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ELECTRICALLY STABILIZED LIQUID TONERS**FIELD AND BACKGROUND OF THE INVENTION**

This invention relates to the field of electrostatic imaging and, more particularly, to the preparation of liquid toners containing components for improving the stabilization of the electrical properties due to the charge directors contained therein.

In the art of electrostatic photocopying or photo-printing, a latent electrostatic image is generally produced by first providing a photoconductive imaging surface with a uniform electrostatic charge, e.g. by exposing the imaging surface to a charge corona. The uniform electrostatic charge is then selectively discharged by exposing it to a modulated beam of light corresponding, e.g., to an optical image of an original to be copied or to a computer generated image, thereby forming an electrostatic charge pattern on the photoconductive imaging surface, i.e. a latent electrostatic image having a background portion at one potential and a "print" portion at another potential. The latent electrostatic image can then be developed by applying to it charged pigmented toner particles, which adhere to the "print" portions of the photoconductive surface to form a toner image which is subsequently transferred by various techniques to a copy sheet (e.g. paper).

It will be understood that other methods may be employed to form an electrostatic image, such as, for example, providing a carrier with a dielectric surface and transferring a preformed electrostatic charge to the surface. The charge may be formed from an array of styluses. This invention will be described in respect of office copiers and the like, though it is to be understood that it is applicable to other uses involving electrostatographics including electrostatographic printing.

In liquid-developed electrostatic imaging, the toner particles are generally dispersed in an insulating non-polar liquid carrier, generally an aliphatic hydrocarbon fraction, which generally has a high-volume resistivity above 10^9 ohm cm, a dielectric constant below 3.0 and a low vapor pressure

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1 (less than 10 torr. at 25°C). The liquid developer system
2 further comprises so-called charge directors, i.e. compounds
3 capable of imparting to the toner particles an electrical
4 charge of the desired polarity and uniform magnitude so that
5 the particles may be electrophoretically deposited on the
6 photoconductive surface to form a toner image.

7 In the course of the process, liquid developer is
8 applied to the photoconductive imaging surface. Under the
9 influence of the electrical potential present in the latent
10 image and a developing electrode which is usually present,
11 the charged toner particles in the liquid developer film
12 migrate to the "print" portions of the latent electrostatic
13 image, thereby forming the developed toner image.

14 Charge director molecules play an important role in the
15 above-described developing process in view of their function
16 of controlling the polarity and magnitude of the charge on
17 the toner particles. The choice of a particular charge
18 director for use in a specific liquid developer system, will
19 depend on a comparatively large number of physical
20 characteristics of the charge director compound, inter alia
21 its solubility in the carrier liquid, its chargeability, its
22 high electric field tolerance, its release properties, its
23 time stability, the particle mobility, etc., as well as on
24 characteristics of the developer. All these characteristics
25 are crucial to achieve high quality imaging, particularly
26 when a large number of impressions are to be produced.

27 A wide range of charge director compounds for use in
28 liquid-developed electrostatic imaging are known from the
29 prior art. Examples of charge director compounds are ionic
30 compounds, particularly metal salts of fatty acids, metal
31 salts of sulfo-succinates, metal salts of oxyphosphates,
32 metal salts of alkyl-benzenesulfonic acid, metal salts of
33 aromatic carboxylic acids or sulfonic acids, as well as
34 zwitterionic and non-ionic compounds, such as
35 polyoxyethylated alkylamines, lecithin, polyvinyl-
36 pyrrolidone, organic acid esters of polyvalent alcohols,
37 etc.

38 Notwithstanding the undoubted utility of charge



1 directors, however, the charging caused thereby is generally
2 unstable. In particular, lecithin, basic barium petronate
3 (BBP) and calcium petronate (CP), which are used as negative
4 charge directors, are unstable under high voltage
5 conditions. Thus, when a solution of charge director (or a
6 dispersion of toner particles in carrier liquid and
7 containing charge director) is subjected to a high electric
8 field, e.g. during the development process, the charge
9 transport characteristics and conductivity suffer from
10 transient suppression, and it may take several minutes for
11 these characteristics to recover. This leads to unstable
12 printing performance when long print runs are undertaken.
13 Further, such solutions or dispersions containing
14 particularly BBP, CP and to a lesser extent lecithin, tend
15 to lose conductivity in the course of time (after dilution
16 with Isopar or other carrier liquids), so that, e.g.,
17 solutions or dispersions containing BBP or CP, when diluted
18 with Isopar, will change their conductivity by about one
19 order of magnitude in a day and a half. In this connection,
20 it may be noted that in US Patent No. 4,897,332 (Gibson),
21 there is described the use of alkylated
22 polyvinylpyrrolidones in liquid toners, for the purpose of
23 promoting their electrical stability under high voltage
24 conditions.

