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LIQUID TONER

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No Drawing. Continuation-in-part of applications Ser. No. 165,254, Jan. 9, 1962, and Ser. No. 300,910, Aug. 8, 1963. This application Jan. 10, 1966, Ser. No. 519,520
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U.S. Cl. 252—62.1 11 Claims

This application is a continuation-in-part of my prior applications Ser. Nos. 300,910 filed Aug. 8, 1963 and 165,254 filed Jan. 9, 1962, entitled, "Liquid Developer," and now abandoned.

This invention relates to novel non-uniform coating methods and compositions for use in electrophotographic processes in which a latent electrostatic image existing as a charge pattern on a surface is converted into a visible image by electro-deposition of solid particles from a liquid suspension to form a coating on the charge surface in accordance with the intensity of the charge pattern.

The developer or toner compositions of this invention are generally applicable in copying processes in which a latent electrostatic image is formed and subsequently converted into a visible image by application of a liquid developer, such as disclosed, for example, in U.S. Patent No. 2,991,754 to Johnson. These developers are particularly useful in the processes carried out in the developing apparatus disclosed in U.S. Patent No. 3,202,526 to Ralph Ostensen.

Liquid electrostatic developer compositions have been known as shown, for example, by U.S. Patent No. 2,890,-174 to Mayer and U.S. Patent No. 2,891,911 to Mayer et al. The improved compositions of the present invention, however, afford a combination of advantages and improved image quality and control (especially when used in the apparatus of the aforesaid copending application) not obtainable by the use of prior art developers. These advantages reside primarily in providing a developer or toner which may be easily applied uniformly over the entire surface area of a page; is "self-fixing" in that evaporation of the dispersant renders the image permanent without the necessity of applying heating or pressure, etc.; produces extremely fine images with high degrees of resolution; requires only a simple means for application to the charged paper; and enables the user to replenish and maintain uniformity very easily and yet eliminates problems of cleaning the copying apparatus.

Accordingly, a major object of the present invention is to provide a novel coating method for developing negative electrostatic latent images which comprises dispersing pigment particles in a high resistivity liquid carrier material and then adding to the dispersion a sufficient amount of metal ions to visually improve the quality of the finally developed image when the dispersion is applied to a surface having a negative electrostatic image thereon.

A further object is to provide a novel toner or coating composition capable of developing negative electrostatic latent images which contains an effective amount of a metal salt of an organic acid therein to add a sufficient amount of metal ions to the composition to visually improve the quality of the finally developed images.

A further object resides in providing improved positive-acting electrostatic toner compositions and methods which produce images that are sharper, clearer and more intense than those produced by the prior art through incoporation in the composition of a metal salt of an organic acid in sufficient quantity to add up to 0.2% by weight of metal ions to said composition.

Another object is to provide a novel method and composition for depositing coated or uncoated pigment particles bearing a positive charge from a liquid dispersion on

the negatively charged regions of a latent electrostatic image.

Still another object of this invention is the provision of novel, liquid, electrostatic toner compositions including an evaporative liquid system which will very rapidly produce a permanent, dry image, and which, when used, will dispose of waste products into the surrounding atmosphere, thus eliminating the need for plumbing, cleaning and mixing baths, and other fixing means required with some prior liquid electrostatic toner compositions.

Other objects and advantages of this invention will become apparent to those skilled in this art from the following description and appended claims.

In general, the novel liquid electrostatic toner compositions provided by the present invention include finely divided, opaque, electrostatically attractable, pigment particles dispersed in a liquid carrier. The particles may be uncoated or coated as will be described. To this dispersion is added a minor amount of an image quality enhancing agent which sharply increases the quality of images obtainable from liquid electrostatic toners. In addition, a dispersant may be added to the composition, if desired, to assist in maintaining the pigment particles in suspension.

The essential ingredients of the novel compositions of the present invention are: (a) a liquid carrier; (b) a pigment particle; and (c) an image quality enhancing agent. Optionally a stabilizer may also be added to the composition and the pigment particles may be coated with a paste having one or more of a charge control agent, a fixer and a dye toner therein. The foregoing ingredients are employed normally in the following proportions:

Ingredient	Operative range (by weight)	Preferred range (by weight)
Pigment particles (either coated or uncoated).	0.00005 to 5.0%	0.025 to 1.25%.
Dispersant	None to 0.75%	None to 0.625%.
Image quality enhancing agent.	Trace to amount which causes image quality deterioration, i.e. 10%.	0.001 to amount which optimizes image quality, i.e. about 0.10%.
Liquid carrier	Remainder	Remainder (approx. 94.20–99.45%).

