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# [54] PROCESS FOR PREPARING ELECTROPHOTOGRAPHIC LIQUID DEVELOPING COMPOSITIONS

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[58] **Field of Search** .................. 252/62.1; 8/72, 79; 96/97, 84 A

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## [57] ABSTRACT

An electrophotographic liquid developer may be prepared by admixture of a dye and a mordant therefor in the presence of (1) a suitable binder, (2) a solvent for the binder and (3) a liquid precipitation medium; the solvent for the binder is substantially removed; and the resultant dope is added to a suitable liquid carrier to form a dispersion of finely divided toner particles in the liquid carrier. The toner particles thus formed contain a dye-mordant salt precipitate dispersed in the binder.

**16 Claims, No Drawings**

# PROCESS FOR PREPARING ELECTROPHOTOGRAPHIC LIQUID DEVELOPING COMPOSITIONS

This invention relates to electrophotography and to liquid compositions containing mordantable dyes which are useful for developing a visible image from a latent electrostatic image existing as a charge pattern on electrophotographic elements.

Processes for producing a visible image from a latent electrostatic image by developing with an electrostatically attractable dry powder having optical density are well-known and have been described in numerous U.S. patents including the Carlson U.S. Pat. No. 2,297,691 issued Oct. 6, 1942, and No. 2,357,809 issued Sept. 12, 1944. To develop a latent electrostatic image, the dry granular electroscopic powders have in the past ordinarily been cascaded over latent electroscopic images or brought in the form of powder clouds into intimate contact with the charged image to be rendered visible. Dry developers of this type have been described in such U.S. Pats. as No. 2,618,552 by Wise issued Nov. 18, 1952, and No. 2,753,308 by Landigram issued July 3, 1956. More recently, it has been proposed to develop latent electrostatic images using liquid media rather than the above-described "dry" process. Straughan in U.S. Pat. No. 2,899,335 issued Aug. 11, 1959, for example, proposed the development of an electrostatic image using a liquid developer in which the charged solid developing particles are carried into contact with the electrostatic image in a liquid medium instead of in air or a gaseous medium as in the aforesaid Carlson patents, for example. Another type of charged pigment suspending liquid developer of electrostatic images has been described by Metcalfe and Wright in Australian Pat. No. 212,315 patented Dec. 6, 1956.

A particularly useful liquid electrophotographic developer is shown in York, U.S. Pat. No. 3,135,695. This patent shows an electrophotographic liquid developer prepared by surrounding or dispersing electrophotographic-type pigment particles with a suitable resinous-binder envelope and treating the pigment-binder combination with a small amount of an alkylaryl compound before suspending the combination in a liquid aliphatic carrier. This type of liquid electrophotographic developer is especially useful due to its relatively high stability.

One problem associated with most types of liquid developers noted in the patents cited hereinabove is that the time required simply to prepare the toner particles, i.e., particles comprising a combination of colorant and resinous binder, especially finely divided toner particles on the order of about 1 micron, is frequently quite lengthy; for example, a preparation time of several days in not unusual. Usually this is done by a rapid high-speed blending operation, or in cases where very small toner particle size is required by lengthly ball-milling and super ball-milling procedures. The present invention overcomes, quite unexpectedly, such lengthy preparation times by a relatively simple process such that quite small toner particles of colorant and binder having a uniform size on the order of 0.5 micron may be obtained in a matter of minutes or a very few hours.

It is, therefore, a primary objective of the present invention to provide a process for preparing liquid electrophotographic developers having excellent stability and which contain toner particles requiring relatively short preparation times. Another object of the present invention is to provide novel liquid electrophotographic developers having toner particles of uniformly small particle size. A further object of the invention is to provide a stabilized liquid developer composition having toner particles of a uniformly small size dispersed therein. other objects will become apparent on a reading of the specification and appended claims.

The objects of the present invention are accomplished by a process utilizing a dye and a mordant for said dye to form the colorant contained in the toner particles of a liquid developer In this process, the dye and mordant therefor are admixed in the presence of (1) a suitable polymeric resinous binder, (2) a solvent for said binder and (3) a liquid precipitation medium which is a solvent or a colloidal dispersive medium for the polymeric binder and which also is miscible with a suitable liquid carrier; the solvent for the binder is substantially removed; and the resultant dope or mixture is added to the dispersed liquid carrier to form a dispersion of finely divided toner particles in the liquid carrier. The toner particles thus suspended in the liquid carrier contain a core of a dye-mordant salt precipitate dispersed in the resinous polymeric binder. Suitable polymeric resinous binders include those resins which are soluble in the liquid precipitation medium or which are capable of forming a colloidal dispersion therein and which are insoluble or at least only slightly soluble in the liquid carrier of the developer. If desired, the liquid precipitation medium utilized in the process of the present invention and which is further described hereinafter may serve both as the solvent for the binder and as the liquid precipitation medium, in which case, however, a portion, but not all, of the liquid precipitation medium is removed prior to dispersal of the dope in the liquid carrier. The liquid carrier used can be any of the well-known liquid aliphatic carriers. These liquids have low dielectric constants and a resistivity of greater than about $10^{10}$ ohm-centimeters to preclude the possibility of discharging the latent electrostatic image. The low dielectric constant of the liquid carrier is provided so that the energy in the image field is not dissipated in aligning and moving highly polar molecules. If the admixture of dye, mordant for the dye, polymeric resinous binder and solvent for the binder is dispersed in the liquid carrier without first treating it with the liquid precipitation medium, the system coagulates badly. Where the process of the present invention is utilized to prepare a liquid developer, it is found that the resultant developer exhibits excellent stability. Horover, no ball-milling of any sort is needed to prepare liquid developers having finely divided toner particles dispersed therein having a uniform small particle size.