25 In an attempt to improve the quality of the image
26 formed, particularly when using liquid toners containing
27 charge directors, it has been suggested to use adjuvants in
28 the toner compositions, such as polyhydroxy compounds,
29 aminoalcohols, polybutylene succinimide, an aromatic
30 hydrocarbon, a metallic soap or a salt of a Group Ia, IIa,
31 or IIIa metal.

32 US Patent No. 4,924,766 (Elmasry et al), while
33 mentioning in passing possible use of oligomers containing
34 amine groups as charge directors, is principally concerned
35 with sterically stabilizing the thermoplastic resin in
36 liquid toners; this patent does not address the subject of
37 electrical stabilization.

38 Two US Patents of Kosel (3,753,760 and 3,991,226) list



1 many components of liquid toners, including charge
2 directors. The isopropylamine salt of dodecylbenzenesulfonic
3 acid is one of many charge directors disclosed in these two
4 patents. The present inventors have found, however, that
5 this salt is a poor charge director. This finding is not
6 entirely surprising, because the utility of an amine as
7 charge director is believed to depend on its ability to form
8 salts with the polycarboxylic resin particles, from which
9 cations may be split off leaving a charged residue; amine
10 salts could thus not readily perform this function.

11 Use of an alkylhydroxybenzylpolyamine as an adjuvant in
12 liquid toners, in addition to charge director, is disclosed
13 in US Patent No. 4,977,056 (El-Sayed), while in US Patent
14 No. 4,783,388 (El-Sayed et al), there are disclosed liquid
15 toners containing charge directors and an additional
16 component which is a quaternary ammonium hydroxide. There
17 is no suggestion in either patent that the additive
18 stabilizes the electrical stability of the toners.

19 SUMMARY OF THE INVENTION

20 It is an object of the present invention to provide a
21 method for producing improved liquid toner compositions
22 containing charge directors and components which stabilize
23 the electrical properties of the charge directors. Other
24 objects of the invention will appear from the description
25 which follows.

26 The present invention accordingly provides in one
27 aspect, a homogeneous liquid composition, for use in the
28 preparation of liquid toners containing at least one charge
29 director and in which the electrical properties of the
30 charge director(s) is/are stabilized, which composition
31 comprises: (1) insulating non-polar carrier liquid
32 compatible with liquid toners for electrostatic imaging; (2)
33 at least one charge director other than an amine salt; and
34 (3) at least one stabilizing component in an amount
35 effective to stabilize the electrical properties of said at
36 least one charge director, said component being selected
37 from non-quaternary amine salts and being soluble in the
38 carrier.



1 In another aspect, the invention provides a liquid
2 toner for electrostatic imaging which comprises
3 thermoplastic resin particles dispersed in an insulating
4 non-polar carrier liquid having a volume resistivity above
5 10^9 ohm-cm and a dielectric constant below 3.0; colorant
6 particles micro-dispersed in said carrier liquid; at least
7 one charge director other than an amine salt; and at least
8 one stabilizing component (3) as just defined, in an amount
9 effective to stabilize the electrical properties of said at
10 least one charge director.

11 In yet another aspect, the invention provides a method
12 for producing liquid toner compositions containing charge
13 directors other than amine salts and in which the electrical
14 properties of the charge directors are stabilized, which
15 method comprises the steps of: (A) first making a
16 homogeneous liquid composition comprising components (1),
17 (2) and (3), as defined above, and (B) mixing the with
18 homogeneous liquid composition from step (A) in any order
19 colorant particles, thermoplastic resin particles, and if
20 desired further non-polar carrier liquid, in such manner
21 that the colorant particles and the thermoplastic resin
22 particles are micro-dispersed in the toner composition.

