

1

3,417,019

XEROGRAPHIC DEVELOPMENT

George L. Beyer, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Dec. 27, 1962, Ser. No. 247,525

11 Claims. (Cl. 252—62.1)

This invention relates to xerography. Particularly, the invention relates to improved liquid suspensions of toner particles for use in liquid development of xerographic images, and to improved xerographic development methods employing such liquid suspensions.

Methods are known for developing exposed xerographic plates with a liquid suspension of toner particles. A liquid developer, consisting of toner particles suspended in an insulating liquid, such as a hydrocarbon liquid, is washed onto the surface of an exposed xerographic plate. Charged toner particles in the liquid developer are attracted to, and deposited on, oppositely charged image areas on the xerographic plate. The particles can then be transferred from the plate to form a printed image on a transfer sheet according to any of several known methods, or they can be fixed directly to the xerographic plate. Toner particles that can be used for liquid develop-

2

graphic developers much like the types known, but in which the static charge on the toner particles is enhanced by presence of a "charge agent." Another object is to provide methods of xerographic image development using such improved liquid developers.

We have found that presence of certain agents in a liquid suspension of toner particles will exert a substantial influence on the charge characteristics of suspended particles in the developer and consequently will improve quality of the developed xerographic image. We call these agents "charge agents." According to the present invention useful charge agents are members of the group consisting of soaps of magnesium and heavier metals and organic surface active agents of a non-ionic, anionic, and cationic types. A charge agent selected from this group is incorporated in a liquid suspension of toner particles to regulate the static charge on particles in suspension. In order to exert an appreciable influence on the static charge, a charge agent of the class described must be present in an amount equal to at least about 3% of the weight of the toner particles. Magnesium and heavier metal soaps of fatty acids and aromatic acids are useful charge agents for liquid developers. Following is a partial list of examples of metal soaps that are useful according to the invention.

TABLE 1.—METAL SOAPS AS CHARGE AGENTS

Name	Type	Source	Charging Effect
Uversol Cobalt Liquid.....	Cobalt Naphthenate.....	Harshaw Chemical Co.....	Strong.
Uversol Cobalt Solid.....	do.....	Harshaw.....	Do.
Uversol Mn Solid.....	Manganese Naphthenate.....	do.....	Do.
Zinc Resinate.....	Precipitated.....	do.....	Do.
Zirex.....	Zinc Resinate.....	Newport Indust. Inc.....	Do.
Uversol Ca Liquid.....	Calcium Capthenate.....	Harshaw.....	Do.
Calcium Stearate.....	do.....	Metasap Chem. Co.....	Do.
Aluminum Resinate.....	Precipitated.....	Harshaw.....	Do.
Lead Resinate.....	do.....	do.....	Do.
Zinc Stearate.....	USP-60.....	Metasap.....	Do.
Manganese Paste.....	5.6% Mn.....	Harshaw.....	Moderate.
Copper Resinate.....	Precipitated.....	do.....	Do.
Cobalt Soyate.....	8.5% Co, solid.....	do.....	Mod-low.
Lead Stearate.....	do.....	Metasap.....	Low.
Cobalt Acetylacetonate.....	do.....	Union Carbide.....	Do.
Quillon S.....	Chromium Complex.....	DuPont.....	Do.

ment may consist for example of pigmented and unpigmented thermoplastic polymer particles, inks including those comprising discrete particles of pigment each surrounded by a coating of varnish, or simply particles of pigment without such binder or coating. To produce a satisfactory image the toner particles and suspension must carry a sufficiently strong static charge to be attracted to the oppositely charged image area. An object of the present invention is to provide improved liquid xero-

The metal soap that we have found most effective as a charge agent is cobalt naphthenate. However, a great many other soaps of magnesium and heavier metals have been found effective.

Also useful as charge agents in liquid suspension developers are organic surface active agents of the cationic, anionic and non-ionic types. Following is a partial list of examples of organic surface active agents that have been used.