In a preferred embodiment of the process of the present invention, the admixture of the dye and mordant for the dye is accomplished by dissolving the dye and mordant in separate solutions; that is, the dye is dissolved in a first mixture of polymeric binder and solvent therefor and the mordant for the dye is dissolved in a separate second mixture of polymeric binder and solvent. The second mixture containing the mordant is then quickly added with rapid stirring to the first mixture containing the dye in the presence of the liquid precipitation medium. If desired, the resultant mixture may be washed with water to produce a product containing oily globules dispersed in water. The water may be removed by decanting most of it and running the remainder of the product through filter paper. The washing step is useful because it generally removes most if not all of the binder solvent, provided a water-miscible solvent has been used.

The resulting dope contains a very fine dispersion of the dye-mordant salt precipitate in a mixture of the polymeric binder and liquid precipitation medium. Usually no visible particles are present. Any particles that may be present are present in the form of very loose agglomerates which may readily be broken up. A developer composition is then formed by dispersing the dope in the liquid aliphatic carrier.

In a second embodiment of the present invention, the admixture of the dye and mordant is accomplished by forming a solution of a dye-mordant salt in an organic solvent for said dye-mordant salt and admixing the dye-mordant salt solution with a mixture of the polymeric binder, a solvent for the binder and a liquid precipitation medium. A dope without visible particles results. The solvent for the polymeric binder may be removed by water-washing as described above or by air-drying such as by placing the dope in an evaporating dish and allowing it to stand until all that remains is a dry powder. This dry powder may then readily be taken up in a small amount of additional liquid precipitation medium. The liquid developer composition may then be formed in the same manner as indicated previously by dispersing the resulting dope of particulate dye-mordant salt precipitate, polymeric binder and liquid precipitation medium in the liquid carrier vehicle.

In a variation of either of the above-described embodiments of the present invention, a small quantity of surfactant which is soluble in the liquid carrier may be added prior to or simultaneously with the addition of the liquid precipitation medium and before the dope containing the liquid precipitation medium, binder and dye-mordant salt combination is admixed with the liquid carrier. The addition of this small quantity of surfactant provides an even more finely divided suspension of toner particles in the liquid carrier. Examples of surfactants suitable for use in the present invention include Strodex Super V-8, a polyphosphoric co-ester of an alkylphenol and a polyoxyethylene sorbitan fatty ester; Tween 85, polyoxyethylene sorbitan trioleate; Tergitol 3A6, polyoxyethylene tridecylphenol; Sterox DF, polyoxyethylene dodecylphenol; Unamide SOA a fatty alkanolamide; etc.

In carrying out the present invention, an electrostatic latent image can be produced by any of a number of procedures recognized in the art. For example, a sensitive element may be produced by coating the support with a suitable photoconductor, such as those described in the Carlson patents cited above, the organic-metallic photoconductors such those described in U.S. Pat. application Ser. No. 650,664 filed July 3, 1967 now U.S. Pat. No. 3,647,429 the "organic amine" photoconductors described in U.S. Pat. No. 3,240,597 issued Mar. 15, 1966, and the polyarylalkane photoconductors such as those described in U.S. Pat. No. 3,274,000, etc., and imparting a uniform charge to said sensitive element by any of the known means such as corona discharge and by rubbing as also described in the Carlson patents. Fnally, the charged sensitive element is exposed to a pattern of light and shadow illumination whereby the illuminated areas are discharged and a charged image pattern remains which is developed to a visible image by flowing a developer of the present invention over the differentially charged surface. The electrostatically attractable particles carried in the insulating liquid carrier of the developer are brough into contact with the electrostatic image which results in the particles being deposited on the charged areas of the sensitive element so that the charged areas are immediately rendered visible because of the optical characteristics of the toner particles. Because of the highly volatile nature of the aliphatic carriers of the developer composition, fast drying results and a visible, permanent image is rapidly obtained.