23 In still another aspect, the present invention provides
24 an electrostatic imaging process which comprises the steps
25 of: forming a charged latent electrostatic image on a
26 photoconductive surface; applying to said surface oppositely
27 charged colorant particles from a liquid toner of the
28 invention as defined herein (or as prepared by the method
29 defined in the preceding paragraph); and transferring the
30 resulting toner image to a substrate.

31 The carrier liquid, i.e. component (1) as defined
32 above, is preferably an insulating non polar carrier liquid
33 hydrocarbon having a volume resistivity above 10^9 ohm-cm and
34 a dielectric constant below 3.0.

35 The amine salts utilized in accordance with the present
36 invention as component (3), as described above, may be for
37 example a salt of an amine with an inorganic acid such as
38 HCl or HBr, or with an organic acid such as a carboxylic

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1 acid or a sulfonic acid. Presently preferred organic acids
2 are sulfonic acids, more preferably alkyl-substituted
3 aromatic sulfonic acids and particularly where there is a
4 total within the range of 8-18 carbon atoms in such alkyl
5 substituent(s). The amine component of the amine salt may
6 be for example an aliphatic amine, most preferably a
7 primary, secondary or tertiary aliphatic amine containing
8 from 3 to 8 carbon atoms in the molecule. Non-limiting
9 examples of amine salts which may be utilized in accordance
10 with the present invention are diethylammonium chloride and
11 isopropylamine dodecylbenzenesulfonate.

12 It has been found that the present toner compositions
13 exhibit excellent time stability of charge and reduction of
14 conductivity loss under high voltage conditions, as well as
15 excellent recovery of charge after subjection to high
16 voltage conditions. Also, use of such toner compositions
17 results in images of very good copy quality and long term
18 stability.

19 BRIEF DESCRIPTION OF THE DRAWINGS

20 Figs. 1-4 show the effect of the stabilizing component
21 of the invention on the electrical stability of carrier
22 liquid compositions containing charge directors; and Fig. 5
23 shows the effect of an exemplary stabilizing component of
24 the invention on the conductivity of compositions containing
25 charge director.

26 DETAILED DESCRIPTION OF THE INVENTION

27 The thermoplastic resins, insulating non-polar carrier
28 liquids, colorant particles and charge directors, which may
29 suitably be used in the toner compositions of the invention
30 are known in the art. Illustratively, the insulating non-
31 polar liquid carrier, which should preferably also serve as
32 the solvent for the charge directors, is most suitably an
33 aliphatic hydrocarbon fraction having suitable electrical
34 and other physical properties. Preferred solvents are the
35 series of branched-chain aliphatic hydrocarbons and mixtures
36 thereof, e.g. the isoparaffinic hydrocarbon fractions having
37 a boiling range above about 155°C, which are commercially
38 available under the name Isopar (a trademark of the Exxon



1 Corporation).

2 As set forth above, the at least one component for
3 stabilizing the electrical properties of the at least one
4 charge director is selected from carrier soluble non-
5 quaternary amine salts.

6 The weight ratio of stabilizing component to charge
7 director in the liquid toners preferably falls within the
8 range of 0.001-2.0:1.

9 The invention will be illustrated by the following non-
10 limiting Example, in which all "parts" are parts by weight.

11 EXAMPLE

12 (a) Ten parts of Elvax II 5950 (E.I. du Pont) and five
13 parts of Isopar L (Exxon) are mixed at low speed in a
14 jacketed double planetary mixer connected to an oil heating
15 unit set at 130°C for one hour. Five parts of Isopar L are
16 added to the mix in the double planetary mixer and the whole
17 is mixed for a further hour at high speed. Ten parts of
18 Isopar L, preheated to 110°C are added, and the mixing is
19 continued without heating until the temperature of the
20 mixture drops to 40°C.

21 (b) Ninety grams of the product of part (a) is
22 transferred to a Union Process 01 attritor together with 7.5
23 g of Mogul L carbon black (Cabot) and 120 g Isopar L. The
24 mixture is ground for 24 hours with water cooling (=20°C)
25 using 3/16" stainless steel media. The resultant toner
26 particles have an average (weight) diameter of about 2.1 µm.

