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(71) Applicant: **HEWLETT-PACKARD DEVELOPMENT COMPANY, L.P.** [US/US]; 10300 Energy Drive, Spring, Texas 77389 (US).

(72) Inventors: **PINES, Assaf**; Sapier 3 Kiryat Weizmann, 7403626 Nes Ziona (IL). **SANDLER, Mark**; Einstein 10 Kiryat Weizmann, 7403662 Nes Ziona (IL).

(74) Agent: **COSTALES, Shruti** et al.; HP Inc., 3390 E. Harmony Road, Mailstop 35, Fort Collins, Colorado 80528-9599 (US).

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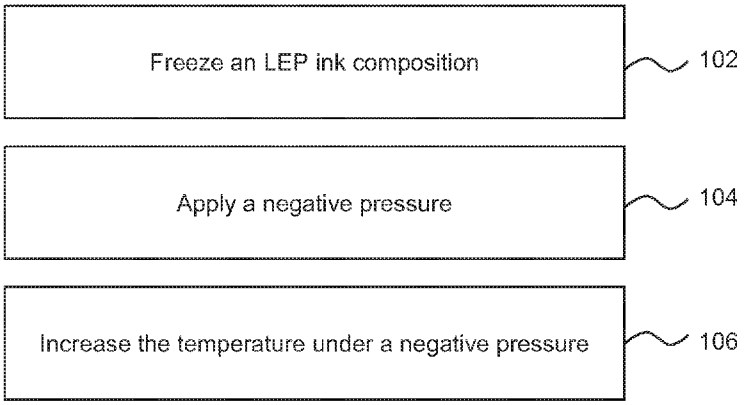

Figure 1

(57) Abstract: Described herein is a method comprising freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles. Also described herein is a freeze-dried LEP ink composition obtainable by the method.

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Concentrating Liquid Electrophotographic Ink Compositions

BACKGROUND

[0001] Printing processes such as electrostatic printing involve creating an image using toner particles. In some examples, the toner particles may be suspended in a carrier fluid providing a liquid print agent, which may be used in liquid electrophotographic printing (LEP) processes. A LEP print agent (also referred to as a "liquid ink" herein) may be formed by mixing g chargeable particles comprising a resin (which may be a thermoplastic resin) with a carrier fluid to create the suspension.

BRIEF DESCRIPTION OF DRAWINGS

[0002] Non-limiting examples will now be described with reference to the accompanying drawings, in which:

[0003] Figure 1 is a flowchart of an example method for concentrating a liquid electrophotographic ink composition;

[0004] Figure 2 is a flowchart of an example method for concentrating liquid electrophotographic ink composition and then re-dispersing the liquid electrophotographic ink composition in liquid carrier;

[0005] Figure 3 shows the volume-based particle size distribution of a magenta LEP ink composition a) before freeze drying, b) after immediate re-dispersion; and c) after being stored for 2 months at room temperature and pressure and then being re-dispersed;

[0006] Figure 4 shows the electrical charging characteristics of the magenta LEP ink composition before freeze drying and after immediate re-dispersion;

[0007] Figure 5 shows the volume-based particle size distribution of a yellow LEP ink composition a) after immediate re-dispersion in tetrachloroethylene; and b) after being stored for 2 months at room temperature and pressure and then being re-dispersed in Isopar L.

DETAILED DESCRIPTION

[0008] Before the present disclosure is disclosed and described, it is to be understood that this disclosure is not limited to the particular process steps and materials disclosed herein because such process steps and materials may vary somewhat. It is also to be understood that the terminology used herein is used for the purpose of

describing particular embodiments. The terms are not intended to be limiting because the scope is intended to be limited by the appended claims and equivalents thereof.

[0009] It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

[0010] As used herein, “carrier fluid”, “carrier liquid,” “carrier,” or “carrier vehicle” refers to the fluid in which pigment particles, resin, charge directors and other additives can be dispersed to form a liquid electrostatic ink composition or liquid electrophotographic ink composition. The carrier liquid may include a mixture of a variety of different agents, such as surfactants, co-solvents, viscosity modifiers, and/or other possible ingredients.

[0011] As used herein, “liquid electrostatic ink composition” or “liquid electrophotographic composition” generally refers to an ink composition that is typically suitable for use in an electrostatic printing process, sometimes termed an electrophotographic printing process. It may comprise pigment particles having a thermoplastic resin thereon. The electrostatic ink composition may be a liquid electrostatic ink composition, in which the pigment particles having resin thereon are suspended in a carrier liquid. The pigment particles having resin thereon will typically be charged or capable of developing charge in an electric field, such that they display electrophoretic behaviour. A charge director may be present to impart a charge to the pigment particles having resin thereon.

[0012] As used herein, “co-polymer” refers to a polymer that is polymerized from at least two monomers.

[0013] As used herein, “melt flow rate” generally refers to the extrusion rate of a resin through an orifice of defined dimensions at a specified temperature and load, usually reported as temperature/load, e.g. 190°C/2.16 kg. Flow rates can be used to differentiate grades or provide a measure of degradation of a material as a result of molding. In the present disclosure, unless otherwise stated, “melt flow rate” is measured per ASTM D1238 Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, as known in the art. If a melt flow rate of a particular polymer is specified, unless otherwise stated, it is the melt flow rate for that polymer alone, in the absence of any of the other components of the liquid electrostatic ink composition.

[0014] As used herein, “acidity,” “acid number,” or “acid value” refers to the mass of potassium hydroxide (KOH) in milligrams that neutralizes one gram of a substance. The acidity of a polymer can be measured according to standard techniques, for example as described in ASTM D1386. If the acidity of a particular polymer is specified, unless otherwise stated, it is the acidity for that polymer alone, in the absence of any of the other components of the liquid toner composition.

[0015] As used herein, “melt viscosity” generally refers to the ratio of shear stress to shear rate at a given shear stress or shear rate. Testing is generally performed using a capillary rheometer. A plastic charge is heated in the rheometer barrel and is forced through a die with a plunger. The plunger is pushed either by a constant force or at constant rate depending on the equipment. Measurements are taken once the system has reached steady-state operation. One method used is measuring Brookfield viscosity @ 140°C, units are mPa·s or cPoise, as known in the art. Alternatively, the melt viscosity can be measured using a rheometer, e.g. a commercially available AR-2000 Rheometer from Thermal Analysis Instruments, using the geometry of: 25mm steel plate-standard steel parallel plate, and finding the plate over plate rheometry isotherm at 120°C, 0.01 Hz shear rate. If the melt viscosity of a particular polymer is specified, unless otherwise stated, it is the melt viscosity for that polymer alone, in the absence of any of the other components of the electrostatic composition.

[0016] A certain monomer may be described herein as constituting a certain weight percentage of a polymer. This indicates that the repeating units formed from the said monomer in the polymer constitute said weight percentage of the polymer.

[0017] If a standard test is mentioned herein, unless otherwise stated, the version of the test to be referred to is the most recent at the time of filing this patent application.

[0018] As used herein, “electrostatic printing” or “electrophotographic printing” generally refers to the process that provides an image that is transferred from a photo imaging substrate either directly or indirectly via an intermediate transfer member to a substrate, such as a paper or plastic substrate. As such, it may be the case that the image is not substantially absorbed into the photo imaging substrate on which it is applied. Additionally, “electrophotographic printers” or “electrostatic printers” generally refer to those printers capable of performing electrophotographic printing or electrostatic printing, as described above. “Liquid electrostatic printing” is a type of electrostatic printing in which a liquid composition is employed in the electrophotographic process rather than a powder toner. An electrostatic printing process may involve subjecting the

electrostatic composition to an electric field, for example, an electric field having a field gradient of 50-400 V/μm, or more, in some examples, 600-900V/μm, or more.

[0019] As used herein, "NVS" is an abbreviation of the term "non-volatile solids".

[0020] As used herein, the term "about" is used to provide flexibility to a numerical range endpoint by providing that a given value may be a little above or a little below the endpoint to allow for variation in test methods or apparatus. The degree of flexibility of this term can be dictated by the particular variable and would be within the knowledge of those skilled in the art to determine based on experience and the associated description herein.

[0021] As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de facto equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary.

[0022] Concentrations, amounts, and other numerical data may be expressed or presented herein in a range format. It is to be understood that such a range format is used merely for convenience and brevity and thus should be interpreted flexibly to include not just the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. As an illustration, a numerical range of "about 1 wt.% to about 5 wt.%" should be interpreted to include not just the explicitly recited values of about 1 wt.% to about 5 wt.%, but also to include individual values and sub-ranges within the indicated range. Thus, included in this numerical range are individual values such as 2, 3.5, and 4 and sub-ranges such as from 1-3, from 2-4, and from 3-5, etc. This same principle applies to ranges reciting a single numerical value. Furthermore, such an interpretation should apply regardless of the breadth of the range or the characteristics being described.

[0023] As used herein, unless otherwise stated, wt.% values are to be taken as referring to a weight-for-weight (w/w) percentage of solids in the ink composition, and not including the weight of any carrier fluid present.

[0024] Unless otherwise stated, any feature described herein can be combined with any aspect or any other feature described herein.

[0025] In an aspect, there is provided a method comprising:

freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid;

subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and

increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles.

[0026] In another aspect, there is provided a freeze dried LEP ink composition. The freeze dried LEP ink composition may be obtainable by a method comprising:

freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid;

subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and

increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles.

[0027] Currently, many liquid electrophotographic ink compositions are supplied at 22 to 42 wt.% non-volatile solids content. However, liquid electrophotographic printing presses recirculate the majority of the liquid carrier, producing excess liquid that is disposed of after printing.

[0028] To reduce this surplus of liquid carrier, a method for concentrating liquid electrophotographic ink compositions has been sought that provides higher non-volatile solids contents without altering the physical and chemical properties of the particles in the ink. The method described herein has been found to produce concentrated liquid electrophotographic ink compositions that largely maintain the particle size distribution of the liquid electrophotographic ink composition before it was concentrated. After re-dispersion to form a print ready liquid electrophotographic ink composition, the particle size distribution was still largely maintained. Additionally, the physical and chemical properties of the liquid electrophotographic ink compositions were also largely maintained after re-dispersion to form a print ready liquid electrophotographic ink composition.

Method of concentrating an LEP ink

[0029] In an aspect, there is provided a method of concentrating a liquid electrophotographic (LEP) ink composition. The method may comprise: freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles. This method provides a concentrated LEP ink composition, which may be termed a freeze dried LEP ink composition herein.

[0030] In some examples, the sublimation and desorption of carrier liquid reduces the amount of liquid present to an amount no more than 5% by weight. In some examples, the sublimation and desorption of carrier liquid reduces the amount of liquid present to an amount no more than 4.5% by weight, for example, no more than 4% by weight, no more than 3.5% by weight, no more than 3% by weight, no more than 2.5% by weight, no more than 2% by weight, no more than 1.5% by weight, no more than 1% by weight, no more than 0.5% by weight, no more than 0.4% by weight, no more than 0.3% by weight, no more than 0.2% by weight, or no more than 0.1% by weight. In some examples, the sublimation and desorption of carrier liquid removes all of the liquid present. In some examples, the sublimation and desorption of carrier liquid reduces the amount of liquid present to an amount up to 0.1% by weight, for example, up to 0.2% by weight, up to 0.3% by weight, up to 0.4% by weight, up to 0.5% by weight, up to 1% by weight, up to 1.5% by weight, up to 2% by weight, up to 2.5% by weight, up to 3% by weight, up to 3.5% by weight, up to 4% by weight, up to 4.5% by weight, or up to 5% by weight. In some examples, the sublimation and desorption of carrier liquid reduces the amount of liquid present to an amount of 0% by weight to 5% by weight, 0.1% by weight to 4.5% by weight, 0.2% by weight to 4% by weight, 0.3% by weight to 3.5% by weight, 0.4% by weight to 3% by weight, 0.5% by weight to 2.5% by weight, 1% by weight to 2% by weight, 0.5% by weight to 1.5% by weight, or 0.5% by weight to 1% by weight.

[0031] In some examples, freezing an LEP ink composition comprises lowering the temperature of the LEP ink composition. In some examples, freezing an LEP ink composition comprises lowering the temperature of the LEP ink composition to a temperature of −35°C or less, for example, −40°C or less, −45°C or less, −50°C or less, −55°C or less, −60°C or less, −65°C or less, −70°C or less, or −75°C or less. In some examples, freezing an LEP ink composition comprises lowering the temperature of the

LEP ink composition to a temperature of −75°C or more, for example, −70°C or more, −65°C or more, −60°C or more, −55°C or more, −50°C or more, −45°C or more, −40°C or more, or −35°C or more. In some examples, freezing an LEP ink composition comprises lowering the temperature of the LEP ink composition to a temperature in the range of from −35°C to −75°C, for example, −35°C to −70°C, −40°C to −65°C, −45°C to −60°C, or −50°C to −55°C.