The polymeric resinous binder material utilized in the present invention to form an enveloping capsule about the dye-mordant salt colorant is characterized by being soluble in the precipitation medium, but insoluble or only slightly soluble in the liquid carrier of the developer. The preferred resinous binders should also be non-chalking should dry to a tought wear-resistant film and should have a refractive index conducive to enhance color or transparency. On the other hand, suitable resinous materials should have no adverse effect on particle charge or on developer stability. Those resinous materials which have been found to be suitable for use in the process of the present invention can be selected from a number of synthetic resins, modified resins, etc. Examples of suitable resins are given in Table 1

TABLE 1

| Trade Name | Resin Type | Manufacturer |
|---|---|---|
| Epon 100 | polyethylene | Shell Oil Co. |
| Amberol 226 | phenol formaldehyde rosin-modified | Rohm and Haas Co. |
| Amberol B/S-1 | phenol formaldehyde rosin-modified | Do. |
| Amberol F-7 | phenol formaldeyhyde rosin-modified | Do. |
| Amberol F-77 | phenol form rosin modified | Do. |
| Amberol K12A | phenol form rosin modified | Do. |
| Amberol M-88 | phenol form rosin modified | Do. |
| Amberol M-93 | phenol form rosin modified | Do. |
| Amberol 800 | maleic rosin type | Do. |
| Amberol 801 | maleic rosin type | Do. |
| Amberol 801P | maleic rosin type | Do. |
| Amberol 808 | maleic rosin type | Do. |
| Amberlac D-96 | maleic rosin type | Do. |
| Beckosol 7 | soya-modified alkyd | Reichold Chemical Co. |
| Cellolyn 102 | modified pentaerythritol ester of rosin | Hercules Powder Co. |
| Gellolyn 104 | modified pentaerythritol ester of rosin | Do. |
| Lewisol 2L | maleic alkyd-modified rosin ester | Do. |
| Lewisol 28 | maleic alkyd-modified rosin ester | Do. |
| Neolyn 23 | rosin-derived alkyd-type resin | Do. |
| Neolyn 35 | rosin-derived alkyd-type resin | Do. |
| Pentalyn B25 | phenol-modified pentaerythritol ester of rosin | Do. |
| Pentalyn 802A | phenol-modified pentaerythritol ester of rosin | Do. |
| Arochem 75 | modified phenolic | Archer Daniels Midland Co. |
| Arochem 333 | modified phenolic | Do. |
| Arochem 335 | modified phenolic | Do. |
| Arochem 337 | modified phenolic | Do. |
| Arochem 339 | modified phenolic | Do. |
| Arochem 365 | modified phenolic | Do. |
| Arochem 402 | modified phenolic | Do. |
| Arochem 404 | modified phenolic | Do. |
| Arochem 520 | modified maleic | Do. |
| Arochem 533 | modified penta ester | Do. |
| Arochem 542 | modified maleic | Do. |

| | | |
|---|---|---|
| | | Daniels Midland Co. |
| Arochem 545 | modified maleic | Do. |
| Arochem 595 | modified maleic | Do. |
| Arochem 650 | lacquer resin | Do. |
| Arofene 753 | pure phenolic resin | Do. |
| LXH 403 | modified pentaerythritol | Sherwin-Williams Co. |
| XLH 504 | modified pentaerythritol | Do. |
| Dymal XLM 110 | maleic alkyd | Do. |
| Dymal XLM 101 | maleic alkyd | Do. |
| Dymal XLM 103 | maleic alkyd | Do. |
| Dymal XLM 106 | maleic alkyd | Do. |

Other suitable resinous materials and mixtures of such materials have been described in such U.S. Pat. as No. 2,891,011 by Insalaco issued June 16, 1959, and No. 2,940,934 by Carlson issued June 14, 1963. Especially useful types of resins are the alkyd and mofidied alkyd resins, including mofidied alkyds such as soya oil-modified and linseed oil-modified alkyds, phthalic, maleic and stryenated alkyds, etc., and the phenolic resins, including modified phenolic resins such as phenol formaldehyde resins and derivatives thereof such as alkylphenol formaldehyde resins, e.g., methylphenol formaldehyde, xylenol formaldehyde resins, and the like.

The dyes which can be used in preparing the dye-mordant salts which serve as colorants in preparing the toner particles for the liquid developers of the present invention can vary widely. Both acid dyes and basic dyes which are mordantable may be used. The principal requirement of the mordantable dyes used in the present invention is that the dye-mordant salt colorant formed from the dye is capable of carrying an electrostatic charge.

The acid dyes useful in the present invention are strongly acid dyes, and the basic dyes useful herein are strongly basic dyes. The strongly acid dye typically contains two or more acid groups and may be further characterized in that a saturated aqueous solution of the free acid form of the dye has a pH less than about 5. In a similar manner, the strongly basic dye typically contains two or more basic groups and may be characterized in that a saturated aqueous solution of the free base form of the dye has a pH greater than about 8. Typically, the acid groups of the acid dyes include sulfonic acid or carboxy acid radicals which are capable of forming salts with alkali metals commonly used in the dye trade, such as sodium, potassium and lithium. Typically, the basic groups of the basic dye include amino or substituted amino radicals. The basic dye is typically used as the hydrohalide (e.g., hydrochloride, etc.), sulfate, nitrate, etc. Substituents for the amino group can be an alkyl group having from 1 to about 8 carbon atoms and which can be a straight-chain or branched-chain alkyl group, e.g, methyl, ethyl, isopropyl, hexyl, octyl, 2,2,4-trimethylpentyl, etc., an aryl group, e.g., phenyl, naphthyl, etc., including substituted aryl group bearing such substituents as alkyl as defined above, amino including substituted amino, nitro, halogen and the like, an aralkyl group, eg., methylphenyl, benzyl, dimethylnaphthyl and the like.