TABLE 2.—SURFACTANTS AS CHARGE AGENTS

Surfactant No.	Name	Type ¹	Source	Charging Effect
1	Rexobase PW	C Naphthenic deriv	Emkay Chem. Co.	+ strong.
2	Sodium maleo pimeryl glutamate	A Na carboxylate	Eastman Kodak Co.	Do.
3	Duomeen T Dioleate	C+A Diquat. + oleate	Armour & Co.	Do.
4	Peregal OK	C Polyethanol quat.	Antara Chem. Co.	Do.
5	Priminox 32	C Alkyl PEG amine	Rohm and Haas	Do.
6	Rexobase XX	A Amide Condensate	Emkay Chem. Co.	+ mod-high.
7	Rexobase GA		do.	Do.
8	Priminox 10	C Alkyl PEG amine	Rohm and Haas	Do.
9	Oleylmethyltaurine	A Na sulfonate	Syn. Chem. Div.	Do.
10	Victawet 58B	A Pentacaprylphosphate	Victor Chem. Co.	Do.
11	Alkaterge T	C Oxazoline	Commercial Solv. Corp.	Do.
12	Hyamine 1622	C Aromatic ammonium	Rohm and Haas	Do.
13	Sipex TEA	A TEA lauryl sulfate	Am. Alcolac Corp.	Do.
14	Adogen 401, 402	C Quaternary	Archer-Daniels	Do.
15	Duomeen T	C Diamine	Armour & Co.	Do.
16	Ethomeen T/25	C Tertiary amine	Armour Chem. Co.	+ mod.
17	Ethomeen 18/15	C Tertiary amine	Armour & Co.	Do.
18	Tween 85	N PEG sorbitan oleate	Atlas Powder Co.	Do.
19	Octimet	C Quaternary	Fairfield Labs.	Do.
20	Nopcoen 16S	C Stearic polyamine	Nopco Chem. Co.	Do.
21	Alkanol B	A Naphthalene sulfonate	DuPont	Do.
22	Aerosol OT	A Alkyl sulfonate	Amer. Cyanamid	Do.
23	Lipal 4ML	N PEG ester	E. F. Drew Co.	+ low.
24	Cetyl trimethylammonium stearate	C+A as described	Fine Organics, Inc.	Do.
25	Negamine 142A	C Amine ester	Synthetic Chem. Inc.	Do.
26	Daxad 11	A Polyaromatic sulfate	Dewey and Almy	Do.
27	Tween 61	N PEG sorbitan stearate	Atlas Powder Co.	Do.
28	Renex 648	N PEG aryl ether	do.	Do.
29	Sulfocolaurate	A Sulfonate	Witco Chem. Co.	- low.
30	Octylphenoxy PEG glutamate	A Na Carboxylate	Eastman Kodak Co.	- and + low.
31	Nalcamine G-13	C Subst. pyrimidine	Nalco Chem. Co.	+ mod. - mod-low.
32	Nalquat G-8-11, G-9-13	C Quat. pyrimidine	Nalco Chem. Co.	+ and - mod.
33	Aliquat 726	C Diquaternary	General Mills	- mod-high, + mod.

¹ C=cationic; A=anionic; N=nonionic.

The most effective surface active agent that we have found for use as a charge agent for liquid xerographic developers is Rexobase PW, but again a large number of others may be used. Because of the especially good results obtained with Rexobase PW it appears that the following two general classes of surfactants will be especially useful—(1) derivatives of polyethylene glycol that contain cationic groups, such as the quaternary ammonium group (examples being Rexobase PW, Peregal OK, acetylated Priminox 32, and Atlas G-3780A quaternized with N-butylidiodide); and (2) derivatives of polyethylene glycols containing amino groups (examples being Priminox 32, Priminox 10, Atlas G-3780A, Ethomeen T/25, and Ethomeen 18/15).

The mechanism by which our charge agents affect charge characteristics of the developers is not fully understood. The effects of a selected charge agent may differ from one toner composition to another. Generally the metal soaps and organic surfactants will have the effect, when included in a liquid xerographic developer, of increasing the existing charge on toner particles. That is, the charge agent usually will increase a weak negative charge or a weak positive charge existing on the particles to a stronger charge of the same polarity. However, there are exceptions and we have found that with some toner suspensions, a charge agent of the class described when added to a toner suspension will reverse a weak negative charge on the toner particles and cause a strong positive charge. In Tables 1 and 2 in the columns headed "Charging Effect," the relative effect of each charge agent on the net charge of the toner particles is rated with respect to other charge agents in the same table.

Toner particles for use in liquid xerographic development may range in size from 0.1 to 30 microns, preferably from 1 to 3 microns for optimum image sharpness and definition. The method for making the toner particles of the invention is not critical, and any suitable method may be employed. We have used ball milling, spray drying, and spray precipitation methods, the latter being especially suitable for making uniformly small fusible particles.