[0032] In some examples, freezing of the LEP ink composition may additionally comprise adjusting the pressure. In some examples, the pressure during freezing of the LEP ink composition may be 100 Torr or more, for example, 150 Torr or more, 200 Torr or more, 250 Torr or more, 300 Torr or more, 350 Torr or more, 400 Torr or more, 450 Torr or more, 500 Torr or more, 550 Torr or more, 600 Torr or more, 650 Torr or more, 700 Torr or more, 750 Torr or more, 780 Torr or more, or 800 Torr or more. In some examples, the pressure during freezing of the LEP ink composition may be from 100 Torr to 800 Torr, for example, 150 Torr to 780 Torr, 200 Torr to 750 Torr, 250 Torr to 700 Torr, 300 Torr to 650 Torr, 350 Torr to 600 Torr, 400 Torr to 550 Torr, or 450 Torr to 500 Torr. In some examples, the pressure during freezing of the LEP ink composition may be atmospheric pressure. One Torr is about 133.32 Pa.

[0033] In some examples, freezing the LEP ink composition comprises lowering the temperature for at least 6 hours, for example, at least 6.5 hours, at least 7 hours, at least 7.5 hours, at least 8 hours, at least 8.5 hours, at least 9 hours, at least 9.5 hours, at least 10 hours, at least 10.5 hours, at least 11 hours, at least 11.5 hours, or at least 12 hours. In some examples, freezing the LEP ink composition comprises lowering the temperature for up to 24 hours, for example, up to 23 hours, up to 22.5 hours, up to 22 hours, up to 21.5 hours, up to 21 hours, up to 20.5 hours, up to 20 hours, up to 19.5 hours, up to 19 hours, up to 18.5 hours, up to 18 hours, up to 17.5 hours, up to 17 hours, up to 16.5 hours, up to 16 hours, up to 15.5 hours, up to 15 hours, up to 14.5 hours, up to 14 hours, up to 13.5 hours, up to 13 hours, up to 12.5 hours, or up to 12 hours. In some examples, freezing the LEP ink composition comprises lowering the temperature for from 6 hours to 24 hours, for example, 6.5 hours to 24 hours, 7 hours to 23.5 hours, 7.5 hours to 23 hours, 8 hours to 22.5 hours, 8.5 hours to 22 hours, 9 hours to 21.5 hours, 9.5 hours to 21 hours, 10 hours to 20.5 hours, 10.5 hours to 20 hours, 11 hours to 19.5 hours, 11.5 hours to 19 hours, 12 hours to 18.5 hours, 12.5 hours to 18 hours, 13 hours to 17.5 hours, 13.5 hours to 17 hours, 14 hours to 16.5 hours, 14.5 hours to 16 hours, or 15 hours to 15.5 hours.

[0034] In some examples, subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid may comprise subjecting the frozen LEP ink composition to a negative pressure whilst maintaining the temperature at the temperature used to freeze the LEP ink composition. In some examples, subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid may comprise subjecting the frozen LEP ink composition to a negative pressure whilst increasing the temperature above the temperature used to freeze the LEP ink composition.

[0035] In some examples, the negative pressure may be 20 mTorr or lower, for example, 19 mTorr or lower, 18 mTorr or lower, 17 mTorr or lower, 16 mTorr or lower, 15 mTorr or lower, 14 mTorr or lower, 13 mTorr or lower, 12 mTorr or lower, 11 mTorr or lower, 10 mTorr or lower, 9 mTorr or lower, 8 mTorr or lower, 7 mTorr or lower, 6 mTorr or lower, 5 mTorr or lower, for example, 4.5 mTorr or lower, 4 mTorr or lower, 3.5 mTorr or lower, 3 mTorr or lower, 2.5 mTorr or lower, or 2 mTorr or lower. In some examples, the negative pressure may be at least 2 mTorr, for example, at least 2.5 mTorr, at least 3 mTorr, at least 3.5 mTorr, at least 4 mTorr, at least 4.5 mTorr, or at least 5 mTorr, at least 6 mTorr, at least 7 mTorr, at least 8 mTorr, at least 9 mTorr, at least 10 mTorr, at least 11 mTorr, at least 12 mTorr, at least 13 mTorr, at least 14 mTorr, at least 15 mTorr, at least 16 mTorr, at least 17 mTorr, at least 18 mTorr, at least 19 mTorr, or at least 20 mTorr. In some examples, the negative pressure may be from 2 mTorr to 20 mTorr, for example, 2.5 mTorr to 20 mTorr, 3 mTorr to 19 mTorr, 3.5 mTorr to 18 mTorr, 4 mTorr to 17 mTorr, 4.5 mTorr to 16 mTorr, 5 mTorr to 15 mTorr, 2 mTorr to 14 mTorr, 2.5 mTorr to 13 mTorr, 3 mTorr to 12 mTorr, 4 mTorr to 11 mTorr, 3.5 mTorr to 10 mTorr, 4 mTorr to 9 mTorr, 4.5 mTorr to 8 mTorr, 5 mTorr to 7 mTorr, or 2 mTorr to 6 mTorr. One mTorr is 0.001 Torr, which corresponds to about 0.13 Pa.

[0036] In some examples, the frozen LEP ink composition is subjected to a negative pressure for at least 10 hours, for example, at least 12 hours, at least 18 hours, at least 24 hours, at least 36 hours, at least 48 hours, at least 60 hours, at least 72 hours, at least 84 hours, at least 96 hours. In some examples, the frozen LEP ink composition is subjected to a negative pressure for up to 120 hours, for example, up to 108 hours, up to 96 hours, up to 84 hours, up to 72 hours, up to 60 hours, up to 48 hours, up to 36 hours, up to 24 hours, up to 18 hours, up to 12 hours or up to 10 hours. In some examples, the frozen LEP ink composition is subjected to a negative pressure for from 10 hours to 120 hours, in some examples, 12 hours to 108 hours, 18 hours to 96 hours, 24 hours to 84

hours, 36 hours to 72 hours or 48 hours to 60 hours. In some examples, the negative pressure is maintained until sublimation of the liquid carrier is completed. In some examples, the sublimation rate is monitored by monitoring the temperature of the LEP ink composition and the negative pressure is maintained until sublimation of the liquid carrier is completed.

[0037] In some examples, the pressure is reduced over a period of time from the pressure at which the LEP ink composition is frozen to a lower pressure at which the carrier liquid is sublimed. In some examples, the pressure is reduced over a period of time from the pressure at which the LEP ink composition is frozen to the negative pressure. In some examples, the pressure is reduced over a period of at least 5 hours, for example, at least 10 hours, at least 12 hours, at least 18 hours, at least 24 hours, at least 36 hours, at least 48 hours, at least 60 hours, at least 72 hours, at least 84 hours, at least 96 hours. In some examples, the pressure is reduced over a period of up to 120 hours, for example, up to 108 hours, up to 96 hours, up to 84 hours, up to 72 hours, up to 60 hours, up to 48 hours, up to 36 hours, up to 24 hours, up to 18 hours, up to 12 hours or up to 10 hours. In some examples, the pressure is reduced over a period of from 10 hours to 120 hours, in some examples, 12 hours to 108 hours, 18 hours to 96 hours, 24 hours to 84 hours, 36 hours to 72 hours or 48 hours to 60 hours.

[0038] In some examples, the frozen LEP ink composition may be subjected to the negative pressure at a temperature of up to 50°C higher than the temperature at which the LEP ink composition was frozen, for example, up to 45°C higher, up to 40°C higher, up to 35°C higher, up to 30°C higher, up to 25°C higher, up to 20°C higher, up to 15°C higher, up to 10°C higher, up to 5°C higher, or up to 0°C higher than the tempearture at which the LEP ink composition was frozen. In some examples, the frozen LEP ink composition may be subjected to the negative pressure at a tempearture of 0°C higher to 50°C higher than the temperature at which the LEP ink composition was frozen, 5°C higher to 45°C higher, 10°C higher to 40°C higher, 15°C higher to 35°C higher, 20°C higher to 30°C higher, or 20°C higher to 25°C higher than the temperature at which the LEP ink composition was frozen.

[0039] In some examples, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles may comprise increasing the temperature over a period of time. In some examples, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable

particles may comprise increasing the temperature to room temperature (which may be from 20°C to 25°C) over a period of time. In some examples, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles may comprise increasing the temperature from the temperature at which the frozen LEP ink composition was subjected to a negative pressure to a higher temperature. In some examples, the higher temperature may be at least −40°C, for example, at least −35°C, at least −30°C, at least −25°C, at least −20°C, at least −15°C, at least −10°C, at least −5°C, at least 0°C, at least 5°C, at least 10°C, at least 15°C, at least 20°C, or at least 25°C. In some examples, the higher temperature may be up to up to 25°C, up to 20°C, up to 15°C, up to 10°C, up to 5°C, up to 0°C, up to −5°C, up to −10°C, up to −15°C, up to −20°C, up to −25°C, up to −30°C, up to −35°C, or up to −40°C. In some examples, the higher temperature may be from −40°C to 25°C, for example, −35°C to 20°C, −30°C to 15°C, −25°C to 10°C, −20°C to 25°C, −15°C to 20°C, −10°C to −15°C, −5°C to 10°C, 0°C to 20°C, −35°C to 5°C.

[0040] In some examples, the temperature may be increased over a period of up to 24 hours, for example, up to 18 hours, up to 12 hours, up to 10 hours, up to 8 hours, up to 7 hours, up to 6 hours, up to 5 hours, up to 4 hours, or up to 2 hours. In some examples, the temperature may be increased over a period of at least 2 hours, for examples, at least 4 hours, at least 5 hours, at least 6 hours, at least 7 hours, at least 8 hours, at least 10 hours, at least 12 hours, at least 18 hours, or at least 24 hours. In some examples, the temperature may be increased over a period of from 2 hours to 24 hours, for example, from 4 hours to 18 hours, 5 hours to 12 hours, 6 hours to 10 hours, or 7 hours to 8 hours.

[0041] In some examples, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles may comprise increasing the temperature over a period of time and then maintaining that temperature for a further period of time. In some examples, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles may comprise increasing the temperature to room temperature (which may be from 20°C to 25°C) over a period of time and then maintaining that temperature for a further period of time. In some examples, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles may comprise increasing the temperature from the temperature at which the

frozen LEP ink composition was subjected to a negative pressure to a higher temperature and then maintaining that temperature for a further period of time. In some examples, the further period of time may be at least 1 hour, for example, at least 2 hours, at least 3 hours, at least 4 hours, at least 5 hours, at least 6 hours, at least 7 hours, at least 8 hours, at least 9 hours, or at least 10 hours. In some examples, the further period of time may be up to 10 hours, up to 9 hours, up to 8 hours, up to 7 hours, up to 6 hours, up to 5 hours, up to 4 hours, up to 3 hours, up to 2 hours or up to 1 hour. In some examples, the further period of time may be from 1 hour to 10 hours, for example, from 2 hours to 9 hours, from 3 hours to 8 hours, from 4 hours to 7 hours, from 1 hour to 6 hours, from 2 hours to 5 hours, or from 5 hours to 10 hours.

[0042] In some examples, the method may comprise freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid by lowering the temperature to a temperature in the range −35°C to −75°C at a pressure of 600 mTorr to 800 mTorr for at least 6 hours; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid by maintaining the frozen LEP ink composition at −35°C to −75°C and reducing the pressure to 20 mTorr or lower (e.g., 5 mTorr or lower) for at least 12 hours; and increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of the carrier liquid from within the chargeable particles by increasing the temperature to at least 10°C over a period of at least 2 hours, and maintaining that temperature for at least 2 further hours.

[0043] In some examples, the method further comprises storing the freeze dried location for a period of time and/or transporting the freeze dried LEP ink composition to another location.

[0044] In some examples, the method further comprises adding the freeze dried LEP ink composition to a carrier liquid. In some examples, the method comprises freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles; and adding the freeze dried LEP ink composition to a carrier liquid. In some examples, the method comprises freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier

liquid; increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles to form a freeze dried LEP ink composition; and adding the freeze dried LEP ink composition to a carrier liquid. In some examples, the carrier liquid to which the freeze dried LEP ink composition is added may be the same or different from the carrier liquid that is removed from the LEP ink composition by sublimation and desorption. In some examples, the carrier liquid to which the freeze dried LEP ink composition is added may be a hydrocarbon.