The dyes used as the starting materials in the present invention can 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, acridine, thiazole, azine, anthraquinone, phthalocyanine, etc. These and other useful classes of dyes can be found in the Preamble to the Color Index, Volume 3, Second Edition, 1956.

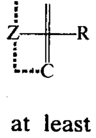
Useful acidic dyes include Brilliant Alizarine Light Red B, Color Index Acid Red 58; copper phthalocyanine tetrasodium sulfonate, C.I. 74220; 4,8-disulfonaphthyl-2-azo-4(3-methyl-1-p-sulfophenyl-5-pyrazolone); anthraquinone Blue B, C.I. 73010; Solantine Pink 4 BL, C.I. 25380; and the like.

Useful basic dyes include Astraphloxine FF, C.I. 48070; Rhodamine B, C.I. 45170; Rhodamine 6G, C.I. 45160; methylene blue, C.I. 52015; Toluidine Blue, C.I. 52040; Auramine G, C.I. 41005; and the like.

Suitable mordant compounds for use with the dyes of the present invention, of course, will depend upon the particular mordantable dye chosen. Naturally, an acid dye will require a basic mordant compound and a basic dye will require an acidic mordant compound. Like the mordantable dyes utilized in the process of the present invention the principal requirement of any mordant, either acid or basic, used in the present process is that these mordants be capable of reacting with the mordantable dye to form colorant particles capable of carrying an electrostatic charge. Mordants useful with basic dyes include such materials as phosphomolybdic acid, phosphotungstic acid, tungsto-silicic acid, molybdosilicic acid, naphthalene-1,5-disulfonic acid, tannic acid, 2-sulfoanthraquinone, mixtures thereof, etc. Suitable mordants for use with acidic dyes include triphenylguanidine, di-o-tolyguanidine, α-naphthyl-amine, dioctylamine, N,N,-dimethyldodecylamine mixtures thereof, etc. In general, the molar ratio of mordant to dye should be within the range of from about 1:1 to about 2.5:1.0, the actual ratio being previously determined by titration. Normally, a slight excess of mordant is preferred.

The amounts of the dye and dye mordant used in the present invention are generally quite small in comparison with the amount of polymeric binder used. Ordinarily, the ratios of the weight amounts of both the dye and dye mordant to the polymeric binder vary from about 0.05:1 to about 0.3:1.0, preferably from about 0.1:1.0 to about 0.2:1.0, or smaller or larger amounts of binder could be utilized, if desired.

According to the present invention, the liquid precipitation medium utilized in the process thereof can be characterized as a compound which is capable of dissolving or serving as a colloid-dispersive medium for the polymeric resinous binder and which also is miscible with the liquid carrier of the developer. Suitable compound which have been found useful as the liquid precipitation medium employed in the present invention are the alkylated aromatic-like hydrocarbons, including the alkylated cyclic alkenes, represented by the following general formula:



wherein R represents at least one straight-chain or branched-chain alkyl group having from 1 to about 12 carbon atoms, and Z represents the nonmetallic atoms necessary to complete a carbocyclic nucleus containing 1 to 3 carbocyclic rings, 5 to 7 carbon atoms being present in each ring. Typical examples of useful aromatic-like carbocyclic nuclei comprise benzene, naphthalene, anthracene, etc.

Examples of various liquid precipitation media of the type described hereinabove comprise xylene, mesitylene, ethyl-benzene, n-propylbenzene, n-butylbenzene, isobutylbenzene, n-pentylbenzene, n-hexylbenzene, n-propylnaphthalene, butylnaph-thalene, propylanthracene, butylanthracene, and the like. Useful results are obtained using isomers, as well as the normal aliphatic hydrocarbons and mixtures of each thereof. The preferred liquid precipitation media are compounds in which the cyclic nucleus is an aromatic nucleus such as benzene. Especially useful results are obtained where the aromatic substituent is benzene and the alkyl group is selected from those having from 3 to 6 carbon atoms. Preparation of any of the liquid precipitation media useful in the present invention can be by any of the well-known methods.