The carrier liquid must have the property of high electrical resistivity (about 10^{10} ohm-cm.) and be of a substance in which the finely divided pigment can be dispersed. The carrier should exhibit relatively low solvency for the electrostatic coating of the paper (normally ZnO) or other material on which the electrostatic image is formed, should be substantially free of odor and toxicity, and should possess a relatively high flash point (above 100° F.) and have a boiling range of between 250° F. and 410° F. to minimize fire and explosion hazards. One carrier liquid which has been found to provide excellent results in accordance with this invention is Shel-Sol 72, an odorless alkylate-type hydrocarbon consisting essentially of at least 92% by weight of isoparaffinic hydrocarbons boiling within the range of about 300° F. to 470° F. The most particularly preferred hydrocarbon of this class has a flash point of 128° F. (Tag closed cup) and solubility rated as Kauri Butanol No. 26.7. Another similar hydrocarbon liquid, which also provides excellent results, is Shell-Sol 71, a mixture of isoparaffins having between 9 and 14 carbon atoms. The foregoing hydrocarbons are very weak solvents for most organic resins which make them ideal for use with organic coated papers. Their rates of evaporation are fast enough to provide dry copies on a properly designed machine, yet slow enough to permit retention of the developer in an open tray for several weeks.

With the preferred alkylate type hydrocarbon liquid as the liquid toner constituent, an evaporative liquid system

is established which disposes of waste products into the air, thus eliminating the need for plumbing, cleaning and mixing baths, and/or fixing by other means. These liquids also permit rapid production of a dry copy which is very important in successful use in commercial equipment. The amount of hydrocarbon molecules distributed in the air upon evaporation is so small that it is barely detectable when the toner is exposed in open trays.

For a more complete description of suitable alkylate type thinners, reference is hereby made to United States Patent No. 2,795,563.

Chlorinated-fluorinated hydrocarbons such as trichlorotrifluoroethane and dichlorodifluoromethane may be added to the toner as diluents to reduce the toner viscosity and maintain good flowability. These materials also act as volatizers for increasing the toner evaporation rate and most of these chlorine and fluorine substituted hydrocarbons are highly dielectric so the dielectric properties of the liquid carier are enhanced by their addition.

The present invention, however, is not limited to and is not dependent for novelty on the use of the foregoing liquid carriers. For example, the proprietary hydrocarbon mixtures disclosed in the United States Patent No. 2,899,335; the dimethyl polysiloxanes disclosed in United States Patent No. 3,053,688; or the substituted hydrocarbons disclosed in United States Patent No. 3,058,914 may be employed if desired. The Shell-Sol hydrocarbons are preferred, however, because of their above-discussed advantages and because of their relatively low cost.

The pigment particles may be virtually any of a wide variety of electrostaticaly attractable, organic and inorganic, finely divided, opaque, intensely colored powders which are essentially insoluble in the carrier liquid and capable of being dispersed in the carrier to provide particles bearing an electrical charge of proper magnitude. The pigment particles are preferably of a size ranging from 0.1 to 10 microns in diameter although slightly larger or smaller particles may be used in some cases. Several suitable pigments are described in United States Patents Nos. 2,297,691, 2,907,674 and 2,877,133 which patents are hereby incorporated by reference into this specification for the purpose of illustrating the nature of the pigments which may be used. Examples of suitable pigments include carbon black, charcoal, talcum powder, metallic pigments, and organic pigments such as lakes and dye toners. These are used with or without a coating of natural and synthetic resins and oils such as asphaltum, alkyds, epoxies, and hydrocarbon resins. The resins are primarily added to give the pigment particles a positive or more positive electrostatic charge.

Some pigment particles, however, such as carbon black are inherently positive and can be used without a coating in the developer composition. Even with carbon black, a material such as asphaltum is preferably added to aid in fixing the particles in position on the copy sheet, however. Asphaltum, as defined in the condensed Chemical Dictionary (Rheinhold Publishing Corporation, 1950, page 72), has about 27.2% mineral matter. Its non-mineral constituents are fusible and largely soluble in carbon disulfide and it may be obtained as a residue from the distillation of asphaltic and mixed base crude oils. As well as acting as a fixer, it may also provide an incidental positive charge to the pigment particles when used.