[0045] In some examples, the method further comprises adding the freeze dried LEP ink composition to a carrier fluid; and agitating the carrier fluid containing the freeze dried LEP ink composition to disperse particles of the toner particles in the fluid to form a liquid ink. In some examples, the method comprises freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles; adding the freeze dried LEP ink composition to a carrier liquid; and agitating the carrier fluid containing the freeze dried LEP ink composition to disperse particles of the toner particles in the fluid to form a liquid ink. In some examples, the method comprises freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles to form a freeze dried LEP ink composition; adding the freeze dried LEP ink composition to a carrier liquid; and agitating the carrier fluid containing the freeze dried LEP ink composition to disperse particles of the toner particles in the fluid to form a liquid ink. In some examples, the carrier liquid to which the freeze dried LEP ink composition is added may be the same or different from the carrier liquid that is removed from the LEP ink composition by sublimation and desorption. In some examples, the carrier liquid to which the freeze dried LEP ink composition is added may be a hydrocarbon. Adding the freeze dried LEP ink composition to a liquid carrier and agitating the liquid carrier containing the freeze dried LEP ink composition to disperse the chargeable particles in the liquid carrier may be referred to as re-dispersing the freeze dried LEP ink composition in a liquid carrier. In some examples, the re-

dispersed freeze dried LEP ink composition may be referred to as a print ready LEP ink composition.

[0046] In some examples, agitating the liquid carrier containing the freeze dried LEP ink composition to disperse the chargeable particles in the liquid carrier may comprise mixing, for example, stirring, low shear mixing or high shear mixing.

[0047] The present disclosure is described with reference to flow charts and/or block diagrams of the method, devices and systems according to examples of the present disclosure. Although the flow diagrams described above show a specific order of execution, the order of execution may differ from that which is depicted. Blocks described in relation to one flow chart may be combined with those of another flow chart.

[0048] Figure 1 shows an example of a method for concentrating an LEP ink composition. The method comprises, in block 102, freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; in block 104, subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and in block 106, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles.

[0049] Figure 2 shows an example of a method for concentrating an LEP ink composition and re-dispersing the concentrated LEP ink composition in a liquid carrier. The method comprises, in block 202, freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; in block 204, subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; in block 206, increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles; and, in block 208, adding the freeze dried LEP ink composition to a liquid carrier; and agitating the liquid carrier containing the freeze dried LEP ink composition to disperse the chargeable particles in the liquid carrier to form a print ready LEP ink composition.

LEP ink composition

[0050] The initial LEP ink composition, that is, the LEP ink composition before the method of concentrating the LEP ink composition is performed, may comprise chargeable particles comprising a resin suspended in a carrier liquid. In some examples,

the initial LEP ink composition comprises chargeable particles comprising a resin, wherein the chargeable particles are suspended in a carrier liquid.

[0051] In some examples, the initial LEP ink composition comprises chargeable particles suspended in a liquid carrier. In some examples, the chargeable particles of the initial LEP ink composition comprise a resin and a colorant.

[0052] In some examples, the initial LEP ink composition further comprises a charge adjuvant. In some examples, the initial LEP ink composition further comprises a charge director. In some examples, the initial LEP ink composition further comprises a charge director and a charge adjuvant. In some examples, the initial LEP ink composition further comprises other additives. In some examples, the initial LEP ink composition further comprises a charge adjuvant, a charge director and other additives.

[0053] In some examples, the initial LEP ink composition, that is, the LEP ink composition before the method of concentrating an LEP ink composition is performed, comprises at least 25 wt.% liquid carrier, for example, at least 30 wt.%, at least 40 wt.%, at least 45 wt.%, or at least 50 wt.% liquid carrier. In some examples, the initial LEP ink composition comprises up to 50 wt.% liquid carrier, for example, up to 45 wt.%, up to 40 wt.%, up to 35 wt.%, up to 30 wt.%, or up to 25 wt.% liquid carrier. In some examples, the initial LEP ink composition comprises 25 wt.% to 50 wt.% liquid carrier, for example, 30 wt.% to 45 wt.%, or 35 wt.% to 40 wt.% liquid carrier.

Freeze dried LEP ink composition

[0054] In another aspect, there is provided a freeze dried LEP ink composition. In some examples, the freeze dried LEP ink composition may be obtainable by any method described herein. In some examples, the freeze dried LEP ink composition may be obtainable by a method comprising: freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid; subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles.

[0055] In some examples, the freeze dried LEP ink composition may comprise carrier liquid present in an amount no more than 5% by weight. In some examples, the freeze dried LEP ink composition may comprise carrier liquid present in an amount no more than 4.5% by weight, for example, no more than 4% by weight, no more than 3.5% by weight, no more than 3% by weight, no more than 2.5% by weight, no more than 2%

by weight, no more than 1.5% by weight, no more than 1% by weight, no more than 0.5% by weight, no more than 0.4% by weight, no more than 0.3% by weight, no more than 0.2% by weight, or no more than 0.1% by weight. In some examples, the freeze dried LEP ink composition may comprise 0% by weight carrier liquid. In some examples, the freeze dried LEP ink composition may comprise carrier liquid present in an amount up to 0.1% by weight, for example, up to 0.2% by weight, up to 0.3% by weight, up to 0.4% by weight, up to 0.5% by weight, up to 1% by weight, up to 1.5% by weight, up to 2% by weight, up to 2.5% by weight, up to 3% by weight, up to 3.5% by weight, up to 4% by weight, up to 4.5% by weight, or up to 5% by weight. In some examples, the freeze dried LEP ink composition may comprise carrier liquid in an amount of 0% by weight to 5% by weight, 0.1% by weight to 4.5% by weight, 0.2% by weight to 4% by weight, 0.3% by weight to 3.5% by weight, 0.4% by weight to 3% by weight, 0.5% by weight to 2.5% by weight, 1% by weight to 2% by weight, 0.5% by weight to 1.5% by weight, or 0.5% by weight to 1% by weight.

[0056] In some examples, the concentrated LEP ink composition, which may be termed a freeze dried LEP ink composition herein, comprises up to 5 wt.% liquid carrier, for example, up to 4.5 wt.%, up to 4 wt.%, up to 3.5 wt.%, up to 3 wt.%, up to 2.5 wt.%, up to 2 wt.%, up to 1.5 wt.%, up to 1 wt.%, or up to 0.5 wt.% liquid carrier. In some examples, the freeze dried LEP ink composition comprises 0 wt.% to 5 wt.% liquid carrier, for example, 0.5 wt.% to 5 wt.%, 1 wt.% to 4.5 wt.%, 1.5 wt.% to 4 wt.%, 2 wt.% to 3.5 wt.%, or 2.5 wt.% to 3 wt.% liquid carrier.

[0057] In some examples, the freeze dried LEP ink composition comprises chargeable particles comprising a resin. In some examples, the chargeable particles comprising a resin further comprise a colorant, such as a pigment.

[0058] In some examples, the freeze dried LEP ink composition further comprises a charge adjuvant. In some examples, the freeze dried LEP ink composition further comprises a charge director. In some examples, the freeze dried LEP ink composition further comprises a charge adjuvant and a charge director.

[0059] In some examples, the chargeable particles have an average diameter of 5 μm or less, for example, 4.5 μm or less, 4 μm or less, 3.5 μm or less, 3 μm or less, 2.5 μm or less, 2 μm or less, 1.5 μm or less, 1 μm or less, or 0.5 μm or less. In some examples, the chargeable particles have an average diameter of at least 0.5 μm, for example, at least 1 μm, at least 1.5 μm, at least 2 μm, at least 2.5 μm, at least 3 μm, at least 3.5 μm, at least 4 μm, at least 4.5 μm, or at least 5 μm. In some examples, the

chargeable particles have an average diameter of 0.5 μm to 5 μm, 1 μm to 4.5 μm, 1.5 μm to 4 μm, 2 μm to 3.5 μm, or 2.5 μm to 3 μm. In some examples, the average diameter of the chargeable particles is the volume-based average particle size as measured by laser diffraction. In some examples, the average diameter of the chargeable particles may be measured by using a Malven™ Mastersizer 2000. In some examples, the chargeable particles may be plate shaped.

[0060] In some examples, the freeze dried LEP ink composition is dispersible in a carrier liquid to form a liquid electrophotographic (LEP) ink composition. In some examples, the dispersed (which may be referred to herein as re-dispersed) LEP ink composition may comprise at least 90 wt.% liquid carrier, for example, at least 91 wt.%, at least 92 wt.%, at least 93 wt.%, at least 94 wt.%, at least 95 wt.%, at least 96 wt.%, at least 97 wt.%, at least 98 wt.%, or at least 99 wt.% liquid carrier. In some examples. The re-dispersed LEP ink composition may comprise 90 wt.% to 99 wt.% liquid carrier, for example, 91 wt.% to 99 wt.%, 92 wt.% to 98 wt.%, 93 wt.% to 97 wt.%, 94 wt.% to 98 wt.%, 95 wt.% to 99 wt.%, 96 wt.% to 99 wt.% liquid carrier.

Re-dispersed LEP ink composition

[0061] In some examples, the freeze dried LEP ink composition may be re-dispersed in a liquid carrier. In some examples, re-dispersing the freeze dried LEP ink composition in a liquid carrier may provide a print ready LEP ink composition.

[0062] In some examples, the freeze dried LEP ink composition may be re-dispersed in a liquid carrier by mixing the freeze dried LEP ink composition with liquid carrier. In some examples, the mixing may comprise high shear mixing. High shear mixing may comprise mixing with a shear rate of at least 20,000 s^{-1}. In some examples, the freeze dried LEP ink composition and liquid carrier may be mixed for 5 s or more, for example, 10 s or more. In some examples, the freeze dried LEP ink composition and liquid carrier may be mixed for up to 1 minute, for example, 30 seconds or less, 25 seconds or less, 20 seconds or less, 15 seconds or less, 10 seconds or less. In some examples, the freeze dried LEP ink composition may be mixed for 5 s to 1 minute, for example, 10 seconds to 30 seconds.

[0063] In some examples, the liquid carrier in which the LEP ink composition is re-dispersed is the same liquid carrier as the liquid carrier removed during the method of concentrating the LEP ink composition. In some examples, the liquid carrier in which the LEP ink composition is re-dispersed is a different liquid carrier to the liquid carrier

removed during the method of concentrating the LEP ink composition. In some examples, the LEP ink composition is re-dispersed in a carrier liquid comprising hydrocarbons.

[0064] In some examples, the re-dispersed LEP ink composition comprises at least 90 wt.% liquid carrier, for example, at least 91 wt.%, at least 91.5 wt.%, at least 92 wt.%, at least 92.5 wt.%, at least 93 wt.%, at least 93.5 wt.%, at least 94 wt.%, at least 94.5 wt.%, at least 95 wt.%, at least 95.5 wt.%, at least 96 wt.%, at least 96.5 wt.%, at least 97 wt.%, at least 97.5 wt.%, at least 98 wt.%, at least 98.5 wt.%, or at least 99 wt.% liquid carrier. In some examples, the re-dispersed LEP ink composition comprises up to 99 wt.% liquid carrier, for example, up to 98 wt.%, up to 97.5 wt.%, up to 97 wt.%, up to 96.5 wt.%, up to 96 wt.%, up to 95.5 wt.%, up to 95 wt.%, up to 94.5 wt.%, up to 94 wt.%, up to 93.5 wt.%, up to 93 wt.%, up to 92.5 wt.%, up to 92 wt.%, up to 91.5 wt.%, up to 91 wt.%, up to 90.5 wt.%, or up to 90 wt.% liquid carrier. In some examples, the re-dispersed LEP ink composition comprises 90 wt.% to 99 wt.% liquid carrier, for example, 90.5 wt.% to 99 wt.%, 91 wt.% to 98.5 wt.%, 91.5 wt.% to 98 wt.%, 92 wt.% to 97.5 wt.%, 92.5 wt.% to 97 wt.%, 93 wt.% to 96.5 wt.%, 93.5 wt.% to 96 wt.%, 94 wt.% to 95.5 wt.%, or 94.5 wt.% to 95 wt.% liquid carrier.

Liquid Carrier

[0065] The liquid carrier can include or be a hydrocarbon, silicone oil, vegetable oil, etc. The liquid carrier can include, for example, an insulating, non-polar, non-aqueous liquid that can be used as a medium for chargeable particles, for example, the chargeable particles comprising the resin and, in some examples, a colorant. The liquid carrier can include compounds that have a resistivity in excess of about 10^9 ohm·cm. The liquid carrier may have a dielectric constant below about 5, in some examples, below about 3.

[0066] In some examples, the carrier liquid comprises a hydrocarbon, a halogenated hydrocarbon or a mixture thereof. In some examples, the carrier liquid comprises a carrier liquid with a freezing temperature of −200°C or more, for example, −195°C or more, −190°C or more, −180°C or more, −150°C or more, −100°C or more, −75°C or more, −50°C or more, −45°C or more, −40°C or more, −35°C or more, −30°C or more. In some examples, the carrier liquid comprises a carrier liquid with a freezing temperature of −5°C or less, for example, −10°C or less, −15°C or less, −20°C or less, −30°C or less. In some examples, the carrier liquid comprises a carrier liquid with a freezing

temperature of from −5°C to −200°C, for example, −10°C to −190°C, −15°C to −150°C, −20°C to −100°C, −25°C to −50°C, −30°C to −40°C.