The precise function of the liquid precipitation medium in the process of the present invention is not entirely understood. Accordingly, it will be understood that the invention should not be limited or restricted to a specific theory of operation. However, it is believed that the liquid precipitation medium aids in the formation of a resinous binder envelope around the particles of dye-mordant salt colorant formed in the process of the invention and also acts to stabilize the resultant liquid developer by effectively preventing the binder envelope from diffusing away from the dye-mordant salt particles. It is believed that at some time after removal of the binder solvent and the solvent(s) for the dye, mordant for the dye, and/or dye-mordant salt, if solvents for these latter materials are used, the particles of dye-mordant salt precipitate which are present in the resultant dope containing the liquid precipitation medium begin to act as nucleation sites for the resinous binder. With the addition of the dope to the liquid carrier this phenomenon appears to be enhanced. It is believed that this is caused by the liquid precipitation medium beginning to diffuse into the liquid carrier with which it is miscible and the simultaneous exposure of the resinous binder to the liquid carrier, the resinous binder being insoluble in the liquid carrier. In any case, shortly after addition of the dope to the liquid carrier, finely divider toner particles having particles of the dye-mordant salt colorant dispersed in a coating of the resinous binder are present in the liquid carrier. Moreover, these toner particles remain stable in the liquid carrier over very long periods of time.

Advantageously, the size of the toner particles prepared according to the present invention may vary within the range of from about 0.05 micron to about 20 microns, preferably within the range of from 0.1 micron to about 2.0 microns. A particular advantage of the present invention is that there is provided a process for preparing relatively small toner particles having a uniform size in the order of about 0.5 micron.

In preparing electrostatic developers according to the process of the present invention, the amounts of the liquid precipitation medium employed may vary over a wide range. Ordinarily, in the admixture of dye, dye mordant, binder, various solvents and liquid precipitation medium, there may be present an amount of the liquid precipitation medium varying from about 0.2 to about 8.0 parts by weight of the liquid precipitation medium for every 1.0 part by weight of the remaining components of the admixture (excluding the weight of the solvents), i.e., the dye, dye mordant and binder components. Much larger amounts of liquid precipitation medium may also be used, although it is unnecessary and generally results in simply adding to the expense of the process. Of course, in those embodiments of the invention where the liquid precipitation medium is also used as the solvent for the polymeric binder, larger amounts of the liquid precipitation medium than those specified above may be usefully employed. However, as noted hreinabove, the solvents employed in the present invention are removed before dispersal of the admixture of dye, dye-mordant, binder and liquid precipitation medium in the carrier liquid of the developer composition. Accordingly, in those instances where large amounts of the liquid precipitation medium are used because of its dual role as a binder solvent and as a liquid precipitation medium, it is preferable to remove a substantial amount of the liquid precipitation medium prior to dispersal of the admixture in the liquid carrier.

Suitable liquid carriers for dispersing the toner particles prepared by the present invention comprise liquid possessing a low dielectric constant less than about 3.0. In order to avoid discharge of a latent electrostatic image, the liquid carrier should have a resistivity of greater than about $10^{10}$ ohm-centimeters. Liquids which have been found useful include cyclohexane, carbon tetrachloride, mixed halides such as trichlorotrifluoroethane, sold under the trade name Freon 113 by E. I. du Pont de Nemours & Co., cyclopentane, n-pentane, n-hexane, paraffinic hydrocarbon such as isoparaffinic hydrocarbon liquids having a boiling point in the range of 145° to 185° C., sold under the trade name Isopar G by the Humble Oil and Refining Co., petroleum distillates, mixtures thereof, etc. In addition to these liquids, certain other liquid vehicles may be used, such as dimethyl polysiloxane.

Solvents for the binder materials used in the process of the present invention include a wide variety of materials. Generally useful solvents include organic solvents which either are water-soluble or have a low boiling point relative to the boiling point of the liquid precipitation medium, i.e., boiling at least about 25° C. below the boiling point of the liquid precipitation medium. These properties, i.e., water solubility or low boiling point, are desirable because solvents having these properties may be easily removed from the admixture of dye, dye mordant, liquid precipitation medium, binder material and solvent therefor which is employed in the present invention. Thus, water-soluble organic solvents may be removed by continuous water-washing of the aforementioned admixture, and low-boiling organic solvents may be easily removed by air-drying the admixture. When the above-described liquid precipitation medium also functions as the binder solvent, it is desirable to employ a low-boiling liquid so that most of that portion of the liquid serving as a binder solvent may be readily removed by air-drying. In addition, the particular solvent chosen should be substantially chemically inert with respect to the dye, dye mordant, resinous binder and liquid precipitation at least within the temperature range at which the process of the present invention is carried out. Also, the solvent employed should be compatible, i.e., miscible, with the liquid precipitation medium to avoid formation of a multiphase liquid system. Advantageously, the solvent utilized should have little or no adverse effect on particle charge or developer stability.

As suggested hereinabove, in addition to the binder solvents, auxiliary solvents for the dye, dye mordant or dye-mordant salt may be used in the process of the present invention. If so, these solvents should possess properties which are the same as or quite similar to the binder solvents described immediately above. In addition, these auxiliary solvents should be compatible, i.e., miscible, with both the liquid precipitation medium and the binder solvents. Moreover, these auxiliary solvents should be compatible with the binder material, i.e., incapable of causing the binder to settle out of admixture with the binder solvent, dye, dye mordant and liquid precipitation medium.