27 (c) Three charge directors are used, namely, basic
28 barium petronate (BBP), lecithin, and 50-50 mixtures of
29 lecithin with BBP. 600 g. Isopar L is used to dissolve 60
30 g. charge director(s) until a homogeneous solution is
31 obtained, to which was added the stabilizing component(s)
32 according to the invention to obtain a homogeneous solution.
33 The amount of stabilizing component(s) may be, e.g., 0.25-10
34 wt.% of the Isopar solution, but up to 1 wt.%
35 is usually adequate. It is noted that BBP when added to
36 lecithin improves its humidity tolerance (which is poor when
37 used alone); the stabilizing components do not appear to
38 affect the humidity stability of any of the charge directors



1 including the mixtures.

2 (d) The toner concentrate from part (b) is diluted to
3 a non-volatile solids content of 1.5%, using Isopar L.
4 Charge director solution including stabilizing component,
5 from part (c), is added in an amount of e.g. 5-100 mg.
6 charge director solids per g. of toner solids.

7 The toners thus produced were tested in a Savin 870
8 copier and in a high speed electrophotographic printer in
9 which the image is developed on a photoreceptor with a
10 reverse roller developer and then transferred to the final
11 copy sheet via an intermediate transfer member. Print
12 quality was at least equal to that of toner without the
13 stabilizers and was stable under high speed printing
14 conditions, consistent with the following experiments based
15 on the stabilized charge director alone.

16 Electrical stability under high voltage applications

17 These measurements are made for solutions containing
18 charge directors alone (as control), or with the addition of
19 stabilizing components, prepared according to part (c) of
20 the Example, above, and diluted with the same carrier
21 liquid. A solution of 0.1 wt.% charge director (and, when
22 present, stabilizing component in the concentrations
23 described below) is placed in an electrical cell having a
24 one mm. separation between plate electrodes. A first pulse
25 of 1500 volts having a duration of 8 seconds is applied to
26 the electrodes and the total charge transported is measured.
27 This charge represents the "basis" value for comparison.
28 After a 1 second delay a second pulse of 1500 volts having a
29 duration of 68 seconds is applied; this pulse is designed to
30 cause depletion of the charge director by high voltage
31 loading. After a further 1 second delay a third pulse of
32 1500 volts having a duration of 8 seconds is applied and the
33 total charge transported is measured. This charge
34 represents the diminished charge transport capability of the
35 material after being subjected to a high voltage. After a 1
36 minute wait an additional pulse of 1500 volts having a
37 duration of 8 seconds is applied and the total charge
38 transported is measured; this charge is a measure of the



1 recovery of the charge director after being subjected to
2 high voltage.

3 The results of this study are shown in Figs. 1-4, which
4 show clearly that addition of the stabilizing components in
5 accordance with the invention improved both the pulse
6 loading and recovery characteristics of the charge director.
7 In the Figures, the other abbreviations used have the
8 following meanings:

9 GB = isopropylamine dodecylbenzenesulfonate (ICI G3300B);
10 CC-42 = diethylammonium chloride (WITCO-EMCOL PPG-40); P10-
11 59, S-93 = amine dodecylbenzenesulfonate (WITCONATE P10-59,
12 S-93); PC-200, PC-205, PC-210 = amine alkylarylsulfonates of
13 increasing molecular weights (WITCOR); WIT-918 = amine
14 sulfonate (WITFLOW 918).

15 The charge director compositions in the Figures
16 (concentrations of stabilizing components shown in
17 parentheses) were prepared as follows:

18 Fig. 1: 0.05 g lecithin (LAN) and 0.05 g BBP, with 0.01
19 g of the stated stabilizing component according to the
20 invention, were dissolved in Isopar L to make 100 g total
21 solution.

22 Fig. 2: 0.1 g BBP, with varying amounts of
23 isopropylamine dodecylbenzenesulfonate, were dissolved in
24 Isopar L to make 100 g total solution.

25 Fig. 3: 0.05 g lecithin (LAN) and 0.05 g BBP, with
26 varying amounts of isopropylamine dodecylbenzenesulfonate,
27 were dissolved in Isopar L to make 100 g total solution.