[0067] In some examples, the halogenated hydrocarbon may comprise at least one halogen atom. In some examples, the halogenated hydrocarbon may be a perhalohydrocarbon. In some examples, the halogenated hydrocarbon, for example, the perhalohydrocarbon, may comprise a halogenated alkane, a halogenated alkene or a mixture thereof. In some examples, the halogenated alkane, for example, the perhaloalkane, may be a C1 to C10 alkane, for example, a C1 to C5 alkane, or a C2 to C5 alkane. In some examples, the halogenated alkene, for example, the perhaloalkene, may be a C1 to C10 alkene, for example, a C1 to C5 alkene, a C2 to C5 alkene or a C2 alkene. In some examples, the halogen may be fluorine, chlorine, bromine, iodine or a mixture thereof. In some examples, the halogen may comprise or be chlorine. In some examples, the liquid carrier may comprise or be tetrachloroethylene.

[0068] The liquid carrier can include hydrocarbons. The hydrocarbon can include, for example, an aliphatic hydrocarbon, an isomerized aliphatic hydrocarbon, branched chain aliphatic hydrocarbons, aromatic hydrocarbons, and combinations thereof. Examples of the liquid carrier include, for example, aliphatic hydrocarbons, isoparaffinic compounds, paraffinic compounds, dearomatized hydrocarbon compounds, and the like. In particular, the liquid carrier can include, for example, Isopar-G™, Isopar-H™, Isopar-L™, Isopar-M™, Isopar-K™, Isopar-V™, Norpar 12™, Norpar 13™, Norpar 15™, Exxol D40™, Exxol D80™, Exxol D100™, Exxol D130™, and Exxol D140™ (each sold by EXXON CORPORATION); Teclen N-16™, Teclen N-20™, Teclen N-22™, Nisseki Naphthesol L™, Nisseki Naphthesol M™, Nisseki Naphthesol H™, #0 Solvent L™, #0 Solvent M™, #0 Solvent H™, Nisseki Isosol 300™, Nisseki Isosol 400™, AF-4™, AF-5™, AF-6™ and AF-7™ (each sold by NIPPON OIL CORPORATION); IP Solvent 1620™ and IP Solvent 2028™ (each sold by IDEMITSU PETROCHEMICAL CO., LTD.); Amsco OMS™ and Amsco 460™ (each sold by AMERICAN MINERAL SPIRITS CORP.); and Electron, Positron, New II, Purogen HF (100% synthetic terpenes) (sold by ECOLINK™).

Chargeable particles

[0069] In some examples, the chargeable particles comprise a resin. In some examples, the chargeable particles comprise a resin and a colorant. In some examples, the chargeable particles comprise a resin, a colorant and other additives.

Resin

[0070] In some examples, the chargeable particles comprise a resin. The resin may be referred to as a thermoplastic polymer. A thermoplastic polymer is sometimes referred to as a thermoplastic resin.

[0071] In some examples, the resin may coat the colorant. The chargeable particles may include a core of colorant or colorant particles and have an outer layer of resin thereon. The colorant or colorant particles may be dispersed throughout each resin-containing particle. The outer layer of resin may coat the colorant or colorant particle partially or completely.

[0072] The resin typically includes a polymer. The resin can include, but is not limited to, a thermoplastic polymer. In some examples, the polymer of the resin may be selected from ethylene acrylic acid copolymers; ethylene methacrylic acid copolymers; ethylene vinyl acetate copolymers; copolymers of ethylene (e.g. 80 wt% to 99.9 wt%), and alkyl (e.g. C1 to C5) ester of methacrylic or acrylic acid (e.g. 0.1 wt% to 20 wt%); copolymers of ethylene (e.g. 80 wt% to 99.9 wt%), acrylic or methacrylic acid (e.g. 0.1 wt% to 20 wt%) and alkyl (e.g. C1 to C5) ester of methacrylic or acrylic acid (e.g. 0.1 wt% to 20 wt%); polyethylene; polystyrene; isotactic polypropylene (crystalline); ethylene ethyl acrylate; polyesters; polyvinyl toluene; polyamides; styrene/butadiene copolymers; epoxy resins; acrylic resins (e.g. copolymer of acrylic or methacrylic acid and at least one alkyl ester of acrylic or methacrylic acid wherein alkyl is, in some examples, from 1 to about 20 carbon atoms, such as methyl methacrylate (e.g. 50 wt% to 90 wt%)/methacrylic acid (e.g. 0 wt% to 20 wt%)/ethylhexylacrylate (e.g. 10 wt% to 50 wt%)); ethylene-acrylate terpolymers: ethylene-acrylic esters-maleic anhydride (MAH) or glycidyl methacrylate (GMA) terpolymers; ethylene-acrylic acid ionomers and combinations thereof.

[0073] The resin may comprise a polymer having acidic side groups. The polymer having acidic side groups may have an acidity of 50 mg KOH/g or more, in some examples an acidity of 60 mg KOH/g or more, in some examples an acidity of 70 mg KOH/g or more, in some examples an acidity of 80 mg KOH/g or more, in some examples an acidity of 90 mg KOH/g or more, in some examples an acidity of 100 mg KOH/g or more, in some examples an acidity of 105 mg KOH/g or more, in some examples 110 mg KOH/g or more, in some examples 115 mg KOH/g or more. The polymer having acidic side groups may have an acidity of 200 mg KOH/g or less, in some examples 190 mg or less, in some examples 180 mg or less, in some examples 130 mg KOH/g or less, in some examples 120 mg KOH/g or less. Acidity of a polymer,

as measured in mg KOH/g can be measured using standard procedures known in the art, for example using the procedure described in ASTM D1386.

[0074] The resin may comprise a polymer, in some examples a polymer having acidic side groups, that has a melt flow rate of less than about 60 g/10 minutes, in some examples about 50 g/10 minutes or less, in some examples about 40 g/10 minutes or less, in some examples 30 g/10 minutes or less, in some examples 20 g/10 minutes or less, in some examples 10 g/10 minutes or less. In some examples, all polymers having acidic side groups and/or ester groups in the particles each individually have a melt flow rate of less than 90 g/10 minutes, 80 g/10 minutes or less, in some examples 70 g/10 minutes or less, in some examples 60 g/10 minutes or less.

[0075] The polymer having acidic side groups can have a melt flow rate of about 10 g/10 minutes to about 120 g/10 minutes, in some examples about 10 g/10 minutes to about 70 g/10 minutes, in some examples about 10 g/10 minutes to 40 g/10 minutes, in some examples 20 g/10 minutes to 30 g/10 minutes. The polymer having acidic side groups can have a melt flow rate of in some examples about 50 g/10 minutes to about 120 g/10 minutes, in some examples 60 g/10 minutes to about 100 g/10 minutes. The melt flow rate can be measured using standard procedures known in the art, for example as described in ASTM D1238.

[0076] The acidic side groups may be in free acid form or may be in the form of an anion and associated with one or more counterions, typically metal counterions, e.g. a metal selected from the alkali metals, such as lithium, sodium and potassium, alkali earth metals, such as magnesium or calcium, and transition metals, such as zinc. The polymer having acidic side groups can be selected from resins such as copolymers of ethylene and an ethylenically unsaturated acid of either acrylic acid or methacrylic acid; and ionomers thereof, such as methacrylic acid and ethylene-acrylic or methacrylic acid copolymers which are at least partially neutralized with metal ions (e.g. Zn, Na, Li) such as SURLYN® ionomers. The polymer comprising acidic side groups can be a copolymer of ethylene and an ethylenically unsaturated acid of either acrylic or methacrylic acid, where the ethylenically unsaturated acid of either acrylic or methacrylic acid constitute from 5 wt.% to about 25 wt.% of the copolymer, in some examples from 10 wt.% to about 20 wt.% of the copolymer.

[0077] The resin may comprise a copolymer of an alkylene monomer and a monomer having acidic side groups. In some examples, the alkylene monomer may be selected from ethylene and propylene. In some examples, the monomer having acidic

side groups may be selected from methacrylic acid and acrylic acid. In some examples, the resin may comprise a copolymer of ethylene and a monomer selected from methacrylic acid and acrylic acid.

[0078] The resin may comprise two different polymers having acidic side groups. The two polymers having acidic side groups may have different acidities, which may fall within the ranges mentioned above. The resin may comprise a first polymer having acidic side groups that has an acidity of from 50 mg KOH/g to 110 mg KOH/g and a second polymer having acidic side groups that has an acidity of 110 mg KOH/g to 130 mg KOH/g.

[0079] The resin may comprise two different polymers having acidic side groups: a first polymer having acidic side groups that has a melt flow rate of about 10 g/10 minutes to about 50 g/10 minutes and an acidity of from 50 mg KOH/g to 110 mg KOH/g, and a second polymer having acidic side groups that has a melt flow rate of about 50 g/10 minutes to about 120 g/10 minutes and an acidity of 110 mg KOH/g to 130 mg KOH/g. The first and second polymers may be absent of ester groups.

[0080] The resin may comprise a copolymer of ethylene and acrylic acid and a copolymer of ethylene and methacrylic acid.

[0081] The resin may comprise two different polymers having acidic side groups: a first polymer that is a copolymer of ethylene (e.g. 92 to 85 wt%, in some examples about 89 wt%) and acrylic or methacrylic acid (e.g. 8 to 15 wt%, in some examples about 11 wt%) having a melt flow rate of 80 to 110 g/10 minutes and a second polymer that is a copolymer of ethylene (e.g. about 80 to 92 wt%, in some examples about 85 wt%) and acrylic acid (e.g. about 18 to 12 wt%, in some examples about 15 wt %), having a melt viscosity lower than that of the first polymer, the second polymer for example having a melt viscosity of 15000 poise or less, in some examples a melt viscosity of 10000 poise or less, in some examples 1000 poise or less, in some examples 100 poise or less, in some examples 50 poise or less, in some examples 10 poise or less. Melt viscosity can be measured using standard techniques. The melt viscosity can be measured using a rheometer, e.g. a commercially available AR-2000 Rheometer from Thermal Analysis Instruments, using the geometry of: 25mm steel plate-standard steel parallel plate, and finding the plate over plate rheometry isotherm at 120°C, 0.01 Hz shear rate.

[0082] In any of the resins mentioned above, the ratio of the first polymer having acidic side groups to the second polymer having acidic side groups can be from about

10:1 to about 2:1. In another example, the ratio can be from about 6:1 to about 3:1, in some examples about 4:1.

[0083] The resin may comprise a polymer having a melt viscosity of 15000 poise or less, in some examples a melt viscosity of 10000 poise or less, in some examples 1000 poise or less, in some examples 100 poise or less, in some examples 50 poise or less, in some examples 10 poise or less; said polymer may be a polymer having acidic side groups as described herein. The resin may comprise a first polymer having a melt viscosity of 15000 poise or more, in some examples 20000 poise or more, in some examples 50000 poise or more, in some examples 70000 poise or more; and in some examples, the resin may comprise a second polymer having a melt viscosity less than the first polymer, in some examples a melt viscosity of 15000 poise or less, in some examples a melt viscosity of 10000 poise or less, in some examples 1000 poise or less, in some examples 100 poise or less, in some examples 50 poise or less, in some examples 10 poise or less. The resin may comprise a first polymer having a melt viscosity of more than 60000 poise, in some examples from 60000 poise to 100000 poise, in some examples from 65000 poise to 85000 poise; a second polymer having a melt viscosity of from 15000 poise to 40000 poise, in some examples 20000 poise to 30000 poise, and a third polymer having a melt viscosity of 15000 poise or less, in some examples a melt viscosity of 10000 poise or less, in some examples 1000 poise or less, in some examples 100 poise or less, in some examples 50 poise or less, in some examples 10 poise or less; an example of the first polymer is Nucrel 960 (from DuPont), an example of the second polymer is Nucrel 699 (from DuPont), and an example of the third polymer is AC-5120 (from Honeywell). In some examples, the resin may comprise a first polymer having a melt viscosity of from 15000 poise to 40000 poise, in some examples 20000 poise to 30000 poise, and a second polymer having a melt viscosity of 15000 poise or less, in some examples a melt viscosity of 10000 poise or less, in some examples 1000 poise or less, in some examples 100 poise or less, in some examples 50 poise or less, in some examples 10 poise or less; an example of the first polymer is Nucrel 699 (from DuPont), and an example of the second polymer is AC-5120 (from Honeywell). The first, second and third polymers may be polymers having acidic side groups as described herein. The melt viscosity can be measured using a rheometer, e.g. a commercially available AR-2000 Rheometer from Thermal Analysis Instruments, using the geometry of: 25mm steel plate-standard steel parallel plate, and finding the plate over plate rheometry isotherm at 120°C, 0.01 Hz shear rate.