The preferred coated pigment particle mixtures are produced from a mixture of Rogersol B–280, a surface plate developing ink made by the Harry H. Rogers Company, Inc. of Chicago, Ill., and #853 paste. #853 paste is manufactured by the Braznell Company and consists of carbon black, several dye toners and asphaltum and optionally small quantities of conventional solvents or flushing agents to reduce loss of the dry powders. The carbon black is the pigment particle and primary color imparting ingredient. The dye toners impart a highly desirable bluish-black hue to the pigment particles to thereby brighten the image. Asphaltum is partially soluble in the liquid carrier and adhesively bonds the pigment particles to the stratum on which the image is formed to provide a permanent image. Preferably, the paste contains from 50 to 75% asphaltum. Other suitable fixers or sticking agents which give satisfactory results in the practice of the present invention, are discussed in Australian Patent No. 234,619, which is hereby incorporated by reference.

Another especially effective coated pigment is produced from a mixture of asphaltum, carbon black and an alkali blue dye toner, i.e., a mixture of Rogersol B–280 and Color Base #35712 also manufactured by the Braznell Company, St. Louis, Mo.

My earlier application No. 165,254 disclosed what were termed "control agents" or "control ingredients" which, as pointed out in that application, had a suprisingly beneficial affect on the quality of the developed image. This name was selected because it was originally thought that these agents were adsorbed onto the pigment particles and acted solely by imparting an additional charge to the particles through an ionization process. It is now thought that metal ions are added to the toner by these agents (now termed image quality enhancing agents). It is believed that metal ions must be in sufficient concentration in the liquid composition to surround or actually contact the pigment particles so that they can influence their migration through the liquid to the charged surface. The metal ions are believed to be the important element and may be added to the composition in any suitable manner, the metal salts of organic acids being preferred.

It has been also theorized that these salts (image quality enhancing agents) in developing processes carried out under less than optimum conditions reduce the deposition of pigment particles on the non-image areas (or background) of the carrier on which the electrostatic image is formed. However, in developing processes carried out under optimum conditions where no background development occurs, the image quality enhancing agents still have a markedly visible effect on the image density, clearness and fringe effects. The image quality enhancing agents are believed to contribute to the positive electrostatic charge control characteristics on the pigment particles and it has been theorized that they may also act by reversally developing the background areas with a colorless transparent material consisting of polarized molecules (i.e., molecules having opposite electrical charges on their two ends). It has been theorized that the charge on one end of these molecules sticks them to the poorly charged background areas (the latent electrical image is formed by selectively discharging a uniformly charged surface) and that the opposite charge on the other end then repels the charged pigmented particles of coloring agent. Regardless of the theory, the primary effect of the image quality enhancing agents, however, has been observed to be derived from the influence these agents have on the migration of the pigment particles through the carrier liquid to the negatively charged image areas.

It has been found that a larger group of materials will provide the beneficial image quality enhancing function than was previously thought possible since the principal consideration is whether the material ionizes to get metal ions into the carrier liquid. More specifically, it has been found by experimentation that the metal salts of all organic acids, which salts are or can be made soluble or can be finely dispersed in the liquid carrier, function as image quality enhancing agents for providing denser, clearer images with a minimum of fringe effects. The solubility of the salt or its ability to be finely dispersed throughout the carrier has been found to be a main factor in determining whether it will function as an image quality enhancing agent. For those metal-organic acid salts which are not soluble in the liquid carrier directly, it has been found that if they are first dissolved in a solvent which can then be dissolved in the liquid carrier, the image enhancing function is still accomplished. While all of the soluble metallic salts of organic acids function satisfac-

torily as image enhancing agents, the divalent and trivalent metallic salts of aliphatic acids (straight and branched) having from 2 to 18 carbon atoms, because of their generally high solubility in the liquid carriers, are particularly suited for use as image quality enhancing agents and are preferred.

For example, the soluble or finely dispersable aluminum, barium, cadmium, calcium, cerium, cobalt, copper, iron, lead, lithium, magnesium, manganese, nickel, potassium, sodium, strontium, zinc and zirconium salts of 2-ethylhexanoic acid, resinic acid, naphthenic acid, abietic acid, linoresinic acid, acetic acid, benzoic acid, phthalic acid, stearic acid, oleaic acid and tallic acid have been found by observation to enhance visibly the image quality when added to liquid toners for developing negatively charged electrostatic latent images.