28 Fig. 4: 0.1 g lecithin (LAN), with varying amounts of
29 isopropylamine dodecylbenzenesulfonate, were dissolved in
30 Isopar L to make 100 g total solution.

31 As is clearly seen from these Figures, the addition of
32 stabilizing components to solutions of charge director
33 material substantially improves the stability of these
34 solutions.

35 Conductivity kinetics (stability of conductivity with time)

36 The effect of an exemplary stabilizer of the invention
37 (isopropylamine dodecylbenzenesulfonate) on conductivity
38 degradation, following dilution to 0.1 wt.% charge director,



1 from a stock solution of 10% BBP or lecithin or a 5%+5% BBP-
2 lecithin mixture, in Isopar L to a 0.1% solution in Isopar
3 L, is presented in Fig. 5. This Figure shows that the
4 conductivity of these solutions was stabilized when they
5 contained (based on charge director) at least approximately
6 7.5 wt.% stabilizer.

7 While the present invention has been particularly
8 described, persons skilled in the art will appreciate that
9 many variations and modifications can be made. Therefore,
10 the invention is not to be construed as restricted to the
11 particularly described embodiments, rather the scope, spirit
12 and concept of the invention will be more readily understood
13 by reference to the claims which follow.

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CLAIMS

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- 2 1. A homogeneous liquid composition, for use in the
3 preparation of liquid toners containing at least one charge
4 director and in which the electrical properties of the
5 charge director(s) is/are stabilized, which composition
6 comprises:
- 7 (1) insulating non-polar carrier liquid compatible
8 with liquid toners for electrostatic imaging;
- 9 (2) at least one charge director other than an amine
10 salt; and (3) at least one stabilizing component in an
11 amount effective to stabilize the electrical properties of
12 said at least one charge director, said component being
13 selected from non-quaternary amine salts and being soluble
14 in the carrier.
- 15
- 16 2. A homogeneous composition according to claim 1, wherein
17 component (3) is selected from non-quaternary salts of
18 aliphatic amines with an acid selected from inorganic acids
19 and alkyl-substituted aromatic sulfonic acids.
- 20
- 21 3. A homogeneous composition according to either claim 1
22 or claim 2, wherein said insulating non-polar carrier liquid
23 comprises an insulating non-polar liquid hydrocarbon having
24 a volume resistivity above 10^9 ohm-cm and a dielectric
25 constant below 3.0.
- 26
- 27 4. A homogeneous composition according to any of the
28 preceding claims, wherein the weight ratio of stabilizing
29 component to charge director falls within the range of
30 0.001-2.0:1.
- 31
- 32 5. A homogeneous composition according to any of the
33 preceding claims, wherein said at least one charge director
34 is selected from lecithin, basic barium petronate and
35 calcium petronate.
- 36
- 37 6. A homogeneous composition according to any of the
38 preceding claims, wherein component (3) is selected from



1 diethylammonium chloride and isopropylamine
2 dodecylbenzenesulfonate.

3

4 7. A liquid toner for electrostatic imaging which
5 comprises thermoplastic resin particles dispersed in a
6 homogeneous composition according to any of claims 1-6,
7 wherein the at least one charge director is operative to
8 charge the particles and the stabilizing compound is present
9 in an amount effective to stabilize the electrical
10 properties of the at least one charge director.

11

12 8. A liquid toner according to claim 7, wherein the weight
13 ratio of stabilizing component to charge director falls
14 within the range of 0.001-2.0:1.

15

16 9. A method for producing liquid toner compositions
17 containing charge directors and in which the electrical
18 properties of the charge directors are stabilized, which
19 method comprises the steps of: (A) first making a
20 homogeneous liquid composition as defined in any of claims 1
21 to 6, and (B) mixing the homogeneous liquid composition
22 from step (A) in any order with colored thermoplastic resin
23 particles, and if desired further liquid carrier, in such
24 manner that the colored thermoplastic resin particles are
25 micro-dispersed in the toner composition.

26

27 10. An electrostatic imaging process which comprises the
28 steps of: forming a charged latent electrostatic image on a
29 photoconductive surface; applying to said surface oppositely
30 charged colorant particles from a liquid toner as defined in
31 claim 7 or claim 8 or as prepared by the method of claim 9;
32 and transferring the resulting toner image to a substrate.

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