The charge agent may be added directly to the developer suspension, or preferably may be incorporated as a component of the toner particle composition before the particles are mixed into an insulating liquid.

Following are examples describing specific embodiments of the invention in which a charge is added directly to the developer suspension.

Example 1

A suspension of 0.08 gram of Spirit Nigrosine in 100 cc. of paint thinner (a non-conductive petroleum distillate having a 95° C. flash point and consisting essentially of branched chain paraffin hydrocarbons) was prepared. A conventional xerographic plate comprising a negatively charged zinc oxide layer which had been exposed to a pattern of light was immersed in the prepared developer liquid. Another plate was developed by flowing the developer liquid over the surface of the plate. Both of these techniques produced line images that were fringed. A grounded electrode of broad area was held at a space of about 0.02 to 0.05 inch from the face of the xerographic plate during development, and again the toner particles were caused to deposit to give a low density, fringed image on the negatively charged image areas of the xerographic plate. Cobalt naphthenate was added to the developer in an amount equal to 6 percent by weight of the solids present. A xerographic plate was developed in this liquid while in close proximity to a grounded electrode. The developer containing cobalt naphthenate produced a deposit of high density in negatively charged image areas of the plate. Similarly, a suspension of 0.05 gram of Azo Oil Blue Black B in 100 ml. of the same paint thinner developed a weak, fringed image on negatively charged image areas, but by addition to the developer of an amount of Rexobase PW equal to 40% of the weight of pigment, a high-density, evenly dispersed image was obtained in broad image areas. Similarly, a suspension of 0.05 gram of Solfast Green in 100 ml. of paint thinner developed a weak fringed image in positively biased image areas of the xerographic plate, whereas after addition of an amount of cobalt naphthenate equal to 6 percent of the weight of the pigment, a heavy de-

5

posit was developed on positively charged image areas. Loose deposits of deposited pigments were transferred to receiver sheets and then fixed there by fusion into a low melting binder layer on the receiver sheets.

Example 2

A mixture of 3 grams of lampblack, 2 ml. of Superior Varnish, H2215 (a copolymer ink vehicle obtained from Superior Varnish Company) and 10 ml. of cyclohexane was ball-milled for five days, then 25 ml. of paint thinner was added and the mixture was further milled for three days. The resulting ink was diluted with 25 ml. of paint thinner and stored. The suspension contained particles ranging in size from about 0.1 to 1 micron. A 3 ml. portion was taken from storage and diluted to 100 ml. with paint thinner, then used for development of positively biased image areas on a xerographic plate in the presence of a closely spaced grounded developer electrode. Only very thin deposits were obtained when a 400 volt bias was applied, with the developer electrode negative and the support for the photoconductive layer positive, a heavy image was produced in the light-exposed areas, indicating that the particles were negatively charged. After addition of cobalt naphthenate to the suspension in an amount equal to 10% of the weight of solid particles, a strong image was developed in unexposed areas without application of bias, indicating that the particles were now positively charged. Similarly, it was found that cobalt naphthenate apparently altered the charge from negative to positive when added to a developer that was prepared by milling 6 grams of lead chromate in 2 grams of boiled linseed oil, and then diluting with 50 ml. of paint thinner before storage, and then further diluting, as above. A yellow image was deposited from this developer in negative image areas. After fixing, the yellow image was blackened by swabbing with an aqueous solution of sodium sulfide.

Example 3

A mixture of 10 grams of S & K Offset PC Black Printing Ink (C. E. Johnson Company) and 40 ml. of odorless paint thinner was ball-milled for three days and

6

areas using no bias. Similar results were obtained using Multilith Black Ink ML 36 and Readi Set Black NY 22615 Litho Ink (Fuchs & Lang Div., Sun Chemical Co.) and Slight and Helmuth Cyan Ink No. 7048 (Slight and Helmuth, Inc.). With each ink a different amount of metal soap was required to produce good quality images. The required amount ranged from 5 to 50% of the solids present in the developer suspension.

In a preferred embodiment of the invention fusible toner particles are provided that comprise (1) a fusible binder which usually will be a thermoplastic polymer, and (2) a charge agent of the class described above. A pigment or dye may also be included in fusible toner particles. Use of fusible polymer toner particles in liquid xerographic developers has been limited because of difficulty in sustaining a charge level on the suspended particles sufficient to attract them to oppositely charged image areas on a xerographic plate. This has been especially true with relatively larger particles and in liquid development of broad image areas. By including a charge agent of the class described in the composition of fusible toner particles, the particles can be made to sustain a stronger charge than they could do without such charge agent.