Preferred solvents useful in the present invention will, of course, vary also depending on the particular binders, dyes, dye mordants, etc., which are employed. Generally, however useful solvents include (1) low-boiling, water-insoluble organic solvents having a boiling point within a range of from about less than 28° C. to about 150° C., such as ethyl and butyl acetates, ethyl propionate, butyl alcohol, ethyl formate, nitroethane, etc., and (2) water-soluble solvents, such as methyl isobutyl ketone, β-ethoxy ethyl acetate, β-butoxy-β-ethoxy ethyl acetate, tetrahydrofurfuryl adipate, diethylene glycol monoacetate, β-methoxymethyl acetate, acetonyl acetone, diacetone alcohol, diethylene glycol monomethyl ether, ethylene glycol, dipropylene glycol, acetone, methanol, ethanol, methylethyl ketone, acetonitrile, dimethylformamide, dioxane, etc.

The final liquid developer prepared by the process of the present invention ordinarily has a composition as follows: the toner particles, i.e., the particles comprising dye-mordant salt colorant dispersed in the polymeric binder material, are present in concentrations within the range of from about 0.01 to about 10 percent by weight, the liquid precipitation medium is present in a concentration within the range of from about 2 to about 35 percent by weight, and the aliphatic liquid carrier can make up from about 45 to about 98 percent by weight.

In addition, the electrostatic-charge polarity of the toner particles of the present invention can be enhanced or altered by the addition of suitable charge control agents, if so desired. A variety of materials can be used as charge control agents. Illustrative of suitable charge agents would be the polyoxyethylated alkyl surfactants such as polyoxyethylated alkylamine, polyoxyethylene palmitate, polyoxyethylene stearate, etc. Other useful materials are magnesium and heavier metal 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 and manganese naphthenate, zinc resinate, calcium naphthenate, zinc linoleate, aluminum resinate, isopropyltitanium stearate, aluminum stearate, and others, many of which are also described in U.S. Pat. No. 3,259,581. Typically, the amount of such materials used is less than about 2 percent by weight based on the weight of toner. In certain instances, the resinous binder per se can function as the charge control agent, as can the colorant.

The following examples further illustrate preferred embodiments of the invention.

## EXAMPLE 1

A stock solution of polymer is prepared as follows:

A 25-gram quantity of Beckosol 7 (a soya-modified alkyd resin containing 42 percent phthalic anhydride and 41 percent soya fatty acids, made by the Reichold Chemical Co.) is dissolved in a mixture of 75 ml. of methanol and 75 ml. of methylethyl ketone by stirring the mixture of resins and solvents for 2½ hours at room temperature.

Solution A: To a 22-gram quantity of the stock solution (containing 4 grams of resin solids) is added 1.0 gram of a basic magenta dye, Astraphloxine FF (Color Index 48070, General Dyestuffs Co.) or Calcozine Red BG (Color Index 48070, American Cyanamid Co.). The dye dissolves readily.

Solution B: To another 22-gram portion of the stock solution are added the following ingredients:

phosphomolybdic acid (dye mordant) — 2.0 g.
methanol (solvent) — 10 ml.
methylethyl ketone (solvent) — 10 ml.
Solvesso 100 (solvent) — 10 ml.

Solvesso 100 is an essentially aromatic petroleum hydrocarbon made by Humble Oil and Refining Co.; flash point, 100° F.; boiling range, 315°–350° F.; percent aromatics, 96 percent of total including xylenes 9 percent, monoalkyl benzenes 16 percent, dialkyl benzenes 36 percent, trialkyl benzene 39 percent; aliphatics 4 percent. The resultant solution is essentially clear.

Solution B is quickly added with vigorous stirring to Solution A. There results an excellent dispersion of the precipitated pigment formed by the mordanting of the dye in Solution A by the acid in Solution B. The dispersion is formed in the polymer solution. A 30-gram portion of Solvesso 100 is then stirred in to serve as the liquid precipitation medium.

To remove most of the above-noted solvents from the pigmented polymer solution, the above-described mixture is dumped into 400 ml. of water. Oily globules result. Most of the water is decanted, and the remaining water is removed by running through a filter paper. The resulting dope contains the liquid precipitation medium and polymeric binder together with colorant particles having an average size of about 0.8 micron, with some very loose agglomerates of up to 6 microns in size. These are readily broken up.

The developer is then made up by adding dropwise, with stirring in a Polytron blender, 2.5 g. of the dope to 250 ml. of a liquid carrier of Isopar G containing 0.2 g. cobalt naphthenate and 0.45 g. of a 1.5 percent by weight solution of aluminum stearate in xylene and shearing for 3 minutes after addition is complete. The resultant liquid developer is found to contain toner particles having an average size of about 0.8 micron. These particles contain the dye-mordant salt colorant dispersed in the Beckosol 7 polymeric binder.

The toner particles are positively charged.

## EXAMPLE 2

The procedure of Example 1 is followed using 0.56 gram of an acid dye, Brilliant Alizarine Light Red B (Sandoz, Color Index acid Red 58), in 22 grams of the stock polymer solution for Solution A, and 0.29 gram of triphenylguanidine as a mordant in 22 grams of the stock solution for Solution B. Recovery and developer preparation are carried out as in Example 1. The toner particles are positively charged.

