

[54] ELECTROSTATIC LIQUID DEVELOPER
COMPOSITION

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abandoned, which is a continuation of Ser. No.
575,970, Aug. 30, 1966, abandoned, which is a
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1964, abandoned.

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[58] Field of Search..... 252/62.1

[56]

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UNITED STATES PATENTS

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[57]

ABSTRACT

The present invention is directed to a liquid toner
composition comprised of a carrier liquid having toner
particles suspended therein and also containing a tri-
valent or tetravalent metal salt of an organic acid plus
an organic amine dissolved in the carrier.

4 Claims, No Drawings

ELECTROSTATIC LIQUID DEVELOPER COMPOSITION

This is a continuation of application Ser. No. 778,006, filed on Nov. 18, 1968, now abandoned, which is a continuation of application Ser. No. 575,970 filed on Aug. 30, 1966, now abandoned, which latter application is a continuation-in-part of U.S. application Ser. No. 343,130 filed Feb. 6, 1964, also now abandoned.

This invention relates to electrophotography, and more particularly to improvements in the development of visible images from latent electrostatic images by the use of liquid developers.

In electrophotography, latent electrostatic images are formed on a photoconductive surface of a recording element by uniformly charging the surface thereof, as by a corona discharge device in the dark, followed by exposure to light in the desired image pattern. Such images have been heretofore developed or rendered visible by use of liquid developers comprising colored toner particles suspended in an insulating liquid. It is known that the insulating liquid should have high volume resistivity, preferably at least 10^9 ohm-centimeters and low dielectric constant, preferably 3.4 or less. Suitable liquids include aromatic hydrocarbons such as benzene, toluene, xylene, etc.; aliphatic hydrocarbons such as hexane, cyclohexane, heptane, etc.; freons or halogenated hydrocarbons; silicone oils; or mixtures thereof. The suspended toner particles, usually finely-divided pigments or pigmented resins, are electrostatically charged and develop the latent image by migration to the image surface under influence of the image charge. The resulting prints are usually fixed by fusing the toner particles either directly to the image surface or to another surface following transfer of the toner particles thereto.

To obtain a positive print by development as described above, the suspended toner particles should carry an electrostatic charge opposite to the charge present in the electrostatic latent image. Latent images currently used are negatively charged and the toner particles should carry a positive charge to obtain a positive print therefrom. Obtaining satisfactory positive charge of suspended toner particles has heretofore been largely a matter of trial and error. Furthermore, previous liquid suspensions used as developers have been of limited stability and have provided prints with limited definition and density.

It is the principal object of the present invention to provide improved liquid development of latent electrostatic images. Other and further objects include provision of liquid developers with the desired positive charge on the suspended toner particles, which provide prints with improved definition and density, and which are more stable and less subject to settling.

In accordance with this invention the improved liquid toner composition is obtained by dissolving, in the insulating liquid used to suspend the toner particles, a mixture of two substances which remain dissolved at use temperature as follows:

1. a trivalent or tetravalent metal cation salt of an organic acid, and
2. an organic amine, including ammonia and primary, secondary, tertiary and quaternary amines.

While both materials must be present, the amounts thereof are not critical if used in effective quantities which do not seriously lower the dielectric properties

of the resulting solution in the insulating liquid, that is, provided amounts are used which do not lower the volume resistivity of the insulating liquid-additive solution below the 10^9 ohm-centimeters or raise the dielectric constant above about 3.4. Small quantities are beneficial in enhancing the contrast of the print and/or the stability of the developer suspension. Increasing amounts typically improve the developer until a maximum is reached. Beyond such maximum, increasing amounts have little effect until the insulating qualities of the suspending medium are adversely affected. Preferably, from 0.01 to 5% of the metal cation salt (1) and from 0.01 to 6% of the organic nitrogen compound (2) is used, all percentages being based on the total weight of toner particles in the developer. The best combined total amount and the ratio between the additives varies somewhat with the specific system and can best be determined empirically by a series of routine tests with varying amounts and ratios. Generally a total of about 1 to 6% is suitable and the ratio will be within the limits of 60:1 and 1:60.

Examples of suitable metal salts (1) are the trivalent and tetravalent cation salts of aluminum, iron, thorium, zirconium, lanthanum, germanium, tin, vanadium or thallium salts of any organic acid, whether mono or poly basic, for example, octoic, stearic, resin, polymerized rosin, naphthenic, N-tallow B-imino dipropionic, and succinic acids. The salts should be substantially soluble in the insulating liquid and be chemically nonreactive in the developer, and, for stability, are preferably of low volatility.