[0084] If the resin comprises a single type of resin polymer, the resin polymer (excluding any other components of the electrostatic ink composition) may have a melt viscosity of 6000 poise or more, in some examples a melt viscosity of 8000 poise or more, in some examples a melt viscosity of 10000 poise or more, in some examples a melt viscosity of 12000 poise or more. If the resin comprises a plurality of polymers all the polymers of the resin may together form a mixture (excluding any other components of the electrostatic ink composition) that has a melt viscosity of 6000 poise or more, in some examples a melt viscosity of 8000 poise or more, in some examples a melt viscosity of 10000 poise or more, in some examples a melt viscosity of 12000 poise or more. Melt viscosity can be measured using standard techniques. The melt viscosity can be measured using a rheometer, e.g. a commercially available AR-2000 Rheometer from Thermal Analysis Instruments, using the geometry of: 25mm steel plate-standard steel parallel plate, and finding the plate over plate rheometry isotherm at 120°C, 0.01 Hz shear rate.

[0085] The resin may comprise two different polymers having acidic side groups that are selected from copolymers of ethylene and an ethylenically unsaturated acid of either methacrylic acid or acrylic acid; and ionomers thereof, such as methacrylic acid and ethylene-acrylic or methacrylic acid copolymers which are at least partially neutralized with metal ions (e.g. Zn, Na, Li) such as SURLYN ® ionomers. The resin may comprise (i) a first polymer that is a copolymer of ethylene and an ethylenically unsaturated acid of either acrylic acid and methacrylic acid, wherein the ethylenically unsaturated acid of either acrylic or methacrylic acid constitutes from 8 wt% to about 16 wt% of the copolymer, in some examples 10 wt% to 16 wt% of the copolymer; and (ii) a second polymer that is a copolymer of ethylene and an ethylenically unsaturated acid of either acrylic acid and methacrylic acid, wherein the ethylenically unsaturated acid of either acrylic or methacrylic acid constitutes from 12 wt% to about 30 wt% of the copolymer, in some examples from 14 wt% to about 20 wt% of the copolymer, in some examples from 16 wt% to about 20 wt% of the copolymer in some examples from 17 wt% to 19 wt% of the copolymer.

[0086] In an example, the resin constitutes about 5 to 90 %, in some examples about 5 to 80 % by weight of the total solids of the electrostatic ink composition. In another example, the resin constitutes about 10 to 60 % by weight of the total solids of the electrostatic ink composition. In another example, the resin constitutes about 15 to 40 % by weight of the total solids of the electrostatic ink composition. In another example, the

resin constitutes about 60 to 95 % by weight, in some examples from 80 to 90 % by weight, of the total solids of the electrostatic ink composition.

[0087] The resin may comprise a polymer having acidic side groups, as described above (which may be free of ester side groups), and a polymer having ester side groups. The polymer having ester side groups is, in some examples, a thermoplastic polymer. The polymer having ester side groups may further comprise acidic side groups. The polymer having ester side groups may be a copolymer of a monomer having ester side groups and a monomer having acidic side groups. The polymer may be a copolymer of a monomer having ester side groups, a monomer having acidic side groups, and a monomer absent of any acidic and ester side groups. The monomer having ester side groups may be a monomer selected from esterified acrylic acid or esterified methacrylic acid. The monomer having acidic side groups may be a monomer selected from acrylic or methacrylic acid. The monomer absent of any acidic and ester side groups may be an alkylene monomer, including, but not limited to, ethylene or propylene. The esterified acrylic acid or esterified methacrylic acid may, respectively, be an alkyl ester of acrylic acid or an alkyl ester of methacrylic acid. The alkyl group in the alkyl ester of acrylic or methacrylic acid may be an alkyl group having 1 to 30 carbons, in some examples 1 to 20 carbons, in some examples 1 to 10 carbons; in some examples selected from methyl, ethyl, iso-propyl, n-propyl, t-butyl, iso-butyl, n-butyl and pentyl.

[0088] The polymer having ester side groups may be a copolymer of a first monomer having ester side groups, a second monomer having acidic side groups and a third monomer which is an alkylene monomer absent of any acidic and ester side groups. The polymer having ester side groups may be a copolymer of (i) a first monomer having ester side groups selected from esterified acrylic acid or esterified methacrylic acid, in some examples an alkyl ester of acrylic or methacrylic acid, (ii) a second monomer having acidic side groups selected from acrylic or methacrylic acid and (iii) a third monomer which is an alkylene monomer selected from ethylene and propylene. The first monomer may constitute 1 to 50 % by weight of the copolymer, in some examples 5 to 40 % by weight, in some examples 5 to 20 % by weight of the copolymer, in some examples 5 to 15 % by weight of the copolymer. The second monomer may constitute 1 to 50 % by weight of the copolymer, in some examples 5 to 40 % by weight of the copolymer, in some examples 5 to 20 % by weight of the copolymer, in some examples 5 to 15 % by weight of the copolymer. In an example, the first monomer constitutes 5 to 40 % by weight of the copolymer, the second monomer constitutes 5 to 40 % by weight of the

copolymer, and with the third monomer constituting the remaining weight of the copolymer. In an example, the first monomer constitutes 5 to 15 % by weight of the copolymer, the second monomer constitutes 5 to 15 % by weight of the copolymer, with the third monomer constituting the remaining weight of the copolymer. In an example, the first monomer constitutes 8 to 12 % by weight of the copolymer, the second monomer constitutes 8 to 12 % by weight of the copolymer, with the third monomer constituting the remaining weight of the copolymer. In an example, the first monomer constitutes about 10 % by weight of the copolymer, the second monomer constitutes about 10 % by weight of the copolymer, and with the third monomer constituting the remaining weight of the copolymer. The polymer having ester side groups may be selected from the Bynel ® class of monomer, including Bynel 2022 and Bynel 2002, which are available from DuPont ®.

[0089] The polymer having ester side groups may constitute 1% or more by weight of the total amount of the resin polymers in the resin, e.g. the total amount of the polymer or polymers having acidic side groups and polymer having ester side groups. The polymer having ester side groups may constitute 5% or more by weight of the total amount of the resin polymers in the resin, in some examples 8% or more by weight of the total amount of the resin polymers in the resin, in some examples 10% or more by weight of the total amount of the resin polymers in the resin, in some examples 15% or more by weight of the total amount of the resin polymers in the resin, in some examples 20% or more by weight of the total amount of the resin polymers in the resin, in some examples 25% or more by weight of the total amount of the resin polymers in the resin, in some examples 30% or more by weight of the total amount of the resin polymers in the resin, in some examples 35% or more by weight of the total amount of the resin polymers in the resin. The polymer having ester side groups may constitute from 5% to 50% by weight of the total amount of the resin polymers in the resin, in some examples 10% to 40% by weight of the total amount of the resin polymers in the resin, in some examples 15% to 30% by weight of the total amount of the polymers in the resin.

[0090] The polymer having ester side groups may have an acidity of 50 mg KOH/g or more, in some examples an acidity of 60 mg KOH/g or more, in some examples an acidity of 70 mg KOH/g or more, in some examples an acidity of 80 mg KOH/g or more. The polymer having ester side groups may have an acidity of 100 mg KOH/g or less, in some examples 90 mg KOH/g or less. The polymer having ester side groups may have

an acidity of 60 mg KOH/g to 90 mg KOH/g, in some examples 70 mg KOH/g to 80 mg KOH/g.

[0091] The polymer having ester side groups may have a melt flow rate of about 10 g/10 minutes to about 120 g/10 minutes, in some examples about 10 g/10 minutes to about 50 g/10 minutes, in some examples about 20 g/10 minutes to about 40 g/10 minutes, in some examples about 25 g/10 minutes to about 35 g/10 minutes.

[0092] In an example, the polymer or polymers of the resin can be selected from the Nucrel family of toners (e.g. Nucrel 403™, Nucrel 407™, Nucrel 609HS™, Nucrel 908HS™, Nucrel 1202HC™, Nucrel 30707™, Nucrel 1214™, Nucrel 903™, Nucrel 3990™, Nucrel 910™, Nucrel 925™, Nucrel 699™, Nucrel 599™, Nucrel 960™, Nucrel RX 76™, Nucrel 2806™, Bynell 2002, Bynell 2014, and Bynell 2020 (sold by E. I. du PONT)), the Aclyn family of toners (e.g. Aclyn 201 , Aclyn 246, Aclyn 285, and Aclyn 295), AC-5120 and AC 580 (sold by Honeywell), and the Lotader family of toners (e.g. Lotader 2210, Lotader, 3430, and Lotader 8200 (sold by Arkema)).

[0093] In some examples, the resin may constitute 5% to 99 % by weight of the total solids in the electrostatic ink composition, in some examples 50 % to 90 % by weight of the total solids of the electrostatic ink composition, in some examples 70 % to 90 % by weight of the total solids of the electrostatic ink composition.

Colorant

[0094] In some examples, the chargeable particles comprise a colorant. In some examples, the colorant may be a dye or pigment.

[0095] In some examples, the liquid electrostatic ink composition may be a white liquid electrostatic ink composition. In some examples, the liquid electrostatic ink composition comprises a white pigment.

[0096] The liquid electrostatic ink composition may substantially lack or lack a colorant. The liquid electrostatic ink composition may be a transparent liquid electrostatic ink composition. In some examples, the transparent liquid electrostatic ink composition does not contain any colorant, or substantially lacks colorant and thus is a colorant-free composition or substantially colorant-free composition. The transparent liquid electrostatic ink composition may otherwise be termed a colourless liquid electrostatic ink composition or a colourless varnish for liquid electrostatic printing. In some examples, substantially lacks may indicate that the transparent liquid electrostatic ink composition comprises 5 wt.% solids or less of colorant, in some examples, 3 wt.% solids or less of

colorant, in some examples, 1 wt.% solids or less of colorant. “Colorant” may be a material that imparts a colour to the ink composition. As used herein, “colorant” includes pigments and dyes, such as those that impart colours, such as black, magenta, cyan, yellow and white to an ink. As used herein, “pigment” generally includes pigment colorants, magnetic particles, aluminas, silicas, and/or other ceramics or organometallics. Thus, though the present description primarily exemplifies the use of pigment colorants, the term “pigment” can be used more generally to describe not only pigment colorants, but also other pigments such as organometallics, ferrites, ceramics, and so forth.

[0097] The colorant can be any colorant compatible with the carrier liquid and useful for electrostatic printing. For example, the colorant may be present as pigment particles, or may comprise a resin as described herein and a pigment. The pigments can be any of those standardly used in the art. In some examples, the colorant is selected from a cyan pigment, a magenta pigment, a yellow pigment and a black pigment. For example, pigments by Hoechst including Permanent Yellow DHG, Permanent Yellow GR, Permanent Yellow G, Permanent Yellow NCG-71, Permanent Yellow GG, Hansa Yellow RA, Hansa Brilliant Yellow 5GX-02, Hansa Yellow X, NOVAPERM® YELLOW HR, NOVAPERM® YELLOW FGL, Hansa Brilliant Yellow 10GX, Permanent Yellow G3R-01, HOSTAPERM® YELLOW H4G, HOSTAPERM® YELLOW H3G, HOSTAPERM® ORANGE GR, HOSTAPERM® SCARLET GO, Permanent Rubine F6B; pigments by Sun Chemical including L74-1357 Yellow, L75-1331 Yellow, L75-2337 Yellow; pigments by Heubach including DALAMAR® YELLOW YT-858-D; pigments by Ciba-Geigy including CROMOPHTHAL® YELLOW 3 G, CROMOPHTHAL® YELLOW GR, CROMOPHTHAL® YELLOW 8 G, IRGAZINE® YELLOW 5GT, IRGALITE® RUBINE 4BL, MONASTRAL® MAGENTA, MONASTRAL® SCARLET, MONASTRAL® VIOLET, MONASTRAL® RED, MONASTRAL® VIOLET; pigments by BASF including LUMOGEN® LIGHT YELLOW, PALIOGEN® ORANGE, HELIOGEN® BLUE L 690 IF, HELIOGEN® BLUE TBD 7010, HELIOGEN® BLUE K 7090, HELIOGEN® BLUE L 710 IF, HELIOGEN® BLUE L 6470, HELIOGEN® GREEN K 8683, HELIOGEN® GREEN L 9140; pigments by Mobay including QUINDO® MAGENTA, INDOFAST® BRILLIANT SCARLET, QUINDO® RED 6700, QUINDO® RED 6713, INDOFAST® VIOLET; pigments by Cabot including Maroon B STERLING® NS BLACK, STERLING® NSX 76, MOGUL® L; pigments by DuPont including TIPURE® R-101; and pigments by Paul Uhlich including UHLICH® BK 8200. If the pigment is a white pigment, the pigment particle may be selected from the group consisting of TiO_2, calcium carbonate, zinc

oxide, and mixtures thereof. In some examples, the white pigment particle may comprise an alumina-TiO_2 pigment.

[0098] The colorant or pigment may be present in the liquid electrostatic ink composition in an amount of from 10 wt.% to 80 wt.% of the total amount of resin and colorant, in some examples, 15 wt.% to 80 wt.%, in some examples 15 wt.% to 60 wt.%, in some examples, 15 wt.% to 50 wt.%, in some examples, 15 wt.% to 40 wt.%, in some examples, 15 wt.% to 30 wt.% of the total amount of resin and colorant. In some examples, the colorant or pigment particle may be present in the liquid electrostatic ink in an amount of at least 50 wt.% of the total amount of resin and colorant or pigment, for example at least 55 wt.% of the total amount of resin and colorant or pigment.