The composition of fusible toner particles that contain a charge agent according to the present invention preferably is in the following ranges, shown as percent by weight based on total weight of the particles

Component:	Weight percent (range)
Fusible polymer	40-90
Compatible coloring matter (dye or pigment)	0-50
Charge agent	3-30

Any of a number of thermoplastic polymers may be used for making the toner particle. For most uses a thermoplastic polymer having a fusion point in the range from about 50 to about 200° C. will be chosen. In some cases, however, other fusion temperatures may be preferred. Some examples of polymer materials that are suitable for making fusible toner particles according to the present invention are:

TABLE 3.—POLYMERIC BINDERS FOR FUSIBLE TONER PARTICLES

Name	Type	Manufacturer	Softening Point, ° C.	Melt Viscosity	Charge Effect
Styron PS-2	Polystyrene	Dow	75	Mod.	None.
Styron PS-1	do.	Dow	Low	Do.
AYAC	PV Acetate	Bakelite	48	Low	Do.
Amberlac D96	Maleic Rosin	Rohm and Haas	99	Low-mod.	Pos. or 0.
Pentacol 20	Mod. Pentaeryth.	Polymer Corp.	120	Mod.	Pos. or 0.
Costyreneblak	Carbon-polystyrene	Columbian	High	Neg.
Picco 410	Hydrocarbon	Penna. Ind.	100	Mod.	Pos.
Picolastic B75	Styrenated H.C.	Penna. Ind.	75	Low-mod.	None (?)
Nebony 100	Hydrocarbon	Neville	100	Low-mod.	Pos.
Nebony LX769A	Styrenated H.C.	do.	100	Mod.	None (?)
Lucite 29	Methacrylate	DuPont	115	High	Pos.
Lucite 41	do.	do.	do.	Pos.
VYLF	Vinyl Chloride	Bakelite	95	do.	None.
VYHH	do.	do.	do.	Do.
SP-6700	Phenolic	Schenectady	85	Low	Neg.
Amberol 226	Phenol-Rosin	Rohm and Haas	70	V. low	Neg.
Aroclor 5460	Chlor. Phenyl	Monsanto	100	Low	None (?)
Arochem 650	Polyester	Archer-Daniels	76	Low-mod.	Pos. or 0.
Picoflex 100A	Styrene copolym.	Penna. Ind.	100	Mod.	Pos. or 0.
Silicone Z-6018	Silicone	Dow Corning	Mod.	Neg. or 0.
Carbowax 4000	Polyethylene Glyc.	Union Carbide	53	Low	Pos. or 0.

then 0.5 ml. portions were diluted with 100 ml. of paint thinner. This developer would produce only fringe images on negatively charged image areas of a xerographic plate opposite a development electrode with a bias of 400 volts applied, the polarity of the photoconductive support being positive. However, on addition to the developer of an amount of cobalt naphthenate equivalent to 50% of the weight of solids present, black images were produced in the negative image areas with good coverage of broad

The compatible coloring matter, usually a pigment or dye, when included in the fusible toner particle composition, will in most cases affect the net charge on the particles. The charge agent serves to increase this net charge. Following are examples of compatible coloring matter that are suitable for use directly in fusible toner particles and also in other liquid suspensions according to the present invention.

