortlaufenden Farbtonung, umfassend die folgenden Schritte:

(a) Ausbilden eines anfänglichen elektrostatischen Ladungsmusters auf einem Substrat und Entwickeln des anfänglichen Musters mit einer ersten Flüssigentwicklerzusammensetzung nach einem der Ansprüche 1 bis 4, und dann

(b) Ausbilden eines zweiten elektrostatischen Ladungsmusters auf dem Substrat und Entwickeln des zweiten Musters mit einer zweiten Flüssigentwicklerzusammensetzung nach einem der Ansprüche 1 bis 4;

wobei die Schritte (a) und (b) in unmittelbarer Folge ohne zusätzliche Verarbeitungsschritte dazwischen durchgeführt werden.

Revendications

1. Composition de révélateur liquide pour électrophotographie, qui comporte, en dispersion dans un véhicule liquide électriquement isolant :

a) un directeur de charge comprenant un ion d'un métal choisi parmi l'aluminium, le magnésium, le chrome et le fer, et un contre-ion ;

b) des particules de toner comportant une phase résineuse qui contient un colorant et qui est constituée d'un polymère portant des groupes carboxy qui jouent le rôle de sites spécifiques de solvation solvantant efficacement les ions métalliques ; et

c) un acide qui sert à supprimer l'ionisation des sites de solvation.

2. Composition conforme à la revendication 1, dans laquelle le polymère est choisi parmi les copolymères d'éthylène

et d'acide acrylique, les ionomères et leurs mélanges.

3. Composition conforme à l'une des revendications 1 et 2, dans laquelle le directeur de charge est choisi de telle sorte que sa solvatation par le polymère soit une réaction exothermique pour laquelle la valeur de ΔH est inférieure à environ -50 kJ/mol.

4. Composition conforme à l'une des revendications 1 à 3, dans laquelle l'acide est la forme acide du contre-ion du directeur de charge.

5. Procédé permettant de conférer une charge superficielle à des particules de toner employées dans une composition de révélateur liquide pour électrophotographie, qui comporte le fait de préparer une dispersion, dans un véhicule liquide électriquement isolant :

a) d'un directeur de charge comprenant un ion d'un métal choisi parmi l'aluminium, le magnésium, le chrome et le fer, et un contre-ion ;

b) de particules de toner comportant une phase résineuse qui contient un colorant et qui est constituée d'un polymère portant des groupes carboxy qui jouent le rôle de sites spécifiques de solvatation solvantant efficacement les ions métalliques ; et

c) d'un acide qui sert à supprimer l'ionisation des sites de solvatation.

6. Procédé conforme à la revendication 5, dans lequel le polymère est défini comme dans la revendication 2.

7. Procédé conforme à la revendication 5 ou 6, dans lequel le directeur de charge est défini comme dans la revendication 3.

8. Procédé conforme à l'une des revendications 5 à 7, dans lequel l'acide est la forme acide du contre-ion du directeur de charge.

9. Procédé permettant de développer un motif de charges électrostatiques au moyen d'un système d'application successive de toners colorés, et comportant

a) le fait de former sur un substrat un motif initial de charges électrostatiques et de révéler ce motif initial à l'aide d'une première composition de révélateur liquide conforme à l'une des revendications 1 à 4, puis

b) le fait de former sur le substrat un deuxième motif de charges électrostatiques et de révéler ce deuxième motif à l'aide d'une deuxième composition de révélateur liquide conforme à l'une des revendications 1 à 4,

les étapes (a) et (b) se suivant immédiatement l'une l'autre, sans qu'aucune étape supplémentaire de traitement n'ait lieu entre elles.