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ELECTROSTATIC LIQUID DEVELOPER CONTAINING DYE COATED CARBON PARTICLES

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ABSTRACT OF THE DISCLOSURE

New and improved toner particles for use in a liquid developing composition for converting a latent electrostatic image to a visible image and method for their preparation wherein carbon pigment material is treated with a dye carrying a positive electrostatic charge dissolved in a polar organic solvent.

This invention relates to electrostatic printing, and more particularly to a method for treating pigment or toner particles for use in liquid developing compositions for converting an electrostatic image to a visible image.

Processes for forming a latent electrostatic image, existing as an electrostatic charge pattern in a layer of material having high resistance, and for subsequently converting the latent electrostatic image into a visual pattern, are well known.

In one such process, an optical image is produced directly on a film or coating of a photoconductive pigment, such as zinc oxide dispersed in an insulating matrix, such as a synthetic resin, on the surface of a flexible carrier, such as a sheet of paper, metal or other electrically conductive backing. In this process, the photoelectrostatic coating is given an overall electrostatic charge while being protected from light and thereafter it is exposed to a light image of the subject to be reproduced. The electrostatic charge on the coating is dissipated in the areas struck by light and retained in the unexposed areas thereby to provide an electrostatic reproduction of the optical image. This latent electrostatic image is then converted to a visible image by a developing composition containing toner particles which are attracted to the latent electrostatic image in a "positive toning" process, or to the background area in a "negative toning" process.

In another process referred to as the Videograph process described in U.S. Pats. No. 2,996,573 and No. 3,075,859, a latent electrostatic image is inscribed by elements extending through a cathode ray tube directly onto the dielectric coating on the surface of a base sheet of paper or other highly electrically conductive material. The latent electrostatic image is retained on the dielectric coating and later developed into a visible image by the application of a suitable developing composition containing toner particles which are attracted to the latent electrostatic image or the background, as described above.

Liquid developer compositions for use with electrostatic images comprise a dispersion of a pigment or toner particles in a volatile liquid having a high dielectric strength and a high volume resistivity. The dispersed particles may carry either a positive charge or a negative electrical charge, depending on their chemical composition for either positive toning or negative toning respectively. The nonconductivity and the high dielectric strength of the volatile liquid in the liquid developing composition preserves the electrostatic image and permits the deposition of the dispersed toner particles to form a visible image. Liquid toners are described in the U.S. Metcalfe Pat. No. 2,907,674, the U.S. Straughan Pat. No. 2,899,335, the U.S. Mayer et al. Pat. No. 2,390,911, the U.S. York Pat. No. 3,135,095 and the U.S. Dirks Pat. No. 3,155,546, and many others.

Although liquid developing composition represent an improvement over the use of earlier dry powder developers used for conversion of a latent electrostatic image to a visible image, improvement of the liquid developing compositions is desirable from the standpoint of producing permanent visible images which are free from smearing or blurring, especially when rubbed. This deficiency stems from the inability of the toner particles to become permanently fixed on the surface of the copy sheet. In addition, liquid developing composition heretofore known have the further disadvantage in that the pigment or toner particles contained therein have a tendency to agglomerate, whereby destroying the dispersion of the toner particles in the liquid developing composition.

Attempts have been made to overcome these disadvantages and to fix the image onto the copy sheet by subsequent processing, as by heating to fuse the toner particles, but such additional processing steps are often incomplete. Moreover, attempts to provide a more complete dispersion of the toner particles in the liquid developing composition have been made, but have similarly been difficult to achieve.

It is accordingly an object of the present invention to provide new and improved toner particles and method for preparing same wherein the toner particles become permanently fixed to the copy sheet to provide a dense, black image of good resolution on development of the latent electrostatic image.

It is a further object of the present invention to provide a method for treating toner particles whereby the individual toner particles are caused to repel each other to thereby prevent agglomeration of the toner particles over long periods of time.

It is a related object of the present invention to provide new and improved toner particles and a liquid developing composition embodying same for converting an latent electrostatic image to a visible image which provides a clean background on the copy sheet, which promotes good adherenec of the toner particles to the copy sheet to prevent streaking and smearing of the visible images, and which will promote the uniform development of a dense, black image.