TABLE 4.—PIGMENTS AND DYES FOR FUSIBLE TONER PARTICLES

Name	Type	Manufacturer	Charging Effect
Spirit Nigrosine	Aniline	Gen. Aniline	Strong pos.
Nubian Resin Black	Solvent Black 5	Nat. Aniline	Do.
Grasol Fast Black F	Solvent Black 18	Ciba	Do.
Induline Base B	Solvent Blue 7	Gen. Aniline	Do.
Phthalo Blue	Phthalocyanine	Nat. Aniline	Do.
Spirit Blue B	Solvent Blue 3	N.Y. Color and Chem.	Do.
Orasol Blue BLW	Solvent Blue 10	Ciba	Weak pos.
Spirit Blue RBF	Solvent Blue 39	Nat. Aniline	Mod. pos.
Brilliant Blue 6G	Basic Blue 1	do	Mod. pos.
Brilliant Blue 5B	Basic Blue 5	Allied	Mod. pos.
Kiton Pure Blue V	Acid Blue 1	Ciba	Mod. pos.
Brilliant Wool Blue G	Acid Blue 99	Nat. Aniline	Weak pos.
Pyramid Cerise	Pig. Violet 1	Max Marx	Pos. or neg.
Costyreneblak 903	Carbon in Poly S.	Columbian Carbon	Strong neg.
Germantown Black	Carbon	do	Do.
Neo Spectra Black	do	Columbian Carbon	Do.
Orasol Black B	Solvent Black 6	Ciba	Do.
Azsol Fast Black MA	Solvent Black 19	Nat. Aniline	Do.
Solfast Green	Phthalocyanine	Sherwin Williams	Do.
Cyan Green Toner G	do	American Cyanamid	Do.
Iosol Black	Solvent Black 13	Nat. Aniline	Moderate neg.
Spirit Fast Black, NJ	Solvent Black 20	do	Do.
Orasol Black BR	Solvent Black 15	Ciba	Strong neg.
Spirit Fast Black	Solvent Black 14	Nat. Aniline	Moderate neg.
Orasol Black 2RG	Solvent Black 2	Ciba	Weak neg.
Orasol Navy Blue RB	Solvent Blue 1	do	Do.
Azsol Fast Blue HLR	Solvent Blue 42	Gen. Aniline	Do.
Azsol Fast Blue HLD	Solvent Blue 38	do	Do.
Azsol Brilliant Blue B	Solvent Blue 9	do	Do.
Spirit Fast Blue B	Solvent Blue 29	Nat. Aniline	Do.
Iosol Blue 6G	Solvent Blue 31	do	Do.

Following are specific examples illustrating preferred embodiments of the invention in which the charge agent is incorporated as an ingredient of the fusible toner particles.

Example 4

A mixture of 0.3 g. of Spirit Nigrosine plus 3 g. of Dow Styron, Grade PS-2, plus 0.5 g. of Uversol Cobalt Liquid (6% cobalt as the naphthenate) was fused together with frequent stirring. The mix was cooled, crushed, and ball-milled for 18 hours in the presence of 20 ml. of a hydrocarbon liquid having a 95° C. flash point and consisting essentially of branched chain paraffins, sold for use as an odorless paint thinner. After milling, the particles ranged in size from 2-30 microns. The viscous paste was diluted with an additional 50 ml. of paint thinner, and stored. As needed, 3 ml. portions were diluted to 100 ml. with more of the same liquid, and used as a liquid developer. A conventional xerographic plate comprising a negatively charged zinc oxide layer which had been exposed to a pattern of light, was immersed in the developer liquid. Another plate was developed by flowing the developer liquid over the surface of the plate. Both of these techniques produced line images that were fringed. By holding a grounded electrode of broad area at a space of about 0.02 to 0.05 inch from the xerographic plate during development, the toner particles were caused to deposit evenly in the unexposed negative areas of the plate. Upon drying of the plate and fusion of the deposited particles by heat using conventional methods, a dense black image of good quality was obtained. The experiment was repeated, but using particles without a charge agent. Development with these solid particles produced an unsatisfactory image with little or no deposit of particles in broad image areas, even when a grounded electrode was present.

Metal soaps other than cobalt naphthenate, have been used successfully in experiments similar to Example 4 with comparable results. Examples are Zirex and Manganese Paste. Other polymers that have been substituted for Styron are polyvinyl acetate, Grade AYAC, polyvinyl chloride-acetate, Grade VYHH, Picco 410, Nebony 100, and Amberlac D96. Examples of other dyes that can be used in place of Nigrosine are Nubian Resin Black, Spirit Blue, C. P. blue, Phthalo Blue, Orasol Blue BLW, and Pyramid Cerise.

Example 5

A mixture of 0.3 g. of Spirit Nigrosine, plus 3 g. of Dow Styron PS-2, plus 0.5 g. of Rexobase PW was fused together and mixed to uniform composition. The mix was cooled, crushed, and ball-milled with paint thinner as in Example 1. Dilution and application as a liquid developer were also performed as in Example 1. The toner deposits obtained were dense black with sharp lines and broad images when applied in the presence of a closely spaced development electrode. Similar compositions in which surfactant was not incorporated produced weak deposits in the broad areas of the xerographic plate.