As the second additive (2), any organic amine, including ammonia, can be used provided it is substantially soluble and chemically non-reactive in the developer. In addition to ammonia, examples include tetraethyl ammonium chloride; Amine C of the Geigy Chemical Co., a substituted imidazoline alicyclic amine having the formula $\text{CH}_3(\text{CH}_2)_n\text{C}_3\text{H}_4\text{N}_2\text{C}_2\text{H}_4\text{OH}$; N-coco-morpholine, the Armeens and Duomeens of Armour and Co., for example Armeen DMSD, a tertiary dimethyl soya amine, Duomeen TDO, a tallow amine dioleate, and Duomeen 12, n-lauryl propylene diamine; the polyethoxylated aliphatic amines available from Armour and Co. As Ethomeens and Ethoduomeens and preferably the organic acid esters thereof; and polymeric amines such as Lube Oil 564 of Du Pont, a copolymer of laurylmethacrylate and diethyleaminoethylmethacrylate, and similar materials such as those described as oil additives in U.S. Pats. Nos. 2,737,452 and 3,008,813, especially those described in the third column of the latter patent as a second class of polymeric additives, and defined as nitrogen-containing addition-type copolymers of an amine-free monomer containing one ethylene linkage and an aliphatic hydrocarbon chain of from 8 to 18 carbon atoms with a monomer containing a nitrogen atom and one polymerizable ethylene linkage. While the simply organic nitrogen compounds are operative in providing enhanced toner charge and print contrast, the larger materials, preferably polymeric, are preferred for their low volatility and protective colloid function which aids in providing stability in the suspension during storage and use. Tertiary amines of substantial molecular weight are most preferred.

While the additives (1) and (2) are chemically non-reactive in the developer as stated above, no primary bonds of the covalent, ionic or metallic type being

formed in the developer, some secondary association between the additives themselves is believed to occur. For example, mixtures of both additives in Odorless mineral spirits generally have higher conductivities than either alone in like quantities. While the type of association is not understood, it is believed to involve the amine nitrogen atom or atoms and the carboxyate groups of the salt. For example, infrared spectrum of solutions of equal weight quantities of both additives in Odorless mineral spirits, aged at least 48 hours, show a measurable decrease in the absorbance at about 6.3 microns, a peak attributed to the carboxyate group of the salt (1), over the spectra of a like solution of the salt alone.

The following examples are for the purpose of illustration, Example 2(c) being currently preferred. All parts are by weight unless otherwise stated.

The toner particles indicated in the Examples 1-7 were prepared as follows:

Toner Particles

Nigrosine SSB dye	40
Santicizer 9	30
Santowax M	20
Age Rite Resin D	10

The last three ingredients were melted together, the dye dissolved therein and the melt solidified by cooling and then ground. Nigrosine SSB is a black dye obtained from the National Aniline Company, Santowax M and Santicizer 9 are respectively a meta terphenyl and a mixture of ortho and para toluene sulfonamides obtained from the Monsanto Chemical Company, and Age Rite Resin D is a polyquinoline obtained from the R. T. Vanderbilt Company. Many other suitable toner compositions are known and can also be used.

Example 1

Material	Developer Concentrates				
	a	b	c	d	e
Toner particles	10	10	10	10	10
Odorless mineral spirits (OMS)	39	39	39	39	39
Aluminum Tristearate	.01	.05	0.1	0.3	0.5
Lube oil 564	.59	.55	0.5	0.3	0.1

The foregoing concentrates were prepared by dissolving the aluminum salt and the Lube oil 564 in the OMS, adding the toner particles, and ballmilling the mixture in a porcelain mill with steel balls for 16 hours. OMS is a mixture of paraffin hydrocarbons obtained from the American Mineral Spirits Company having a distillation range from 352° to 390°F. and a flashpoint of 125°C.

One-fourth part of each of the above compositions was further diluted with 100 parts of additional OMS. A conventional electrofax recording element compris-

ing paper coated with photoconductive zinc oxide suspended in a resinous binder was processed to provide a latent image by exposure to a corona discharge device at a 6KV negative potential and discharged with light in an image pattern. Recording elements were then developed by immersion in each of the foregoing diluted compositions and fixed by heating for a few seconds above the melting temperature of the toner particles, for example 125°C. Prints with good contrast and good definition were obtained. Composition d having the metal salt and organic esters present in equal weight amounts provided the best prints and the best stability of liquid toner against settling.

Example 2

Additional compositions involving the ingredients of Example 1 were made as follows, the dispersant mixture being equal weight amounts of the aluminum salt and Lube oil 564 stated above.

Material	a	b	c	d	e
Toner particles	10	10	10	10	10
Dispersant mixture	0.3	0.5	1.0	5.0	7.5
OMS	39.5	39.1	38.5	34.3	30.32

Again the dispersant mixture was first dissolved in the OMS, the toner particles added, and the mixture ballmilled for sixteen hours. One-fourth part of each composition was further diluted with 100 parts additional OMS and prints developed as above-described in Example 1. Good contrast and definition were obtained.