### EXAMPLE 3

This is a variation on the procedure of Example 1 which requires no washing step to remove the solvents and recover the dispersion of colorant particles in a dope containing the liquid precipitation medium and the polymeric binder.

A 0.5 gram quantity of the dye-mordant salt, triphenylguanidine salt of copper phthalocyanine tetrasulfonic acid, is dissolved in 10 ml. of methanol and 10 ml. of methylethyl ketone. To this solution are added 22 grams of the stock polymer solution of Example 1. To the mixture are then added a 10-ml. quantity of Solvesso 100 as a solvent and a 50 mg. quantity of surfactant (Tween 85). A clear dope without visible particles results. The dope is placed in an evaporating dish and allowed to stand for 24 hours or until all that remains is a dry powder. This is readily taken up in 15 g. of Solvesso 100, which is now used as the liquid precipitation medium.

A liquid developer is made in the same manner indicated previously. The final toner particles contained therein are under 0.5 micron in size and very uniform. The toner particles are positively charged.

### EXAMPLE 4

In this example, the same liquid serves both as the binder solvent and as the liquid precipitation medium. A stock polymer solution is prepared which contains the following ingredients:

Beckosol 7 (resinous binder) — 27.0 g.
Amberol ST137 (resinous binder) — 81.0 g.
Solvesso 100 (solvent and precipitation medium) — 405.0 g.

A dye solution is prepared by dissolving 0.5 g. of a dye-mordant salt of phosphomolybdic acid complex of Astraphloxine FF in 3.0 ml. of dimethyl sulfoxide. The dye solution, to which also has been added 0.5 g. of Strodex V–8 as a surfactant, is added to 19.0 g. of the above-described stock polymer solution, with stirring, to yield a dope containing a fine dispersion of the pigment; about 16 g. of excess Solvesso 100 are removed by air-drying the dope. The resultant dope is then added to a liquid carrier of Isopar G as described in Example 1 to form a liquid developer composition containing toner particles having the dye-mordant salt dispersed in the Beckosol 7 and Amberol ST137 resin mixture.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

I claim:

**1.** A process for making electrophotographic developers having toner particles dispersed in an organic liquid carrier having a dielectric constant less than about 3.0 and a resistivity greater than about $10^{10}$ ohm-cm. which comprises admixing a dye and a mordant for said dye in the presence of (1) a polymeric binder comprising a material separate and distinct from said mordant, (2) an organic solvent for said binder and (3) an organic liquid precipitation medium which is capable of dissolving or forming a colloidal suspension of the polymeric binder and which is miscible with the liquid carrier; removing the solvent for said binder; and admixing the resultant dope with the liquid carrier to form a substantially stable dispersion of finely-divided toner particles in the liquid carrier, said toner particles having a substantially uniform size within the range of from about 0.05 microns to about 20 microns and comprising particulate dye-mordant salt precipitate dispersed in the polymeric binder.

**2.** The process according to claim **1** wherein admixture of the dye and mordant for the dye occurs in the presence of a surfactant which is soluble in the liquid carrier.

**3.** The process according to claim **1** wherein the same liquid is employed as the liquid precipitation medium and the binder solvent and wherein only a portion of this liquid is removed during removal of said binder solvent.

**4.** The process according to claim **1** wherein admixture of the dye and mordant is accomplished by forming a solution of a dye-mordant salt in an organic solvent for said dye-mordant salt and mixing said dye-mordant salt solution with a mixture of the polymeric binder, the solvent therefor and the liquid precipitation medium.

**5.** The process according to claim **4** wherein said mixture of polymeric binder, solvent therefor and liquid precipitation medium also contains a surfactant which is soluble in the liquid carrier.

**6.** The process according to claim **1** wherein admixture of the dye and mordant is accomplished by dissolving the dye in a first mixture of polymeric binder and solvent therefor, dissolving the mordant for the dye in a second mixture of polymeric binder and a solvent therefor, and mixing said first mixture with said second mixture in the presence of the liquid precipitation medium.

**7.** The process according to claim **6** wherein the mixture of said first mixture and said second mixture occurs in the presence of the liquid precipitation medium and also in the presence of a surfactant which is soluble in the liquid carrier.

**8.** The process according to claim **6** wherein said second mixture of polymeric binder and liquid solvent therefor also contains a surfactant which is soluble in the liquid carrier.