In place of Rexobase PW, the following may be substituted with equivalent high quality: Rexobase XX, Rexobase GA, Peregol OK, Priminox 32, both as received and acetylated with acetic acid, Atlas G-3780A quaternized with N-butyl iodide, Duomeen T Dioleate, and sodium maleopimaril glutamate. Moderately high density results were obtained using the following charge agents: Sodium oleylmethyl tauride, Victawet 58B, Alkaterge T, Hyamine 1622, Sipex TEA, Adogen 401 and 402, Duomeen T, Octimet, Nopcofen 16S, Alkanol B, Aerosol OT, Ethomeen T/25 and 18/15, and Duomeen T Butylbromide. Instead of Spirit Nigrosine, the following colorants may be substituted: Costyrene Black 903, Solfast Green, Pyramid Cerise, Grasol Fast Black F, Nubian Resin Black, or Iosol Black.

Example 6

A mixture of 0.3 g. of Nubian Resin Black plus 2 g. of Lucite 29, plus 0.3 g. of Uversol Cobalt Solid (10% cobalt) were dissolved in a mixture of 3.5 ml. methylene chloride, 6.5 ml. of 1,1,1-trichloroethane, and 10 ml. of acetone. This mixture was sprayed in air and collected in an electrostatic precipitator. The finely divided powder was suspended in paint thinner using 0.1 g. of powder per 100 ml. of solvent, by ball-milling for 1 hour, and the suspension was used for development of an electrostatic image as in Example 1. Upon development the results were comparable with those obtained in Example 1.

Example 7

A mixture of 0.4 g. of Spirit Nigrosine plus 2 g. of Dow Styrene Grade PS-2 plus 0.4 g. of Uversol Cobalt Solid (10% cobalt naphthenate) were dissolved in 40 ml. of methylene chloride and the solution was sprayed at

50 pounds pressure through an orifice 0.2 mm. diameter in a container filled with 900 ml. of the hydrocarbon solvent described in Example 1. The suspended particles were allowed to settle, and most of the liquid was removed by centrifuge. The solid mass was ball-milled for 1 hour with 20 ml. of paint thinner and then diluted to 45 ml. total volume using the same solvent. Portions of 3 ml. each were then diluted to 100 ml. each with the same solvent, and were used in a liquid developing process as described in Example 1. On the xerographic plate heavy black deposits were formed in the image areas and the image had improved sharpness as compared with the image formed by the ball-milled toners prepared in Example 1. The particle sizes of precipitated particles range from about 1 to 3 microns. Particles of this size which do not contain a charge agent generally have a better charge characteristic than do larger particles of the same composition, and in some cases a fairly good deposit of particles of this size without a charge agent can be obtained on a charged plate. However, even in the case of such small particles, presence of a charge agent of the type described above will greatly improve the deposit characteristics and the quality of the image, especially in broad image areas.

A few examples of other high resistance liquid vehicles that can be substituted in the above examples are: n-hexane, n-octane, iso-octane, cyclohexane, toluene, xylene, petroleum ether, kerosene, light mineral oil, carbon tetrachloride, Freon 113, Freon BF, and the like.

The invention has been described with reference to certain preferred embodiments, but it will be understood that variations and modifications can be made within the scope of the invention defined in the following claims.

I claim:

1. A liquid xerographic developer comprising a high resistance liquid vehicle, and fusible toner particles of an average size from 0.1 to 30 microns dispersed in said liquid vehicle, said particles comprising:
 - (1) from 40 to 90 weight percent of a thermoplastic polymer having a fusion point in the range from about 50° C. to about 200° C.
 - (2) from 5 to 30 weight percent of compatible coloring matter, and
 - (3) from 5 to 30 weight percent of a charge agent selected from the group consisting of
 - (a) soaps of magnesium and heavier metals, and
 - (b) cationic, anionic and non-ionic surface active agents.
2. Fusible toner particles defined in claim 1 wherein said charge agent consists of a polyethylene glycol derivative that contains a cationic group.
3. Fusible toner particles defined in claim 1 wherein said charge agent consists of a polyethylene glycol derivative that contains an amino group.
4. Fusible toner particles defined in claim 1 wherein said charge agent consists of a polyethylene glycol derivative that contains a quaternary ammonium group.
5. A liquid xerographic developer consisting essentially of a high resistance liquid vehicle, solid discrete toner particles having an average particle size from 0.1 to 30 microns, and from 3 to 50% by weight based on the weight of solid particles present of a charge agent selected from the group consisting of:
 - (a) soaps of magnesium and heavier metals, and
 - (b) cationic, anionic and non-ionic surface active agents.
6. A liquid xerographic developer comprising a high resistance liquid vehicle, and fusible toner particles of an average size from about 0.1 to about 30 microns dispersed in said liquid vehicle, said particles comprising:
 - (1) from about 40 to about 90 weight percent of a thermoplastic polymer having a fusion point in the range of about 50° C. to about 200° C.,
 - (2) up to about 30 weight percent of a colored marking material, and
 - (3) from about 5 to about 30 weight percent of a