The concepts of the present invention reside in a method for treating toner or pigment particles wherein a carbon pigment material is treated with an organic solvent containing a dye which carries a positive electrostatic charge. It has been found that pigment material treated in this manner provides an increased image intensity, and completely obviates the problem of agglomeration of the toner particles in the developing composition. Without limiting the invention as to theory, it is believed that the method of the present invention causes the carbon pigment material, which inherently carries a negative electrostatic charge, to become coated with a layer of the dye which carries an active positive electrostatic charge. Thus, the complete absence of agglomeration of toner particles formed of the treated pigment materials is believed to result from the repulsion of the actively positively charged toner particles.

In accordance with the practice of the present invention, a dye which carries a strong positive electrostatic charge is dissolved in a polar organic solvent, and the resulting solution is used to treat the carbon pigment material. The solid carbon pigment material is then separated from the liquid phase, dried and powdered, and formulated into a liquid toner concentrate and/or liquid toner developing composition.

In accordance with the preferred practice of the invention, after separation of the liquid phase containing

the polar organic solvent and dissolved dye, the separated liquid phase is either combined with a second organic solvent, and the resulting mixture used to wash the solids comprising the treated carbon pigment material, or the solid carbon pigment material is treated with the second solvent alone and the liquid phase containing the second solvent, which is thereafter separated from the solid carbon pigment material, is mixed with the liquid phase from the first treatment to provide an additional treating medium for the solid carbon pigment material. Thereafter, the treated pigment material can be formulated into a liquid developing composition for converting a latent electrostatic image to a visible image.

A variety of carbon pigment materials may be used in the practice of the present invention, including carbon black, lamp black, channel black or the like. It is generally preferred to make use of carbon blacks, such as Mogul A, Raven 11 or GAF permanent black toner 84–5001.

Similarly, a wide variety of dyes may be used in the treatment of the foregoing carbon materials, with the primary requirement of such dyes being that they must carry a strong positive electrostatic charge. Nigrosine dyes, such as Nigrosine Base B or Nigrosine Base SSB (C.I. 50415), are frequently preferred, although use may also be made of other dyes which carry a positive electrostatic charge, such as methyl violet (C.I. 42435) or alkali blue dyes (e.g. Alkali Blue R Powder 55–4570 (C.I. 42750), marketed by American Cyanamide).

The polar organic solvent used in accordance with the practice of the present invention should be a solvent for the dye. For this purpose, use can be made of aliphatic alcohols having 1–5 carbon atoms, such as methanol, ethanol, isopropanol, etc., or aliphatic ketones having 3–10 carbon atoms, such as acetone, methyl ethyl ketone, diethyl ketone, ethyl propyl ketone, etc. Separation of the solvent from the treated carbon material can be effected by a variety of conventional procedures, although it is generally preferred to filter the mixture of the carbon material with the solvent containing the dissolved dye in order to separate the solid pigment material from the dye-containing solvent. It will be understood that various other means of separation, such as centrifugation may similarly be used.

The second solvent, which may be either combined with the liquid phase containing the polar organic solvent resulting from the initial treatment, or used as a treating medium alone and thereafter combined after separation of the pigment material with the liquid component of the initial treatment to provide a third treating medium can be either a polar or non-polar organic solvent. For example, use can be made of polar solvents of the type described above, such as methanol or methyl ethyl ketone, or non-polar aromatic and cycloaliphatic hydrocarbon solvents, such as benzene, toluene, xylene, cyclopentane, cyclohexane, etc. It will be appreciated by those skilled in the art that mixtures of the foregoing polar or non-polar solvents may be used to provide a second solvent in accordance with this invention.

When both the polar and the second solvent are used in accordance with the preferred embodiment wherein the second solvent serves as an additional treating medium, it has been found that best results are obtained when the polar solvent is ethyl alcohol and the second solvent is an aliphatic ketone of the type described above, such as methyl ethyl ketone. Pigment material treated with this solvent system provides particularly well defined dark images when formulated into a liquid developer composition for converting latent electrostatic images to visible images.