**9.** A process for making electrophotographic developers having toner particles dispersed in an organic liquid carrier having a dielectric constant less than about 3.0 and a resistivity greater than about $10^{10}$ ohm-cm. which comprises admixing an acid dye and a basic mordant for said dye in the presence of (1) a polymeric binder, (2) an organic solvent for said binder and (3) an alkylated aromatic hydrocarbon; removing the solvent for said binder; and admixing the resultant dope with the liquid carrier to form a substantially stable dispersion of finely divided toner particles in the liquid carrier, said toner particles having a substantially uniform size within the range of from about 0.1 microns to about 2.0 microns and comprising a particulate dye-mordant salt precipitate dispersed in the polymeric binder; said acid dye being selected from the group consisting of Brilliant Alizarine Light Red B. C.I. acid Red 58; copper phthalocyanine tetrasodium sulfonate, C.I. 74220; 4,8-disulfonaphthyl-2-azo-4-(3-methyl-1-p-sulfophenyl-5-pyrazolone); anthraquinone Blue B, C.I. 63010; and Solantine Pink 4 BL, C.I. 25380; said basic mordant being selected from the group consisting of triphenylguanidine, di-o-tolylquinidine, α-naphthylamine, dioctylamine and N,N-dimethyldodecylamine.

**10.** The process according to claim **9** wherein admixture of the acidic dye and basic mordant occurs in the presence of a surfactant selected from the group consisting of a polyphosphoric co-ester of an alkylphenol and a polyoxyethylene sorbitan fatty ester, polyoxyethylene sorbitan trioleate, polyoxyethylene tridecylphenol, polyoxyethylene dodecylphenol and a fatty alkanolamide.

**11.** A process for making electrophotographic developers having toner particles dispersed in an organic liquid carrier having a dielectric constant less than about 3.0 and a resistivity greater than about $10^{10}$ ohm-cm. which comprises admixing a basic dye and an acidic mordant for said dye in the presence of (1) a polymeric binder, (2) an organic solvent for said binder and (3) an alkylated aromatic hydrocarbon; removing the solvent for said binder; and admixing the resultant dope with the liquid carrier to form a substantially stable dispersion of finely divided toner particles in the liquid carrier, said toner particles having a substantially uniform size within the range of from about 0.1 microns to about 2.0 microns and comprising a particulate dye-mordant salt precipitate dispersed in the polymeric binder; said basic dye being selected from the group consisting of Astraphloxine FF, C.I. 48070; Rhodamine B, C.I. 45170; Rhodamine 6G, C.I. 45160; methylene Blue, C.I. 52015; Toluidine Blue, C.I. 52040; and Auramine G, C.I. 41005; said acidic mordant being selected from the group consisting of phosphotungstic acid, phosphomolybdic acid, tannic acid, tungstosilicic acid and molybdosilicic acid.

**12.** The process according to claim **11** wherein admixture of the basic dye and the acidic mordant occurs in the presence of a surfactant selected from the group consisting of a polyphosphoric co-ester of an alkylphenol and a polyoxyethylene sorbitan fatty ester, polyoxyethylene sorbitan trioleate, polyoxyethylene tridecylphenol, polyoxyethylene dodecylphenol and a fatty alkanolamide.

**13.** A process for making electrophotographic developers having toner particles dispersed in an organic liquid carrier having a dielectric constant less than about 3.0 and a resistivity greater than about $10^{10}$ ohm-cm. which comprises admixing a dye and a mordant for said dye in the presence of (1) a polymeric binder comprising a material separate and distinct from sad mordant, (2) an organic solvent for said binder, and (3) a first amount of an organic liquid precipitation medium which is capable of dissolving or forming a colloidal suspension of the polymeric binder and which is miscible with the liquid carrier; removing the solvent for said binder and the liquid precipitation medium to form a dry powder admixture of said binder, dye, and mordant for said dye; admixing said dry powder in a second amount of said organic liquid precipitation medium sufficient to form a dope thereof; and admixing the resultant dope with the liquid carrier to form a substantially stable dispersion of finely-divided toner particles in the liquid carrier, said toner particles having a substantially uniform size within the range of from about 0.05 microns to about 20 microns and comprising a particulate dye-mordant salt precipitate dispersed in the polymeric binder.

**14.** The process according to claim **13** wherein admixture of a dye and mordant for the dye occurs in the presence of a surfactant which is soluble in the liquid carrier.

**15.** A process for making electrophotographic developers having toner particles dispersed in an organic liquid carrier having a dielectric constant less than about 3.0 and a resistivity greater than about $10^{10}$ ohm-cm. which comprises admixing a dye and a mordant for said dye in the presence of (1) a polymeric binder comprising a material separate and distinct from said mordant, (2) an organic solvent for said binder, and (3) a first amount of an alkylated aromatic hydrocarbon; removing the solvent for said binder and the alkylated aromatic hydrocarbon to form a dry powder admixture of said binder, dye, and mordant for said dye; admixing said dry powder in a second amount of said alkylated aromatic hydrocarbon sufficient to form a dope thereof; and admixing the resultant dope with the liquid carrier to form a substantially stable dispersion of finely-divided toner particles in the liquid carrier, said toner particles having a substantially uniform size within the range of from about 0.05 microns to about 20 microns and comprising a particulate dye-mordant salt precipitate dispersed in the polymeric binder.

**16.** The process according to claim **15** wherein admixture of the dye and mordant for the dye occurs in the presence of a surfactant which is soluble in the liquid carrier.

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