charge agent comprising a soap of magnesium and heavier metals.

7. The liquid xerographic developer of claim 6 wherein the charge agent comprises cobalt naphthenate.

8. A method of xerographic development comprising contacting liquid developer with the surface of a xerographic plate having a charged photoconductive layer that has been exposed to a light pattern, said developer liquid consisting essentially of a high resistance liquid vehicle, solid discrete toner particles having an average particle size of 0.1 to 30 microns, and from 3 to 50% by weight based on the weight of solid particles present, of a charge agent selected from the group consisting of

- (a) soaps of magnesium and heavier metals, and
- (b) cationic, anionic, and non-ionic surface active agents.

9. A method of xerographic development comprising contacting developer liquid with the surface of a xerographic plate having a charged photoconductive layer that has been exposed to a light pattern, said developer liquid comprising a high resistance liquid vehicle and, dispersed in said liquid vehicle, toner particles of an average size from 0.1 to 30 microns comprising:

- (1) from 40 to 90 weight percent of a thermoplastic polymer having a fusion point in the range from about 50° C. to about 200° C.
- (2) from 5 to 30 weight percent of compatible coloring matter, and
- (3) from 5 to 30 weight percent of a charge agent selected from the group consisting of
 - (a) soaps of magnesium and heavier metals, and
 - (b) cationic, anionic and non-ionic surface active agents.

10. The method defined in claim 9 wherein said developer liquid is contacted with said xerographic plate while said xerographic plate is in close proximity to a grounded electrode.

11. A method of xerographic development comprising contacting developer liquid with the surface of a xerographic plate having a charge photoconductive layer that has been exposed to a light pattern, said developer liquid contacting said xerographic plate while said plate is in close proximity to a grounded electrode, said developer liquid comprising a high-resistance liquid vehicle and, dispersion in said developer liquid from particles of an average size of 0.1 to 30 microns comprising:

- (1) from about 40 to 90 weight percent of a thermoplastic polymer having a fusion point in the range from about 50° C. to about 200° C.
- (2) from about 5 to 30 weight percent of compatible coloring matter, and
- (3) from about 5 to 30 weight percent of a charge agent selected from the group consisting of soaps of magnesium and heavier metals.

References Cited

UNITED STATES PATENTS

2,899,335	8/1959	Straughan	117—37
2,361,740	10/1944	Boggs et al.	106—29
3,165,420	1/1965	Tomanek et al.	252—62.1
3,207,601	9/1965	Gaiamo	96—1
3,215,527	11/1965	Johnson	252—62.1
3,236,776	2/1966	Tomanek	96—1
3,241,957	3/1966	Fauser et al.	96—1
2,877,133	3/1959	Mayer	117—37
2,907,674	10/1959	Metcalfe et al.	117—37
3,051,659	8/1962	Troelstra	252—317
3,032,432	5/1962	Metcalfe et al.	117—37
3,053,688	9/1962	Greig	117—37
3,253,913	5/1966	Smith et al.	96—1.2
3,267,057	8/1966	Spiller	260—22

(Other references on following page)

3,417,019

11

FOREIGN PATENTS

608,901 11/1960 Canada.
866,780 5/1961 Great Britain.
873,080 7/1961 Great Britain.
239,647 7/1962 Australia.
1,261,521 4/1961 France.

OTHER REFERENCES

Weiser, Colloid Chem., 2nd edition, Wiley and Sons 10 96—1; 117—37; 106—27
(1949), pp. 266—270.

12

Schwartz-Perry, Surface Active Agents, Interscience
Publishers Inc., New York (1949), pp. 473—476.

NORMAN G. TORCHIN, *Primary Examiner.*

5 C. E. VAN HORN, *Assistant Examiner.*

U.S. Cl. X.R.