Having described the basic concepts of this invention, reference is now made to the following examples which are provided by way of illustration, and not by way of limitation, of the method for treatment of pigment material in accordance with the practice of this invention.

EXAMPLE 1

A sample of 20 grams of a nigrosine dye (Nigrosine SSB) is dissolved in 200 ml. of ethanol, and then 40 grams of carbon black (Mogul A) are added. The resulting mixture is then vigorously agitated and filtered. The resulting filtrate is then dried and powdered.

EXAMPLE 2

The procedure of Example 1 is repeated except that the solvent employed is methyl ethyl ketone.

EXAMPLE 3

Six grams of carbon black are admixed with one gram of nigrosine dye (Nigrosine SSB) and dissolved in 200 ml. of ethyl alcohol. The resulting mixture is then filtered, and the ethyl alcohol filtrate is used to wash the filter cake. Thereafter, the filter cake is washed with methyl ethyl ketone, and the ketone filtrate is combined with the alcohol filtrate from the first washing are admixed and used to wash the filter cake again.

The filter cake resulting from the third washing is then dried and powdered in the manner described in Example 1.

EXAMPLE 4

The procedure of Example 3 is repeated except that the ethyl alcohol solvent is replaced by methyl ethyl ketone and the methyl ethyl ketone solvent is replaced by benzene.

EXAMPLE 5

The procedure of Example 3 is again repeated except that the methyl ethyl ketone solvent is replaced by cyclohexane.

EXAMPLE 6

The procedure of Example 3 is again repeated except that the ethyl alcohol solvent is replaced by methyl alcohol, and the ketone solvent is replaced by toluene.

EXAMPLE 7

Twenty grams of nigrosine dye (Nigrosine Base B) are dissolved in 200 ml. of ethyl alcohol, and 40 grams of carbon black are added to the mixture. Thereafter, the mixture is filtered, and the filtrate is admixed with 150 ml. of methyl ethyl ketone. The resulting mixture is then used to wash the filter cake, which is then dried and powdered.

EXAMPLE 8

The procedure of Example 7 is repeated except that the methyl ethyl ketone solvent is replaced by toluene.

EXAMPLE 9

The procedure of Example 7 is again repeated except that the methyl ethyl ketone solvent is replaced by cyclohexane.

EXAMPLE 10

Ten grams of alkali blue powder (Alkali Blue R powder 55–4570) are dissolved in 150 ml. of ethyl alcohol, and 25 grams of carbon black are added to the solution. The resulting mixture is then filtered, and the filter cake is washed with the filtrate. Thereafter, the filter cake is washed with methyl ethyl ketone, and the ketone washing liquid is combined with the filtrate from the first wash and used to again wash the filter cake. The resulting treated toner particles are dried and powdered.

EXAMPLE 11

The procedure utilized in Example 10 is repeated except that the ethyl alcohol solvent is replaced by methyl ethyl ketone and the methyl ethyl ketone solvent is replaced by benzene.

EXAMPLE 12

The procedure of Example 10 is again repeated except that the methyl ethyl ketone solvent is replaced by cyclopentane.

EXAMPLE 13

Five grams of the alkali blue dye utilized in Example 10 are dissolved in 150 ml. of methyl alcohol, and 20 grams of carbon black are added to the solution. The resulting mixture is then filtered and the filter cake is washed with 100 ml. of toluene. Thereafter, the alcohol-containing filtrate and the toluene filtrate are combined, and the mixture used to wash the filter cake again.

The treated carbon black filter cake is then dried and powdered.

EXAMPLE 14

The procedure used in Example 13 is repeated except that the toluene solvent is replaced by methyl ethyl ketone.

Toner particles which have been treated in accordance with the present invention as illustrated by Examples 1 to 14 may be formulated into a variety of liquid developer compositions used for converting a latent electrostatic image to a visible image. For example, toner or pigment particles of the present invention may be used in a liquid developer of the type disclosed in the Metcalfe patent (U.S. No. 2,907,674), which generally comprises the pigment or toner particles and a binder component dispersed in an organic solvent which functions as a carrier. Such a developer composition is illustrated by the following example.