Substantially the only limitation on this class of materials is that the material have sufficient solubility in the carrier liquid or that it be soluble in a liquid which can be added to the toner composition without adverse effects or that it be capable of being finely dispersed throughout the carrier. For example, it has been found that the salts of the lower molecular weight organic acids such as acetic acid will work if enough of the salt is brought into solution. Salts such as manganese acetate which are insoluble directly in most liquid carriers can be dissolved in an appropriate solvent (isopropyl alcohol is suitable for manganese acetate) and the solution added to the toner composition. It is preferable, however, to employ a salt that is directly soluble in the carrier liquid for production, economic and similar considerations.

The image quality enhancing agents employed in the novel toner compositions of the present invention are to be distinguished in function and result from the charge control agents employed in the electrostatic developer compositions disclosed in United States Patents Nos. 2,907,674 and 3,078,231 to K. A. Metcalfe et al. The latter are alkyl, epoxy, cresylic, phenolic, and styrene modified epoxy resins, synthetic rubbers, polystyrene and linseed oil with which the pigment particles are coated and which act only by modifying the value or sign of the charge on the particles and in this sense are analogous to the coating pastes employed in this invention.

If the Metcalfe et al. positive acting control agents are used to coat the pigment particles, the final image may be still visibly improved by the addition of an image quality enhancing agent of this invention. Additionally, in contrast to the Metcalfe charge control agents, in the present invention the quality of the print is not so critically affected by the ratio of pigment particles to image quality enhancing agent. It has been found that the amount of image quality enhancing agent needed to produce prints of optimum quality remains approximately the same even though the concentration of pigment in the toner composition is varied from 5% to 1000% (where the normal concentration is 100%).

While the naphthenate compounds employed as a drier by Metcalfe et al. in negative acting developer compositions (i.e., developer compositions used to develop positive charge electrostatic images), can also be used as an image quality enhancing agent of the present invention, the mechanism involved is entirely different. The function of a drier, as is well-known, is to decrease the time required to form a dry coating or surface layer by increasing the oxidation rates of polymerizable drying oils. Metcalfe et al. employ driers in negative acting liquid developers because the negative acting developers contain large quantities of drying oils such as linseed oil to give the pigment particles a negative charge. Metcalfe et al. do not add driers to the positive acting developers.

Observable beneficial results are obtained by adding the most minute amount of the image quality enhancing agent to a liquid developer which is used to develop a negatively charged latent electrostatic image. The degree to which these results are present is roughly proportional to the amount of agent added until the concentration of the metal from the metal salt added to the toner composition reaches in some cases about 0.2% by weight of the total developer. Higher concentrations usually reduce the quality of the developed image. The optimum amount of image quality enhancing agent can be readily determined by adding the agent to a developer solution with an eye dropper and observing the print quality after each drop is added. The quality improves, reaches a peak and then declines in a manner clearly observable with the naked eye. Once an excess of the image quality enhancing agent is introduced into the solution, it is usually not possible to improve the image quality merely by adding the carrier solvent.

The amount of metal added to the developer composition is determined by multiplying the percent of salt added to the developer by the percent metal content of the salt. For example, if a toner requires 0.12% metal for optimum image quality, the addition of this amount of metal can be theoretically accomplished by adding 0.5% of a 24% metal salt or by adding 10% of a 1.2% metal salt. This means that 0.5% of a manganese octasol salt having 24% manganese or 10% of a manganese octasol salt having 1.2% manganese may be added and both accomplish substantially the same image enhancing function since the concentration of the metal ion added determines the effectiveness of the toner. For practical purposes, however, the total upper metal salt content is limited by the solubility limit of the salt in the liquid carrier or by the amount of salt that can be finely dispersed throughout the carrier without a significant amount of precipitation over long periods of time. The upper limit of total salt content is generally 10% by weight of the total developer composition with an upper limit on the metal ion concentration of about 0.20% by weight.

It has also been found that in some cases negative acting toners can be converted to positive acting by adding the image quality enhancing agent in relatively large amounts, and a remaining small quantity may be used for image enhancement. The amount of salt that must be added when the starting developer is negative acting is that amount necessary to change the toner to positive acting plus the amount necessary to add an effective amount of metal ions to the developer to maximize the image quality. Still the maximum amount of image enhancing agent will not normally exceed 10% by weight of the developer with a total free metal ion content of 0.2% by weight of the metal.

A particularly satisfactory image quality enhancing agent is nickel 2-ethylhexoate. This material is highly resistant to oxidation because its inner electron shells are completely filled and it is, therefore, exceptionally stable and has a long shelf life.

As disclosed in my application No. 165,254, it was originally thought necessary to include in the toner compositions of the present invention a stabilizer or dispersant to stabilize the dispersion of particles and prevent settling of the pigmented particles on standing. By continued experimentation in which the proportion of dispersant was successively reduced, it was unexpectedly found that, in many instances, the dispersant could be reduced to an insignificant proportion or even eliminated. The reason for this surprising finding seems to be that the dispersant does not, as originally thought, act by stabilizing the dispersion of pigment particles. Instead, it appears that the dispersant produced its beneficial results by preventing flocculation of the particles. If the manufacturing process is carefully controlled, the proportion of the dispersant may be reduced and it has been found in some controlled test compositions that the quality of prints made from compositions having a zero amount of dispersant were indistinguishable from the quality made from compositions having varying amounts as earlier were regarded to be essential.

Materials which function satisfactorily as dispersants include siloxanes and disiloxanes were alkyl and alkoxy radicals of 4 to 10 carbon atoms, and aliphatic esters of oxygen-containing acids of the non-metallic elements of Groups III, IV, and V and Periods II, III, and IV of the Periodic Table, specificially, the borates, silicates, phosphates and titanates of 2-ethylhexanol and other alcohols with straight or branched carbon chains from 6 to 12 carbon atoms. A preferred dispersant is a mixture containing about 97% of a 2-ethylhexyl silicate such as tetrakis-(2-ethylhexyl) orthosilicate and 3% 2-ethylhexanol. If desired, minor amounts of other ethylhexyl silicates may also be used in the mixture, and small amounts or traces of yet further materials can be tolerated in the mixture without impairment of the resulting image on the copy paper.

Formulation of toner compositions in accordance with this invention may be carried out in several ways for example, the metal salt may be added initially or after all other ingredients have been mixed into the liquid carrier, as by contacting the composition with a surface having soluble metal salts coated thereon; exemplary methods of preparing these toners are as follows:

Example I

(A) A stock solution is prepared by milling 3.20 pounds of #853 paste, 2.75 pounds of Rogersol B–280, and 97.0 pounds of Shell-Sol #71 together with approximately 10 to 30 minutes in an Eppenbach Colloid Mill, Model VT–7–2, at a setting of 20.

(B) The final toner composition is preferred from the following ingredients:

Ingredient	Weight in pounds
Stock solution prepared in Step A	103.0
Shell-Sol #71	[1] 11.6
Tenamene 3	[1] 1.67
Manganese octasol (manganese 2-ethylhexoate)	[1] 0.75

[1] Pre-mix, then add to stock solution.

These ingredients are blended for fifteen minutes in the colloid mill at a setting of 20.

The resulting liquid toner composition consists of pigment particles ranging from about 0.2 to 5.0 microns in diameter dispersed in a continuous liquid phase. The toner will produce a clear, visible, blue-black image of high resolution and uniform density on a surface bearing a latent electrostatic image.

Tenamene 3, used in Example I, is an anti-oxidant and may be omitted without adversely affecting this toner composition insofar as the quality of image it produces is concerned. The purpose of the anti-oxidant and the beneficial results that may be obtained by its use are discussed and claimed in companion application No. 519,534 filed Jan. 10, 1966 by Donald E. Hanson for liquid toners.

Example II

(A) A stock solution is prepared of the coloring ingredient and a portion of the liquid carrier in the following portions:

Coated pigment particle mixtures:	Percent vol.
(a) Rogersol B–280 (150 ml.)	0.75
(b) Color Base #35712 (300 ml.)	1.50
Carrier liquid (Shell-Sol 72) (19,500 ml.)	97.75

These ingredients are milled together for approximately 30 minutes in an Eppenbach Colloid Mill, Model VT–7–2 at a setting of 20.

(B) The final toner composition is prepared from the following ingredients:

	Percent vol.
Stock solution prepared in step (A) (1,000 ml.)	5.000
Dispersant [mixture of 97% tetrakis (2-ethylhexyl) orthosilicate and 3% 2-ethylhexanol] (75 ml.)	0.375
Mn salt (preferably manganese 2-ethylhexoate or manganese linoresinate) (2 ml.)	0.010
Carrier (Shell-Sol 72) (18,925 ml.)	94.615

These ingredients are blended by milling for fifteen minutes in the colloid mill at a setting of 20.

The resulting toner composition consists of particles ranging from about 0.2 to 1.0 micron in diameter dispersed in a continuous liquid phase. A surface bearing a latent electrostatic image charge when contacted with the developer will produce a clear, visible, blue-black image of good resolution and density.

Example III

A toner was prepared in accordance with the procedure of Example II, but in lieu of the coated pigment particle mixture 15 grams of uncoated carbon black was used.

The resultant developer was positive acting and when applied to an electrostatically negatively charged latent image produced clear, sharp, brownish-black, visible images of good resolution and density.

Example IV

A base toner of the following approximate composition wes prepared:

	Approximate percent by weight
Shell-Sol 71	75.0
Alphaltum	5.6
Carbon black	2.0
Alkali blue	1.0
Tenamene-3	2.5
Dispersan (2-ethylhexyl silicate)	1.0
Trichlorotrifluoroethane	12.5
Manganese 2-ethylhexoate	0.4

This base toner solution was then dispersed in Shell-Sol 71 at a ratio of approximately 3.0 cc. of the solution to 200 cc. of Shell-Sol 71. This final toner was then used to develop a negatively charged latent electrostatic image and produced a clear, sharp, dense, black image of high visual quality.

Example V

Another positive acting developer formula which has exhibited excellent characteristics is as follows:

Shell-Sol 72, ml.	4,000
2-ethylhexyl silicate, ml.	30
Carbon black (dispersed in a small amount of a flushing agent such as mineral oil), ml.	30
Manganese linoresinate, drops	3

Examples VI–XXXII

A base toner for use in obtaining the results tabulated in Tables I and II was prepared from the following composition:

	Parts by weight (grams)
Shell-Sol #71	571.0
Tenamene-3	19.4
Dispersant (2-ethylhexyl silicate)	7.6
Rogersol #B280	34.15
#853 paste	34.15
Trichlorotrifluoroethane	106.0

This base toner was then dispersed in Shell-Sol #71 in a ratio of 3 cc. of base toner to 200 cc. of Shell-Sol #71.

Several metal salts of organic acids were then added in the amount necessary to improve the developed image

by the optimum degree. The metal-organic acid salts listed in Table I were added to separate samples of the final toner and each visibly improved the final image clarity compared to the final toner solution having no image quality enhancing agent therein:

TABLE 1

cobalt octasol	copper oleate
zinc octasol	copper naphthenate
iron octasol	calcium tallate
zirconium octasol	sodium stearate
cerium octasol	sodium oleate
nickel octasol	magnesium naphthenate
lead octasol	barium naphthenate
calcium octasol	strontium naphthenate
manganese linoresinate	cadmium naphthenate
manganese resinate [1]	cadmium octasol
manganese naphthenate	lithium naphthenate
manganese acetate [1]	nickel benzoate [2]
manganese tallate	lead benzoate [2]
manganese stearate	

[1] Added during the milling step.
[2] Predissolved in naphthenic acid.

Those metal salts which could not be dissolved in the toner directly were either added during the milling step ([1]) so that they would be finely dispersed throughout the toner even though not actually dissolved or they were predissolved in a solvent compatible with the Shell-Sol #71 liquid carrier ([2]). It should be understood that the above examples have been presented as illustrative of the metal salts which function as image quality enhancing agents and that all soluble metal salts of organic acids tested and those that could be finely dispersed throughout the toner during the milling step have been found to perform the image enhancing function. Furthermore, although Shell-Sol #71 is the preferred liquid carrier, any of the previously discussed high resistivity carriers may be used.

A relative indication of the improved image quality obtained using the soluble or finely dispersable salts of organic acids will be better appreciated from Table 2 which gives photometer readings for representative metal salts of organic acids which were added to the toner used for tabulation of Table 1 in the amount necessary to produce the best visible final image in terms of clarity, sharpness and density.

TABLE 2

Salt:	Photometer reading image density
No salt added	40.0
Cobalt octasol	62.0
Zirconium octasol	59.2
Cerium octasol	55.6
Lead octasol	53.4
Manganese octasol	53.4
Nickel octasol	50.0
Iron octasol	49.9
Zinc octasol	47.5
Manganese octasol	62.0
Manganese resinate	62.0
Manganese naphthenate	57.2
Manganese linoresinate	55.6
Manganese acetate	46.5

The photometer readings given in Table 2 are representative of the relative image densities of a preselected region of a standard image which was developed on copy sheets by separate samples of the final toner with the respective organic acid metal salts added, as indicated. Since the same region of the image was measured for each copy sheet, Table 2 gives an illustration of the relative density of the pigment deposition and effectiveness of the novel liquid toner compositions and method of developing latent electrostatic images of this invention, though such density is not the only or in many cases even the paramount parameter by which the effectiveness of the image quality enhancing agents can be evaluated. There is also a clearly visible improvement in image clarity and sharpness at the image boundaries and in the contrast between the background portions of the copy sheets and the image portions.

Water has been found to be a deleterious contaminant to the liquid developers of this invention. Although small quantities such as would normally be precipitated from the atmosphere of an office or laboratory can be tolerated, larger amounts must be avoided and the developer must be substantially non-aqueous.

The charged nature of the particles in the toner renders them capable of electrophoretic motion in an electric field. Since the particles are maintained in a positive state with reference to the latent image charge on the surface of the paper, the particles move toward and are attracted to the residual charged areas on the paper. These constitute the image areas on the original being copied and therefore a positive reproduction of the original is obtained.

Normally, a surface charge of about 20–30 volts (measured as apparent surface potential) is sufficient to begin attracting toner particles. The relationship between charge and image density is linear up to about 200 volts, depending somewhat upon the specific properties of the toner and paper being used.

By establishing an external electrical field (bias voltage), the maximum and minimum toner threshold voltage values can be shifted. A small amount of current through the coating also appears to increase the contrast or gradation of the paper due to the differential resistivities in exposed and unexposed areas of the photoconductive coating.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description.

What is claimed and desired to be secured by Letters Patent is:

1. The method of developing a negatively charged latent electrostatic image into a visual image, comprising the steps of:

(a) applying to said image a substantially water-free positive acting developer composition consisting essentially of *an evaporative liquid hydrocarbon* carrier having a resistivity of not less than about 10^{10} ohm-cm.; 0.00005 to 5% by weight of finely divided, opaque, insoluble, pigment particles dispersed in said carrier; and a manganese salt of an organic acid in an effective amount equal to not more than about 0.2% by weight of manganese metal based on total developer, for visually improving the quality of the image produced by the pigment particles, said salt being selected from the group consisting of manganese linoresinate, manganese 2-ethylhexoate and manganese naphthenate, and

(b) thereafter removing excess developer from the carrier bearing the electrostatic image.

2. The method of claim **1**, wherein the manganese salt is manganese linoresinate.

3. The method of claim **1**, wherein the manganese salt is manganese 2-ethylhexoate.

4. The method of claim **1**, wherein said pigment particles are coated with asphaltum.

5. A substantially water-free positive acting developer for negatively charged latent electrostatic images consisting essentially of

(a) an evaporative liquid hydrocarbon carrier having a resistivity of not less than about 10^{10} ohm-cm.,

(b) 0.00005 to 5% by weight of finely divided, opaque, insoluble, pigment particles dispersed in said liquid

carrier such that the pigment particles can be electrostatically attracted to negatively charged latent images, and

(c) a manganese salt of an organic acid in an effective amount equal to not more than about 0.2% by weight of manganese metal based on total developer, for visually improving the quality of the image produced by the pigment particles, said salt being selected from the group consisting of manganese linoresinate, manganese 2-ethylhexoate and manganese naphthenate.

6. The developer composition of claim **5**, wherein the manganese salt is manganese linoresinate.

7. The developer composition of claim **5**, wherein the manganese salt is manganese 2-ethylhexoate.

8. The developer composition according to claim **5**, wherein said pigment particles are coated with asphaltum.

9. The developer composition of claim **8**, wherein the manganese salt is manganese linoresinate.

10. The developer composition of claim **8**, wherein the manganese salt is manganese 2-ethylhexoate.

11. The developer composition of claim **8** including up to about 0.75 percent by weight, based on the weight of said composition, of a dispersing agent for the pigment particles, said dispersing agent being selected from the group consisting of siloxanes and disiloxanes containing alkyl or alkoxy radicals of 4 to 10 carbon atoms, and

of aliphatic esters of borates, silicates, phosphates and titanates esterified with an alcohol of 6 to 12 carbon atoms.

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