Charge director

[0099] In some examples, the liquid electrostatic ink composition further includes a charge director. The charge director may be added to a liquid electrostatic ink composition in order to impart and/or maintain sufficient electrostatic charge on the ink particles. In some examples, the charge director may comprise ionic compounds, particularly metal salts of fatty acids, metal salts of sulfo-succinates, metal salts of oxyphosphates, metal salts of alkyl-benzenesulfonic acid, metal salts of aromatic carboxylic acids or sulfonic acids, as well as zwitterionic and non-ionic compounds, such as polyoxyethylated alkylamines, lecithin, polyvinylpyrrolidone, organic acid esters of polyvalent alcohols, etc. The charge director can be selected from, but is not limited to, oil-soluble petroleum sulfonates (e.g. neutral Calcium Petronate™, neutral Barium Petronate™, and basic Barium Petronate™), polybutylene succinimides (e.g. OLOA™ 1200 and Amoco 575), and glyceride salts (e.g. sodium salts of phosphated mono- and diglycerides with unsaturated and saturated acid substituents), sulfonic acid salts including, but not limited to, barium, sodium, calcium, and aluminum salts of sulfonic acid. The sulfonic acids may include, but are not limited to, alkyl sulfonic acids, aryl sulfonic acids, and sulfonic acids of alkyl succinates. The charge director can impart a negative charge or a positive charge on the resin-containing particles of an electrostatic ink composition.

[00100] The charge director may be added in order to impart and/or maintain sufficient electrostatic charge on the ink particles, which may be particles comprising the thermoplastic resin.

[00101] In some examples, the liquid electrostatic ink composition comprises a charge director comprising a simple salt. The ions constructing the simple salts are all hydrophilic. The simple salt may include a cation selected from the group consisting of Mg, Ca, Ba, NH_4, tert-butyl ammonium, Li^+, and Al^{3+}, or from any sub-group thereof. The simple salt may include an anion selected from the group consisting of SO_4^{2-}, PO^{3-}, NO^{3-}, HPO_4^{2-}, CO_3^{2-}, acetate, trifluoroacetate (TFA), Cl^-, BF_4^-, F^-, ClO_4^-, and TiO_3^{4-} or from any sub-group thereof. The simple salt may be selected from $CaCO_3$, Ba_2TiO_3, $Al_2(SO_4)$, $Al(NO_3)_3$, $Ca_3(PO_4)_2$, $BaSO_4$, $BaHPO_4$, $Ba_2(PO_4)_3$, $CaSO_4$, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, NH_4OAc, tert- butyl ammonium bromide, NH_4NO_3, LiTFA, $Al_2(SO_4)3$, $LiClO_4$ and $LiBF_4$, or any sub-group thereof.

[00102] In some examples, the liquid electrostatic ink composition comprises a charge director comprising a sulfosuccinate salt of the general formula MA_n, wherein M is a metal, n is the valence of M, and A is an ion of the general formula (I): $[R^1\text{-}O\text{-}C(O)CH_2CH(SO_3^-)C(O)\text{-}O\text{-}R^2]$, wherein each of R^1 and R^2 is an alkyl group. In some examples each of R^1 and R^2 is an aliphatic alkyl group. In some examples, each of R^1 and R^2 independently is a C6-25 alkyl. In some examples, said aliphatic alkyl group is linear. In some examples, said aliphatic alkyl group is branched. In some examples, said aliphatic alkyl group includes a linear chain of more than 6 carbon atoms. In some examples, R^1 and R^2 are the same. In some examples, at least one of R^1 and R^2 is $C_{13}H_{27}$. In some examples, M is Na, K, Cs, Ca, or Ba.

[00103] In some examples, the charge director comprises at least one micelle forming salt and nanoparticles of a simple salt as described above. The simple salts are salts that do not form micelles by themselves, although they may form a core for micelles with a micelle forming salt. The sulfosuccinate salt of the general formula MA_n is an example of a micelle forming salt. The charge director may be substantially free of an acid of the general formula HA, where A is as described above. The charge director may include micelles of said sulfosuccinate salt enclosing at least some of the nanoparticles of the simple salt. The charge director may include at least some nanoparticles of the simple salt having a size of 200 nm or less, and/or in some examples 2 nm or more.

[00104] The charge director may include one of, some of or all of (i) soya lecithin, (ii) a barium sulfonate salt, such as basic barium petronate (BBP), and (iii) an isopropyl amine sulfonate salt. Basic barium petronate is a barium sulfonate salt of a 21-26 carbon atom hydrocarbon alkyl, and can be obtained, for example, from Chemtura. An example

isopropyl amine sulphonate salt is dodecyl benzene sulfonic acid isopropyl amine, which is available from Croda.

[00105] In some examples, the charge director constitutes about 0.001% to 20% by weight, in some examples 0.01% to 20% by weight, in some examples 0.01% to 10% by weight, in some examples 0.01% to 5% by weight of the total solids of a liquid electrostatic ink composition. In some examples, the charge director constitutes about 1% to 4% by weight of the total solids of the liquid electrostatic ink composition, in some examples 2% to 4% by weight of the total solids of the electrostatic ink composition.

[00106] In some examples, the charge director is present in an amount sufficient to achieve a particle conductivity of 200 pmho/cm or less, in some examples, 190 pmho/cm or less, in some examples, 180 pmho/cm or less, in some examples, 170 pmho/cm or less, in some examples, 160 pmho/cm or less, in some examples, 150 pmho/cm or less, in some examples, 140 pmho/cm or less, in some examples, 130 pmho/cm or less, in some examples, 120 pmho/cm or less, in some examples, 110 pmho/cm or less, in some examples, about 100 pmho/cm. In some examples, the charge director is present in an amount sufficient to achieve a particle conductivity of 50 pmho/cm or more, in some examples, 60 pmho/cm or more, in some examples, 70 pmho/cm or more, in some examples, 80 pmho/cm or more, in some examples, 90 pmho/cm or more, in some examples, about 100 pmho/cm. In some examples, the charge director is present in an amount sufficient to achieve a particle conductivity of 50 pmho/cm to 200 pmho/cm, in some examples, 60 pmho/cm to 190 pmho/cm, in some examples, 50 pmho/cm to 180 pmho/cm, in some examples, 60 pmho/cm to 170 pmho/cm, in some examples, 70 pmho/cm to 160 pmho/cm, in some examples, 80 pmho/cm to 150 pmho/cm, in some examples, 70 pmho/cm to 140 pmho/cm, in some examples, 80 pmho/cm to 130 pmho/cm, in some examples, 90 pmho/cm to 120 pmho/cm, in some examples, 90 pmho/cm to 110 pmho/cm, in some examples, 100 pmho/cm to 110 pmho/cm, in some examples, 90 pmho/cm to 100 pmho/cm.

[00107] In some examples, the charge director is present in an amount of from 3 mg/g to 50 mg/g, in some examples from 3 mg/g to 45 mg/g, in some examples from 10 mg/g to 40 mg/g, in some examples from 5 mg/g to 35 mg/g, in some examples, 20 mg/g to 35 mg/g, in some examples, 22 mg/g to 34 mg/g (where mg/g indicates mg per gram of solids of the liquid electrostatic ink composition).

Charge Adjuvant

[00108] In some examples, the liquid electrostatic ink composition includes a charge adjuvant. A charge adjuvant may promote charging of the particles when a charge director is present. The method as described herein may involve adding a charge adjuvant at any stage. The charge adjuvant can include, for example, barium petronate, calcium petronate, Co salts of naphthenic acid, Ca salts of naphthenic acid, Cu salts of naphthenic acid, Mn salts of naphthenic acid, Ni salts of naphthenic acid, Zn salts of naphthenic acid, Fe salts of naphthenic acid, Ba salts of stearic acid, Co salts of stearic acid, Pb salts of stearic acid, Zn salts of stearic acid, Al salts of stearic acid, Zn salts of stearic acid, Cu salts of stearic acid, Pb salts of stearic acid, Fe salts of stearic acid, metal carboxylates (e.g., Al tristearate, Al octanoate, Li heptanoate, Fe stearate, Fe distearate, Ba stearate, Cr stearate, Mg octanoate, Ca stearate, Fe naphthenate, Zn naphthenate, Mn heptanoate, Zn heptanoate, Ba octanoate, Al octanoate, Co octanoate, Mn octanoate, and Zn octanoate), Co lineolates, Mn lineolates, Pb lineolates, Zn lineolates, Ca oleates, Co oleates, Zn palmirate, Ca resinates, Co resinates, Mn resinates, Pb resinates, Zn resinates, AB diblock copolymers of 2-ethylhexyl methacrylate-co- methacrylic acid calcium and ammonium salts, copolymers of an alkyl acrylamidoglycolate alkyl ether (e.g., methyl acrylamidoglycolate methyl ether- co-vinyl acetate), or hydroxy bis(3,5-di-tert-butyl salicylic) aluminate monohydrate. In an example, the charge adjuvant is or includes aluminum di- or tristearate. In some examples, the charge adjuvant is VCA (aluminium stearate and aluminium palmitate, available from Sigma Aldrich).

[00109] The charge adjuvant may be present in an amount of about 0.1% to 5% by weight, in some examples about 0.1% to 1% by weight, in some examples about 0.3% to 0.8% by weight of the total solids of the liquid electrostatic ink composition, in some examples, about 1 wt.% to 5 wt.% of the total solids of the liquid electrostatic ink, in some examples about 1 wt.% to 3 wt.% of the total solids of the liquid electrostatic ink composition, in some examples about 1.5 wt.% to 2.5 wt.% of the total solids of the liquid electrostatic ink composition.

[00110] The charge adjuvant may be present in an amount of less than 5% by weight of total solids of the liquid electrostatic ink composition, in some examples in an amount of less than 4.5% by weight, in some examples in an amount of less than 4% by weight, in some examples in an amount of less than 3.5% by weight, in some examples in an

amount of less than 3% by weight, in some examples in an amount of less than 2.5% by weight of the total solids of the liquid electrostatic ink composition.

[00111] In some examples, the liquid electrostatic ink composition further includes, e.g. as a charge adjuvant, a salt of multivalent cation and a fatty acid anion. The salt of multivalent cation and a fatty acid anion can act as a charge adjuvant. The multivalent cation may, in some examples, be a divalent or a trivalent cation. In some examples, the multivalent cation is selected from Group 2, transition metals and Group 3 and Group 4 in the Periodic Table. In some examples, the multivalent cation includes a metal selected from Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al and Pb. In some examples, the multivalent cation is Al^{3+}. The fatty acid anion may be selected from a saturated or unsaturated fatty acid anion. The fatty acid anion may be selected from a C_8 to C_{26} fatty acid anion, in some examples a C_{14} to C_{22} fatty acid anion, in some examples a C_{16} to C_{20} fatty acid anion, in some examples a C_{17}, C_{18} or C_{19} fatty acid anion. In some examples, the fatty acid anion is selected from a caprylic acid anion, capric acid anion, lauric acid anion, myristic acid anion, palmitic acid anion, stearic acid anion, arachidic acid anion, behenic acid anion and cerotic acid anion.

[00112] The charge adjuvant, which may, for example, be or include a salt of a multivalent cation and a fatty acid anion, may be present in an amount of 0.1 wt.% to 5 wt.% of the total solids of the liquid electrostatic ink composition, in some examples in an amount of 0.1 wt.% to 3 wt.% of the total solids of the liquid electrostatic ink composition, in some examples about 1 wt.% to 3 wt.% of the total solids of the liquid electrostatic ink composition, in some examples about 1.5 wt.% to 2.5 wt.% of the total solids of the liquid electrostatic ink composition.

Other Additives

[00113] The liquid electrostatic ink composition may include another additive or a plurality of other additives. The other additive or plurality of other additives may be added at any stage of the method. The other additive or plurality of other additives may be selected from a charge adjuvant, a wax, a surfactant, viscosity modifiers, and compatibility additives. The wax may be an incompatible wax. As used herein, "incompatible wax" may refer to a wax that is incompatible with the resin. Specifically, the wax phase separates from the resin phase upon the cooling of the resin fused mixture on a print substrate during and after the transfer of the ink film to the print substrate, e.g. from an intermediate transfer member, which may be a heated blanket. In some examples, the LEP ink composition comprises silica, which may be added, for example,

to improve the durability of images produced using the LEP ink. The other additives may constitute 10 wt.% or less of the total solids of the electrostatic ink composition, in some examples 5 wt.% or less of the total solids of the electrostatic ink composition, in some examples 3 wt.% or less of the total solids of the electrostatic ink composition.

EXAMPLES

[00114] The following illustrates examples of the methods and other aspects described herein. Thus, these Examples should not be considered as limitations of the present disclosure, but are merely in place to teach how to make examples of the present disclosure.

Materials

Resins

[00115] Nucrel® 699: a copolymer of ethylene and methacrylic acid, made with nominally 11 wt.% methacrylic acid (available form DuPont).

[00116] AC-5120: a copolymer of ethylene and acrylic acid with an acrylic acid content of 15 wt.% (available from Honeywell).

Carrier Liquid

[00117] Isopar L™: an isoparaffinic oil comprising a mixture of C11-C13 isoalkanes (produced by Exxon Mobil™; CAS number 64742-48-9.

[00118] Tetrachloroethylene

Charge Adjuvant

[00119] VCA: an aluminium stearate (available from Fisher Scientific™).

Charge Director

[00120] NCD (natural charge director): KT (natural soya lecithin in phospholipids and fatty acids), BBP (basic barium petronate, i.e., a barium sulfonate salt of a 21-26 carbon hydrocarbon alkyl, available from Cemtura™), and GT (dodecyl benzene sulfonic acid isopropyl amine, supplied by Croda™). The composition being 6.6 wt.% KT, 9.8 wt.% BBP and 3.6 wt.% GT and balance (80 wt.%) Isopar L™.

Example 1

[00121] An 8 wt.% NVS magenta liquid electrophotographic (LEP) ink composition comprising tetrachloroethylene as the liquid carrier and chargeable particles comprising

a resin (a 4:1 mixture of Nucrel™ 699 and A-C 5120), magenta pigment and a charge adjuvant (VCA) was provided.

[00122] The LEP ink compositions was frozen by lowering the temperature to −45°C and reducing the pressure to 500 Torr overnight. The frozen LEP ink composition was then subjected to a negative pressure of 10 mTorr to 4 mTorr over 3 days, maintaining the temperature at −45°C throughout. The temperature was then increased slowly while maintaining the negative pressure of 4 mTorr, by using the following temperature profile: −20°C for 1 h, −5°C for 1 h, 10°C for 1 h; and 20°C for 4 h. This method produced a freeze-dried LEP ink composition. The non-volatile solids content of the freeze-dried LEP ink composition was determined to be 99 wt.%.

[00123] A portion of the freeze-dried LEP ink composition was re-dispersed in tetrachloroethylene by high shear mixing for 30 seconds. A second portion of the freeze-dried LEP ink composition was stored at room temperature and pressure for 2 months before being re-dispersed in tetrachloroethylene by high shear mixing for 10 seconds.

[00124] The volume-based particle size distribution of each re-dispersed LEP ink composition was determined by laser diffraction by using a Malven™ Mastersizer 2000. A comparison with the volume-based particle size distribution of the initial magenta LEP ink composition showed no measurable change in the particle size distribution (see Figure 3 a to c).

[00125] The particle charge of the re-dispersed magenta LEP ink composition was measured by measuring the response of the ink to high voltage. The electrical charging characteristics of the re-dispersed magenta LEP ink composition are compared with those of the initial magenta LEP ink composition in Figure 4 and show acceptable response to high voltage, indicating that the re-dispersed LEP ink composition can be charged by using a charge director such as NCD.

Example 2

[00126] An 8 wt.% NVS yellow LEP ink composition comprising tetrachloroethylene as the liquid carrier and chargeable particles comprising a resin (a 4:1 mixture of Nucrel™ 699 and A-C 5120), yellow pigment and a charge adjuvant (VCA) was provided.

[00127] The LEP ink compositions was frozen by lowering the temperature to −65°C at a pressure of 780 Torr overnight. The frozen LEP ink composition was then subjected to a negative pressure of 12 mTorr to 7 mTorr over 18 hours at a temperature of −60°C. The frozen LEP ink composition was then subjected to a negative pressure of 5 mTorr

over 2.5 days at a temperature of −55°C. The temperature was then increased slowly while maintaining the negative pressure of 5 mTorr, by using the following temperature profile: −20°C for 1 h, −5°C for 1 h, 10°C for 1 h; and 20°C for 4 h. This method produced a freeze-dried LEP ink composition. The non-volatile solids content of the freeze-dried LEP ink composition was determined to be 99 wt.%.

[00128] A portion of the freeze-dried LEP ink composition was re-dispersed in tetrachloroethylene by high shear mixing for 30 seconds. A second portion of the freeze-dried LEP ink composition was stored at room temperature and pressure for 2 months before being re-dispersed in Isopar L by high shear mixing for 10 or 20 seconds.

[00129] The volume-based particle size distribution of each re-dispersed LEP ink composition was determined by laser diffraction using a Malven™ Mastersizer 2000 (Figure 5 a and b).

[00130] While the method, apparatus and related aspects have been described with reference to certain examples, various modifications, changes, omissions, and substitutions can be made without departing from the spirit of the present disclosure. It is intended, therefore, that the method, apparatus and related aspects be limited only by the scope of the following claims and their equivalents. It should be noted that the above-mentioned examples illustrate rather than limit what is described herein, and that those skilled in the art will be able to design many alternative implementations without departing from the scope of the appended claims.

[00131] The word “comprising” does not exclude the presence of elements other than those listed in a claim, “a” or “an” does not exclude a plurality, and a single processor or other unit may fulfil the functions of several units recited in the claims.

[00132] The features of any dependent claim may be combined with the features of any of the independent claims or other dependent claims.

CLAIMS

1. A method comprising:

freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid;

subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and

increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles.

2. The method as claimed in claim 1, wherein the sublimation and desorption of carrier liquid reduces the amount of liquid present to an amount no more than 5% by weight.

3. The method as claimed in claim 1 wherein freezing comprises lowering the temperature of the LEP ink composition.

4. The method as claimed in claim 3, wherein the temperature is lowered to a temperature in the range −35°C to −75°C.

5. The method as claimed in claim 1, wherein the negative pressure is 20 mTorr or lower.

6. The method as claimed in claim 1, wherein increasing the temperature comprises increasing the temperature to 10°C or higher.

7. The method as claimed in claim 1, wherein freezing comprises lowering the temperature for at least 6 hours.

8. The method as claimed in claim 1, wherein the frozen ink composition is subjected to a negative pressure for at least 12 hours.

9. The method as claimed in claim 1 wherein:

the freezing comprises lowering the temperature to a temperature in the range −35°C to −75°C at a pressure of 600 mTorr to 800 mTorr for at least 6 hours;

subjecting the frozen LEP ink composition to a negative pressure comprises maintaining the ink composition at −35°C to −75°C and reducing the pressure to 20 mTorr or lower for at least 12 hours; and

increasing the temperature comprises increasing the temperature to at least 10°C over a period of at least 2 hours, and maintaining that temperature for at least 2 further hours.

10. The method as claimed in claim 1, wherein the method produces a freeze dried LEP ink composition and wherein the method further comprises:

adding the freeze dried LEP ink composition to a liquid carrier; and

agitating the liquid carrier containing the freeze dried LEP ink composition to disperse the chargeable particles in the liquid carrier to form a print ready LEP ink composition.

11. The method as claimed in claim 1, wherein the sublimation and desorption of carrier liquid reduces the amount of liquid present to an amount of from 0% to 5% by weight.

12. The method as claimed in claim 1, wherein the carrier liquid comprises a hydrocarbon, a halogenated hydrocarbon, or a mixture thereof.

13. A freeze dried LEP ink composition obtainable by a method comprising:

freezing an LEP ink composition comprising chargeable particles comprising a resin suspended in a carrier liquid;

subjecting the frozen LEP ink composition to a negative pressure to cause sublimation of the carrier liquid; and

increasing the temperature of the frozen ink composition under a negative pressure to cause desorption of carrier liquid from within the chargeable particles.

14. The freeze dried LEP ink composition as claimed in claim 13, wherein the composition comprises carrier liquid present in an amount no more than 5% by weight.

15. The freeze dried LEP ink composition as claimed in claim 13, wherein the carrier liquid comprises a hydrocarbon, a halogenated hydrocarbon or a mixture thereof.

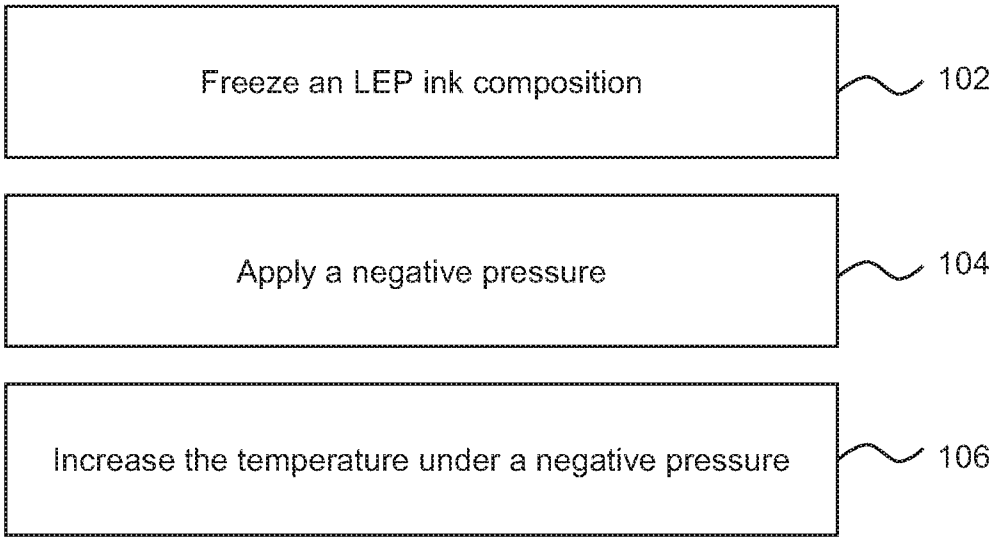


Figure 1

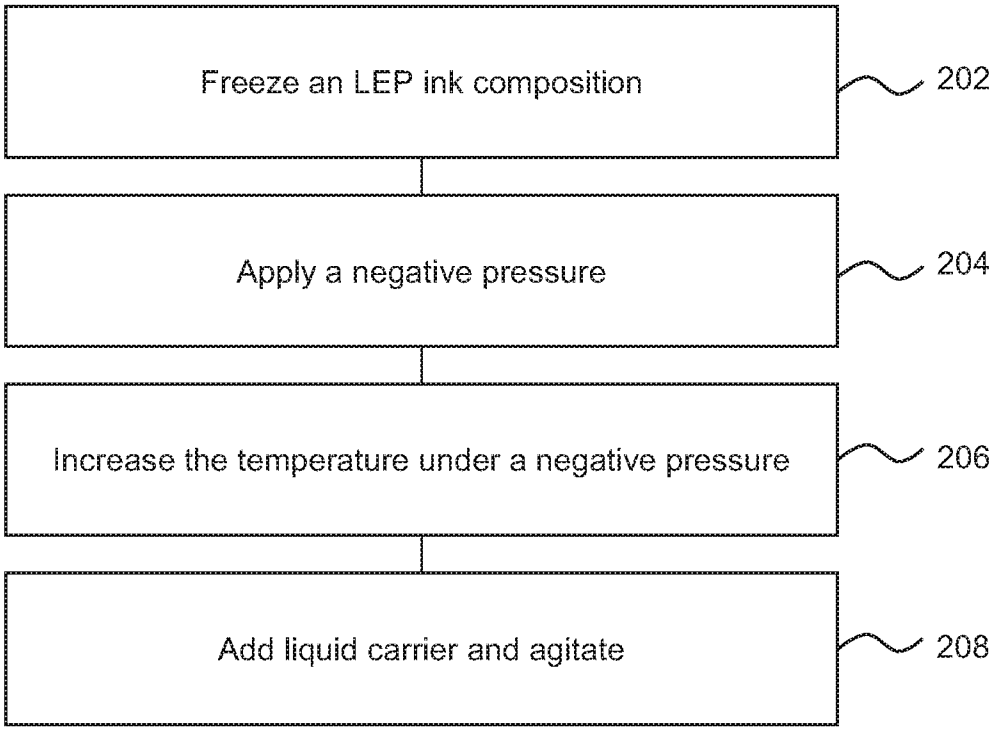
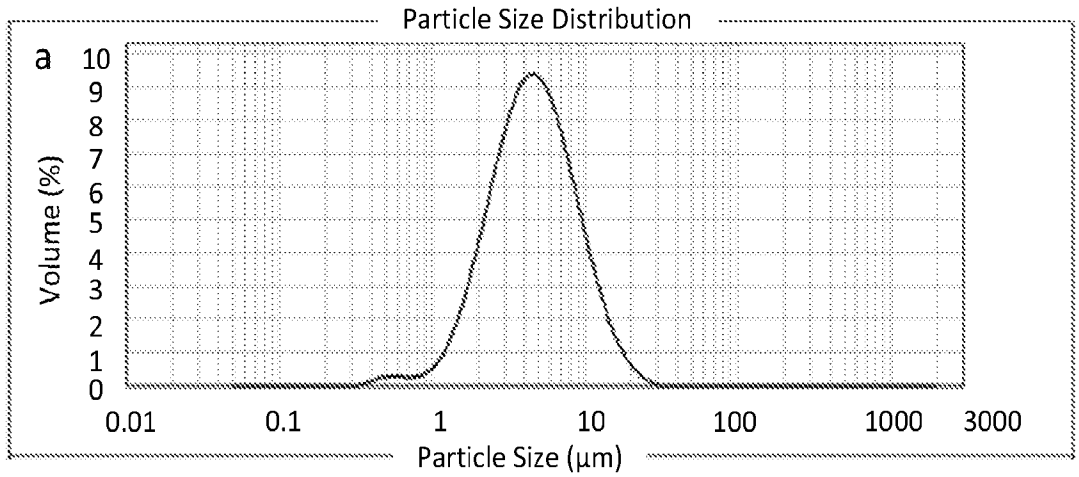
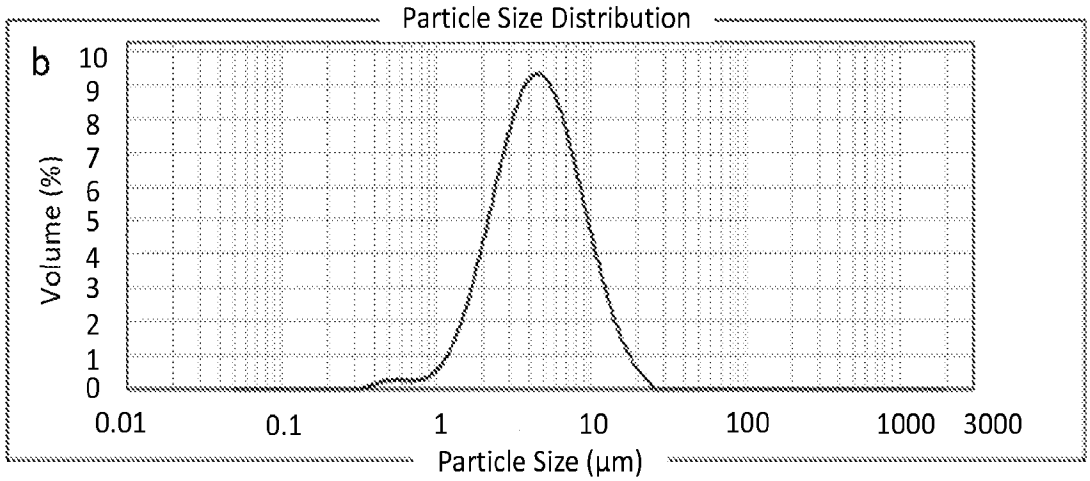


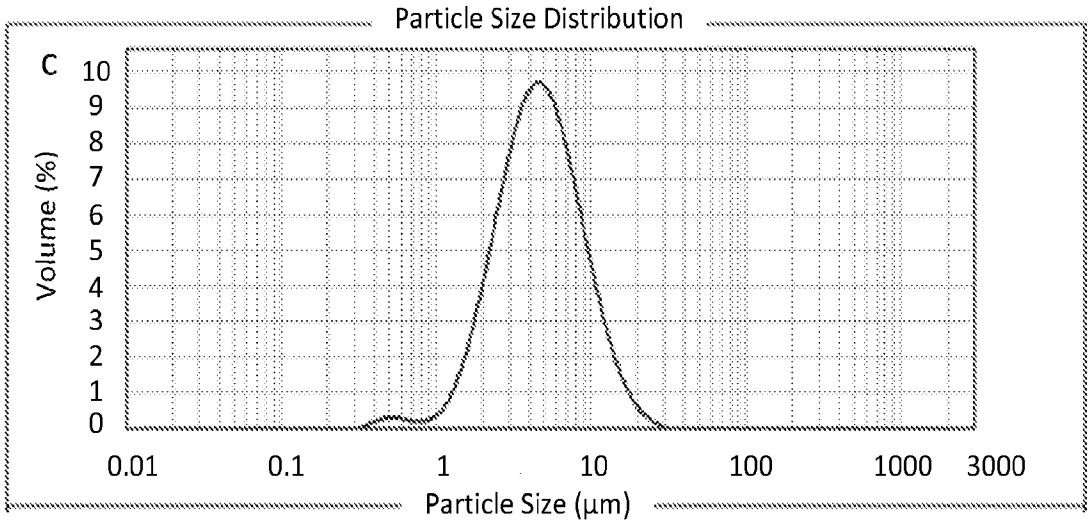
Figure 2



Nectar 8% mix - 30 sec



Nectar Magenta - 30 sec



Nectar pmix magenta - 10 sec

Figure 3

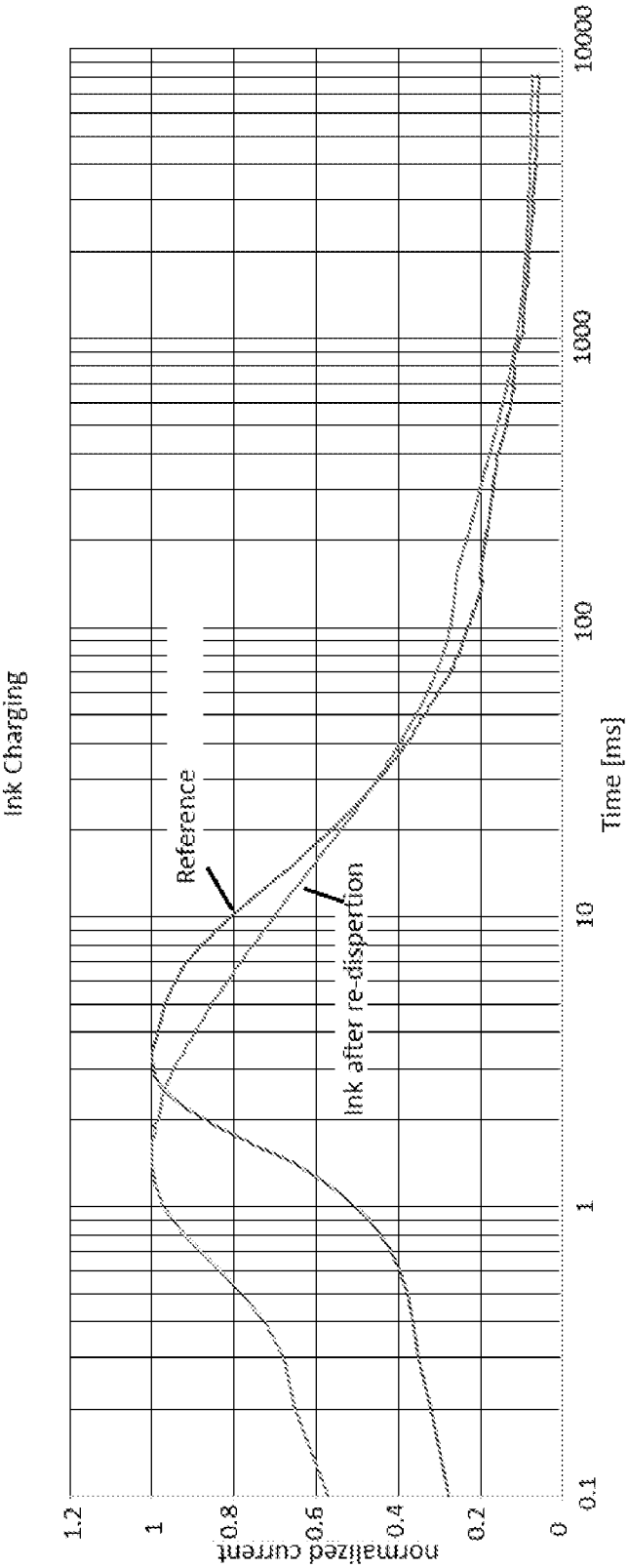
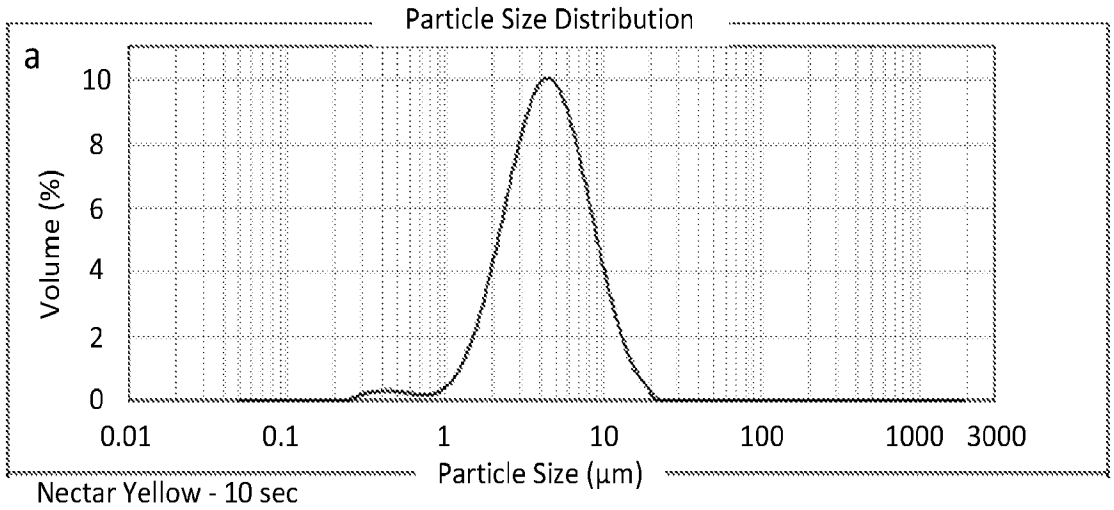

Ink Charging
Reference
Ink after re-dispersion
normalized current
1.2
1
0.8
0.6
0.4
0.2
0
0.1
1
10
100
1000
10000
Time [ms]

Figure 4


Particle Size Distribution
a
Volume (%)
10
8
6
4
2
0
0.01
0.1
1
10
100
1000
3000
Particle Size (µm)
Nectar Yellow - 10 sec

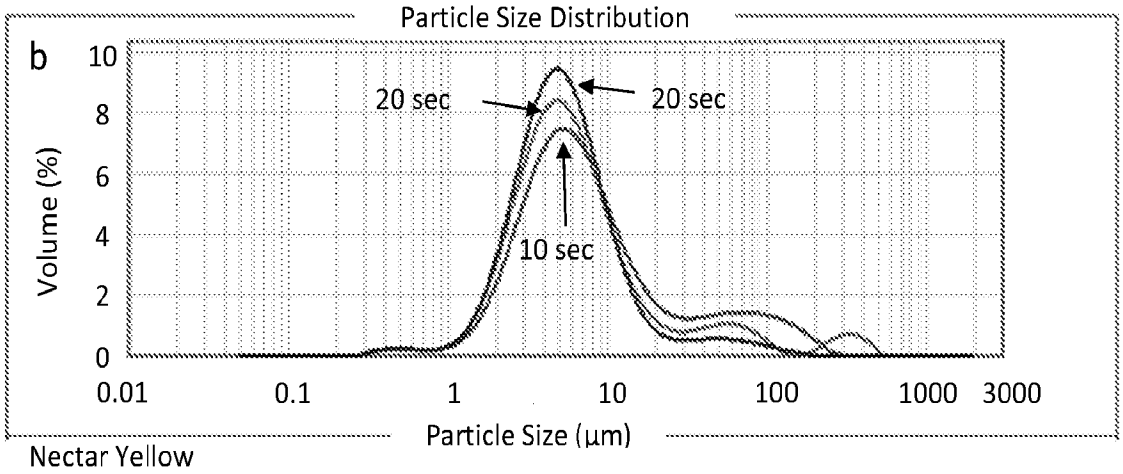

Particle Size Distribution
b
Volume (%)
10
8
6
4
2
0
20 sec
20 sec
10 sec
0.01
0.1
1
10
100
1000
3000
Particle Size (µm)
Nectar Yellow

Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 2020/042108

A. CLASSIFICATION OF SUBJECT MATTER

G03G 13/11 *(2006.01)*
C09D 11/0235 *(2014.01)*
C09D 11/10 *(2014.01)*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G03G 9/00, 9/12-9/135, 13/00, 13/10-13/11, C09D 11/00-11/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSearch (RUPTO internal), Espacenet, DWPI, PAJ, USPTO, CIPO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JPH 0328861 A (NEC CORP et al.) 07.02.1991, column 1-4	1-15
A	EP 1331520 A1 (FUJI XEROX CO LTD) 30.07.2003, abstract	1-15
A	US 2004/0225030 A1 (SAMSUNG ELECTRONICS CO LTD) 11.11.2004, abstract	1-15
A	US 5723252 A (XEROX CORPORATION) 03.03.1998, abstract	1-15

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 February 2021 (25.02.2021)	11 March 2021 (11.03.2021)

Name and mailing address of the ISA/RU:	Authorized officer
Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	A. Grigoryan Telephone No. (499) 240-25-91