EXAMPLE 15

A developer concentrate is prepared by admixing 5 parts by weight of the toner particles prepared in accordance with Example 1 with 7 parts by weight of a lineseed oil-modified alkyd resin (Rhodene L6/100) binder and 15 parts by weight of a high boiling aromatic solvent ("Fusis A"), and ball milling the mixture for several hours to insure and provide the toner concentrate:

	Parts by wt.
Treated carobn black particles	5
Alkyd resin	7
Aromatic solvent	15

The toner concentrate can then be dispersed in a carrier solvent, such as cyclohexane, carbon tetrachloride or the like to provide a toner particles content which may be varied within wide ranges, such as from 0.00001 to 5% by weight of the developer composition.

It will be understood that a wide variety of binder components may be used in lieu of the alkyd resin exemplified in Example 15, the primary requirement being that the binder component have a relatively high dielectric constant. Illustrative of suitable binders are polyvinyl acetate, polyvinyl acetate copolymers containing carboxyl groups (e.g. such as VMCH resin (marketed by Union Carbide which comprises approximately 86% by weight vinyl chloride, 13% by weight vinyl acetate and 1% by weight maleic acid), polyvinyl chloride, polyvinyl acetate copolymers, polystyrene, styrene-butadiene copolymers, alkyd and modified alkyd resins, polyvinyl toluene, such as Pliolite VTL marketed by Goodyear. The binder components of the developing composition are generally insoluble in aliphatic solvents which serve as the carrier for the toner concentrate, and hence it is generally preferred to dissolve the binder component in a small amount of a aromatic solvent, such as Napoleon 100–A marketed by the Deeprock Division of Kerr-McGee Company, and then disperse the dissolved binder in an aliphatic solvent in order to provide a fine dispersion of the binder particles in the aliphatic solvent carrier system. The binder is generally present in the developing composition in an amount within the range of 0.001 to 10% by weight.

As indicated, the compatible carrier system for use in admixture with the toner concentrate to provide the developing composition generally comprises an aliphatic solvent, and preferably a solvent having a high volume resistivity in exces of 10^{10} ohm-cm. so as to avoid dissipation of the charge in the latent electrostatic image. For this purpose, use can be made of aliphatic solvents, such as cyclohexane, carbon tetrachloride, Isopar H, which is an aliphatic solvent marketed by the Humble Oil & Refining Company having a flash point of 123° F., Isopar G, also marketed by Humble, having a flash point of 104° F. The Isopar solvents both have a KB value of 27 and a low odor level. In formualting the liquid developing composition, it is generally desirable to employ between 0.001 and 5 parts by weight of the toner concentrate per 100 parts by weight of the carrier system so as to provide a liquid developing composition containing the toner particles in an amount corresponding to 0.0001 to about 1.0% by weight of the developer composition.

The new and improved toner particles of the present invention may also be used in the developer concentrates and compositions of the type disclosed in copending application Ser. No. 818, filed Jan. 5, 1970, and entitled "Liquid Developer Composition," wherein description is made of a toner concentrate containing toner particles suspended in an organic solvent by means of rosin and derivatives thereof which is adapted to be combined with a compatible carrier system formulated to contain a binder capable of forming a dielectric film to thereby anchor the pigment particles to the copy sheet during the development of a latent electrostatic image. Such developer concentrates and compositions may be formulated in accordance with the following examples.

EXAMPLE 16

Ethyl alcohol (40 grams) is mixed with 20 grams of a mixture of flushed toning blue dissolved in mineral oil and an aliphatic solvent (Isopar G), and the resulting mixture is osterized for four minutes. Thereafter, this flushed blue toning mixture is formulated into the following toner concentrate utilizing pigment particles treated in accordance with Example 1:

	G.
Treated carbon black	5.0
Hydrogenated methyl ester of rosin (Hercolyn D)	50.0
Rosin oil (Rosin Oil 6RS)	5.0
Isobutylene polymers (Paratone 460)	5.0
Flushed blue toner mixture	5.0
Aliphatic solvent	15.0

The foregoing toner concentrate is thoroughly mixed by ball milling for several hours.