Example 3

Toner particles	10
Aluminum tristearate	0.5
Nitrogen Compound	0.5
OMS	38.25

The resulting mixture was ballmilled for 16 hours to provide a fluid dispersion, and one-fourth part thereof

further diluted with 100 parts additional OMS. Electrostatic prints as previously described were prepared and provided excellent contrast. The nitrogen compound used above was prepared by esterifying three moles of oleic acid with one mole of Ethomeen C/15, followed by neutralization of the resulting amine salt with caustic. Ethomeen C/15 is the reaction product of 5 moles ethylene oxide with one mole coco amine. Ethomeen C/15 is useful without esterification but the ester is preferable, apparently due to a reduced tendency to lower the insulating properties of its solution with OMS.

Example 4

The same as Example 3 above, excepting that the ester was a terpolymer of 40 parts laurylmethacrylate, 10 parts diethylaminoethylmethacrylate and 40 parts styrene.

Example 5

The same as Example 4 above, excepting that the thorium salt of rosin acid was substituted for the aluminum tristearate. Prints with good contrast were obtained by following the procedure described in Example 1.

Example 6

The same as Example 5 above, excepting that ferric stearate was used instead of the thorium salt.

Example 7

The same as Example 5 above, excepting the zirconium salt of rosin acid was used in place of the thorium salt.

Example 8

Toner Particles	
Carbon Black	10
Resin	90

The finely divided carbon black was suspended in the melted rosin, the mixture cooled and ground. A developer concentrate was prepared therefrom as follows:

Concentrate	
Toner particles	10
Dispersant mixture of Example 2	1.0
OMS	38.25

One-fourth parts of the above concentrate were diluted with an additional 100 parts OMS and prints prepared therefrom as described in Example 1. Prints with excellent contrast and definition were obtained.

Example 9

Toner Particles	
Nigrosine SSB	600
Santicizer 9	400

Toner particles were prepared by dissolving the dye in the melted Santicizer 9, cooling, and grinding.

Toner Concentrate	
Toner particles, above	10
OMS	37
Aluminum Dresinate 731	0.35
Nitrogen Compound, one of:	
(1) Duomeen TDO	1
(2) Armeen DMSD	1
(3) N-coco-morpholine	1
(4) Duomeen 12	1
(5) Amine C	1
(6) Tetraethyl Ammonium chloride	0.1
(7) Anhydrous ammonia	

The resulting mixtures were ballmilled for 16 hours to provide fluid dispersions and one-fourth part of each further diluted with 100 parts additional OMS. Electro-

static prints prepared as previously described provided excellent contrast. The anhydrous ammonia example was prepared by bubbling the gas through the OMS for about 25 minutes.

Aluminum Dresinate 731 was prepared by aqueous cation exchange between a soluble aluminum salt and Dresinate 731, the sodium salt of rosin acids obtained from Hercules Powder Company.

In all of the foregoing Examples, omission of either of the additives results in a less stable suspension which provides a print with faint or defective contrast. For reasons not thoroughly understood, the two additives, together, materially improve contrast, believed to be due to increasing the electrostatic charge on the suspended toner particles. By proper choice of additive, substantially improved suspension and dispersion properties are simultaneously obtained.

It should be understood that the foregoing description is for the purpose of illustration and that the invention includes all modifications falling within the scope of the appended claims.

I claim:

1. A liquid developer composition for developing a latent electrostatic image consisting essentially of positively charged, finely divided toner particles comprising carbon black suspended in an insulating liquid selected from the group consisting of benzene, toluene, xylene, cyclohexane, and paraffin hydrocarbons and a mixture of (1) a metal cation salt selected from the group consisting of trivalent and tetravalent salts of aluminum, iron, thorium, zirconium, lanthanum, germanium, tin, vanadium, thallium, and an organic acid selected from the group consisting of octoic, stearic, rosin, polymerized rosin, naphthenic, N-tallow B-imino dipropionic and succinic acids and (2) an organic amine, said amine selected from the group of N-cocomorpholine, an imidazole of the formula $\text{CH}_3(\text{CH}_2)_n\text{C}_3\text{H}_7\text{N}_2\text{C}_2\text{H}_4\text{OH}$ wherein n is a positive integer; tertiary dimethyl soya amine; tallow amine dioleate; n-lauryl propylene diamine; and a copolymer of lauryl methacrylate and diethylaminoethylmethacrylate; said salt and amine being chemically non-reactive in the developer and being dissolved in said insulating liquid at printing temperature, said insulating liquid solution of (1) and (2) having a volume resistivity of at least about 10^9 ohm centimeters and dielectric constant less than about 3.5, said salt and amine being present in the amount effective to provide improved image density and definition in developed electrostatic images, said insulating liquid being present in major amounts sufficient to provide a free flowing liquid developer composition.

2. A liquid developer composition according to claim 1 having dissolved therein from about 0.01 to 5% of said metal cation salt (1) and from about 0.01 to 6% of said amine, said percentages being based on the weight of toner particles present in the composition.

3. A liquid developer composition according to claim 1 wherein said metal salt is an aluminum salt of rosin acid and said copolymer is a terpolymer of laurylmethacrylate-diethylaminoethylacrylate and styrene.

4. A liquid developer composition according to claim 1 where said salt is an aluminum salt of rosin acid.

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