As used in the aforementioned application, the term "rosin" is meant to refer to rosin and derivatives thereof, as well as mixtures of various "rosins." Included are tall oils of rosin and decarboxylated rosin oils (e.g. Rosin Oil 6RS) and ester and hydrogenated ester derivatives of tall oils of rosin.

The toner concentrates described above are preferably formulated to include a fixing agent in the form of polymers of isobutylene which operates at least in part to aid in anchoring the pigment particles to the copy sheet during development of the electrostatic image. The solvent which is included in the toner concentrate to maintain the pigment particles is dispersion or suspension is preferably a solvent having a high volume resistivity as described above.

The relative proportions of the components in the concentrate and developer compositions are not critical and can be varied within wide ranges. For best results, it is generally desirable that the concentrate be formulated to include between 10 and 60% by weight of the rosin, up to 10% by weight of the isobutylene polymers, and from .01 to 10% by weight of the treated pigment or toner particles.

It will be appreciated by those skilled in the art that the flushed blue toning component described above may be omitted from the composition as illustrated by the following example, in which use is made of the pigment particles treated in Example 3.

EXAMPLE 17

A toner concentrate is prepared by thoroughly mixing the following compositions in a ball mill:

	G.
Treated carbon black	50.0
Hydrogenated methyl ester of rosin (Hercolyn D)	50.0
Isobutylene polymers (Paratone 460)	5.0
Rosin oil (Rosin Oil 6RS)	5.0
Aliphatic solvent	20.0

The toner concentrates of Examples 16 and 17 may be admixed with a compatible carrier system containing a film forming binder which serves in part to anchor the pigment particles to the copy sheet upon drying. The carrier compositions may be illustrated by the following example.

EXAMPLE 18

One gram of a modified polyvinyl toluene polymer (Pliolite VTL) is dissolved in an aromatic solvent, and the resulting solution is formulated into the following carrier composition.

	Ml.
25% by weight solution of polyvinyl toluene	2
Aliphatic solvent (Isopar G)	1500

The concentrates of Examples 16 and 17 can be added to the above carrier composition to provide a liquid developing composition having a pigment content of 0.00002 to 0.01% by weight. The relative proportions of concentrate and carrier used may be varied between wide ranges. Best results are obtained when the concentrate is added to the carrier in a ratio of .1 to 10 parts by weight concentrate to 1000 parts by weight of the carrier.

It will be appreciated that any of the binders discussed above with reference to Example 15 may be used in place of the polyvinyl toluene exemplified in Example 18.

In use, the copy sheet containing the latent electrostatic image is wet with the liquid developing composition, with the immersion of the sheet in a bath of the developing composition or by flow-coating the composition over the image surface or by application of the liquid developing composition onto the image surface by a roller-coater. The copy sheet which is wet with the developing composition is then advanced through squeeze rolls to remove excess liquid. The toner particles are attracted to the latent electrostatic image for visual development of the image on the copy sheet. After development, the copy is allowed to dry by evaporation of the liquid, with

or without the application of heat. The aliphatic solvents evaporate from the sheet to thereby reduce the binder and the rosin to a tackified or adhesive stage whereby the deposited toner particles become bonded to the underlying coating so as to become permanently fixed on the copy upon complete drying of the sheet.

It will be apparent from the foregoing that we have provided new and improved pigment material for use in liquid developing compositions and a simple method for preparing same, wherein the resulting pigment particles formed of the pigment material are completely free from agglomeration and which provide a well defined image on a clean background.

It will be understood that various changes and modifications may be made in the details of formulation, procedure and use without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. In a liquid developer composition for converting a latent electrostatic image to a visible image comprising a binder and toner particles suspended in an organic solvent having a volume resistivity in excess of 10^{10} ohm-cm., the improvement comprising toner particles formed of carbon pigment particles which have been coated with a nigrosine dye (CI 50415).

2. A composition as defined in claim 1 wherein said pigment particles are selected from the group consisting of carbon black, lamp black and channel black.

3. A composition as defined in claim 1 wherein said pigment material is carbon black.

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,749,670 Dated July 31, 1973

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 5, please delete "Skulby" and insert

therefor -- Skuby --

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents