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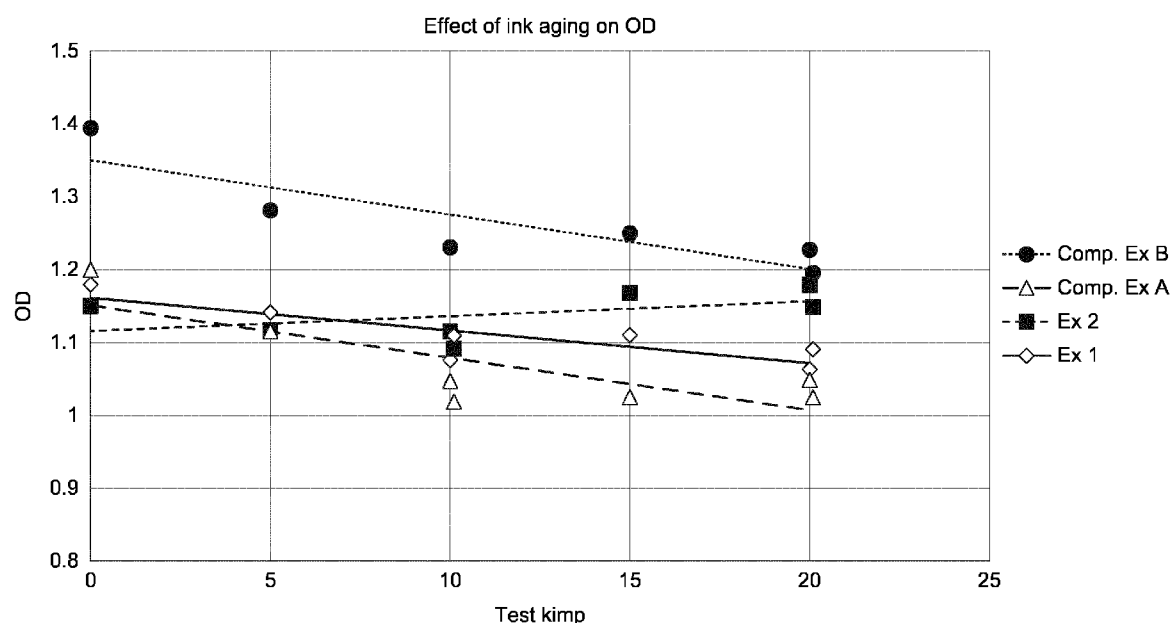


FIG. 1

(57) Abstract: The present disclosure relates to a method for producing a conductive liquid electrophotographic ink composition. The method comprises: heating a polymer resin in a carrier liquid to dissolve the polymer resin; adding conductive metallic pigment particles to the carrier liquid; and cooling the carrier liquid to effect precipitation of the polymer resin from the carrier liquid, such that a coating comprising the resin is formed on the conductive metallic pigment particles; wherein: I) the polymer resin comprises (i) a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, and (ii) an ionomer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, wherein at least a portion of the acrylic acid and/or methacrylic acid groups are neutralised with metal ions; and/or II) a charge adjuvant is included in the coating that is formed on the conductive metallic pigment particles.



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Electrophotographic Composition

BACKGROUND

[0001] An electrophotographic printing process involves creating an image on a photoconductive surface or photo imaging plate (PIP). The image that is formed on the photoconductive surface is a latent electrostatic image having image and background areas with different potentials. When an electrophotographic ink composition containing charged toner particles is brought into contact with the selectively charged photoconductive surface, the charged toner particles adhere to the image areas of the latent image while the background areas remain clean. The image is then transferred to a print substrate (e.g. paper) directly, or by first being transferred to an intermediate transfer member (e.g. a blanket) and then to the print substrate.

BRIEF DESCRIPTION OF THE FIGURES

[0002] Various features will be described, by way of example only, with reference to the following figures, in which:

[0003] Figures 1 and 2 show the effects of aging on the optical densities of images printed according to Example 4; and

[0004] Figure 3 shows the effect of aging on the non-volatile solids content (NVS%) on compositions tested in Example 5.

DETAILED DESCRIPTION

[0005] Before the present disclosure is disclosed and described, it is to be understood that this disclosure is not limited to the particular method steps and materials disclosed herein because such method steps and materials may vary. It is also to be understood that the terminology used herein is used for the purpose of describing particular examples. The terms are not intended to be limiting because the scope is intended to be limited by the appended claims and equivalents thereof.

[0006] 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.

[0007] As used herein, "carrier liquid," "carrier liquid," or "carrier vehicle" refers to liquid in which polymers, pigment particles, colorant, charge directors and other additives can be

dispersed to form a liquid electrostatic composition or electrophotographic composition. The carrier liquids may include a mixture of a variety of different agents, such as surfactants, co-solvents, viscosity modifiers, and/or other possible ingredients.

5 [0008] As used herein, "liquid electrostatic composition" or "liquid electrophotographic composition" generally refers to a composition that is typically suitable for use in an electrostatic printing process, sometimes termed an electrophotographic printing process.

[0009] As used herein, "co-polymer" refers to a polymer that is polymerized from at least two monomers.

10 [0010] 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.

[0011] Unless the context dictates otherwise, the terms "acrylic" and "acrylate" refer to any acrylic or acrylate compound. For example, the term "acrylic" includes acrylic and methacrylic compounds unless the context dictates otherwise. Similarly, the term
15 "acrylate" includes acrylate and methacrylate compounds unless the context dictates otherwise.

[0012] 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 print
20 substrate. As such, 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 electrophotographic printing" is a specific type of electrophotographic printing where a liquid ink is employed in the
25 electrophotographic process rather than a powder toner. An electrostatic printing process may involve subjecting the electrostatic ink composition to an electric field, e.g. an electric field having a field gradient of 50-400V/ μm , or more, in some examples 600-900V/ μm , or more, in some examples 1000 V/cm or more, or in some examples 1500 V/cm or more.

[0013] As used herein, "melt flow rate" generally refers to the extrusion rate of a resin
30 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 moulding. In the present disclosure, "melt flow rate" is measured per ASTM D1238-04c Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, as known in the
35 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 electrostatic composition.

5 **[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.

10 **[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 @
15 140°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
20 the melt viscosity for that polymer alone, in the absence of any of the other components of the electrostatic composition.

[0016] As used herein, "low field conductivity" refers to the electrical conductivity of an ink and is measured by applying a constant amplitude AC voltage to two parallel electrodes and monitoring the current via the liquid. Since the conductivity per definition is
25 proportional to the current and inversely proportional to the voltage inducing the current, the conductivity can be calculated by multiplying the current by a factor depending only on the constant values of the voltage amplitude and geometric parameters, i.e. electrode surface and distance between the electrodes. The present low field conductivities were measured at the following conditions: electrical field amplitude: 5-15 V/mm, frequency: 5-
30 15 Hz, and temperature: 23+/-2 C.

[0017] As used herein, "high field conductivity" refers to the maximum electrical conductivity of the ink measured at the following conditions: electrical field pulse—shape: rectangular; height: 1500 V/mm; duration: 8 sec, rise time: 1 ms or less; ripple: 10 V/mm or less; sampling frequency: 1000 per second; and temperature: 23+/-2 C.

35 **[0018]** As used herein, "particle conductivity" refers to the difference between the high field conductivity and the low field conductivity as defined above. The particle conductivity

is proportional to the ink particle properties; i.e., mobility and electrical charge created on the particles.

[0019] 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.

5 **[0020]** As used herein, "NVS" is an abbreviation of the term "non-volatile solids".

[0021] 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
10 the art to determine based on experience and the associated description herein.

[0022] 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
15 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.

[0023] Concentrations, amounts, and other numerical data may be expressed or presented in this disclosure 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
20 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 include individual
25 values and subranges 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.

30 **[0024]** As used in this disclosure, weight% (wt%) values are to be taken as referring to a weight-for-weight (w/w) percentage of solids in the composition, and not including the weight of any carrier liquid present.

[0025] Unless otherwise stated, any feature described herein can be combined with any aspect or any other feature described herein.

[0026] In an aspect, there is provided a method for producing a conductive liquid electrophotographic ink composition. The method comprises:

[0027] heating a polymer resin in a carrier liquid to dissolve the polymer resin;

[0028] adding conductive metallic pigment particles to the carrier liquid; and

5 **[0029]** cooling the carrier liquid to effect precipitation of the polymer resin from the carrier liquid, such that a coating comprising the resin is formed on the conductive metallic pigment particles; wherein:

[0030] I) the polymer resin comprises (i) a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, and (ii) an ionomer of an
10 alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, wherein at least a portion of the acrylic acid and/or methacrylic acid groups are neutralised with metal ions; and/or

[0031] II) a charge adjuvant is included in the coating that is formed on the conductive metallic pigment particles.

15 **[0032]** It has been found that conductive metallic pigment particles can be coated by precipitating resin over the metallic pigment particles. It has been found, however, the optical density of images printed using a liquid electrophotographic ink composition containing such coated pigment particles may decrease as more print impressions are made using the liquid electrophotographic ink composition stored in the printer. Without
20 wishing to be bound by any theory, this is now believed to be because of variations in the ratio of pigment to resin between coated pigment particles in the ink composition. Particles having relatively higher conductive metallic pigment contents may have a greater tendency to be transferred to the photo-imaging plate (PIP) because of their higher charge. This leaves particles with relatively lower conductive metallic pigment contents behind in the ink
25 storage unit. With time, particles having relatively lower conductive metallic pigment contents may accumulate in the ink storage units, leading to a decrease in optical density.

[0033] One way of addressing this may be to increase the voltage applied to develop the ink in order to improve transfer of the ink particles onto the photo-imaging plate (PIP). The present inventors, however, have found that particle conductivity can also have an
30 influence on long-term optical density stability. In particular, the present inventors have found that, by including an ionomer in the polymer resin and/or including a charge adjuvant in the coating, it may be possible to increase the particle conductivity of the coated conductive metallic pigment particles. This can improve the long-term optical density stability of the resulting images as, despite variations in the relative amounts of pigment
35 and resin in the particles, a greater proportion, if not all, of the particles will have sufficient charge to be effectively transferred onto the photo-imaging plate (PIP).

[0034] The particle conductivity of the coated conductive metallic pigment particles may be at least 100 pmho/cm, for example, at least 110 pmho/cm or at least 130 pmho/cm. In one example, the particle conductivity may be at least 150 pmho/cm, for instance, at least 160 pmho/cm or at least 180 pmho/cm. In another example, the particle conductivity may be at least 200 pmho/cm.

[0035] In another aspect there is provided a liquid electrophotographic ink composition comprising coated conductive metallic pigment particles dispersed in a carrier liquid, wherein the coated conductive metallic pigment particles are coated with a coating comprising particles of charge adjuvant dispersed within a polymer resin matrix.

Alternatively or additionally, the coated conductive metallic pigment particles are coated with a coating comprising a polymer resin, wherein the polymer resin comprises (i) a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, and (ii) an ionomer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, wherein at least a portion of the acrylic acid and/or methacrylic acid groups are neutralised with metal ions.

Conductive Metallic Pigment

[0036] The conductive metallic pigment, in the present disclosure, indicates an electrically conductive metallic pigment. The conductive metallic pigment comprises a metal. The metal may be a metal in elemental form or an alloy of two or more metals. The conductive metallic pigment may comprise a metal selected from aluminium, tin, a transition metal, and alloys of any one of more thereof. The transition metal may be selected from, for example, zinc, copper, silver, gold, nickel, palladium, platinum, and iron. Alloys that may be used include, but are not limited to, brass, bronze, steel and chromium. In one example, the conductive metallic pigment is formed of silver metal or a silver metal alloy.

[0037] The conductive metallic pigment may have any three-dimensional shape. In some examples, the conductive metallic pigment is in the form selected from a flake, a sphere, a rod, or approximations thereof. In the present disclosure, a flake may be a shape with a first dimension, which may be termed a thickness, less than the other two dimensions. In some examples, the flake has a thickness of at least 0.01 μm , in some examples a thickness of at least 0.05 μm , in some examples a thickness of at least 0.1 μm , in some examples a thickness of at least 0.15 μm , in some examples a thickness of at least 0.18 μm . In some examples, the flake has a thickness of 1 μm or less, in some examples a thickness of 0.8 μm or less, in some examples a thickness of 0.5 μm or less, in some examples a thickness of 0.4 μm or less, in some examples a thickness of 0.3 μm or less.

[0038] In some examples, the flake has a diameter, measured in a direction perpendicular to the thickness and excluding any coating on the flake, of at least 1 μm , in some examples a diameter of at least 2 μm , in some examples a diameter of at least 3 μm , in some examples a diameter of at least 4 μm , in some examples a diameter of at least 5 μm , in some examples a diameter of at least 6 μm , in some examples a diameter of at least 7 μm , in some examples a diameter of at least 8 μm . In some examples, the flake has a diameter, measured in a direction perpendicular to the thickness, of 50 μm or less, in some examples a diameter of 40 μm or less, in some examples a diameter of 30 μm or less, in some examples a diameter of 20 μm or less, in some examples a diameter of 15 μm or less.

[0039] In some examples, the conductive metallic pigment, excluding any coating thereon, has an aspect ratio of a diameter (measured in a direction perpendicular to the thickness) to its thickness of $n:1$, where n is at least 2, in some examples at least 5, in some examples at least 10, in some examples at least 20, in some examples at least 30, in some examples at least 35. In some examples, the conductive metallic pigment has an aspect ratio of a diameter (measured in a direction perpendicular to the thickness) to its thickness of $n:1$, where n is 100 or less, in some examples n is 80 or less, in some examples n is 70 or less, in some examples n is 60 or less, in some examples n is 50 or less.

[0040] Unless otherwise stated, the particle size of the pigment particle and the coated pigment particle is determined using laser diffraction on a Malvern Mastersizer 2000 according to the standard procedure as described in the operating manual.

[0041] The pigment particle may be present in the method and/or electrostatic ink composition in an amount of from 10 wt% to 80 wt% of the total amount of resin and pigment, 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 pigment. In some examples, the pigment particle may be present in the method and/or electrostatic ink composition in an amount of at least 50 wt% of the total amount of resin and pigment, for example at least 55 wt% of the total amount of resin and pigment.

[0042] In some examples, the conductive metallic pigments, excluding any coating thereon, constitute 10 % to 60% by weight of the solids in the electrostatic ink composition or composition resulting from the method, which may be an electrostatic ink composition. In some examples, the conductive metallic pigments, excluding any coating thereon, constitute 15 to 50% by weight, in some examples 20 to 45% by weight, in some examples 25 to 40 % by weight of the solids in the electrostatic ink composition or composition

resulting from the method, which may be an electrostatic ink composition. In some examples, the conductive metallic pigments, excluding any coating thereon, 30 to 35% by weight of the solids in the electrostatic ink composition or composition resulting from the method, which may be an electrostatic ink composition.

- 5 **[0043]** In some examples, the conductive metallic pigment particles, including any coating thereon, constitute 60 to 100 % by weight of the solids in the electrostatic ink composition or composition resulting from the method, for example 70 to 100 % by weight, for instance, 80 or 90 to 100 % by weight of the solids in the electrostatic ink composition or composition resulting from the method, which may be an electrostatic ink composition.

10 **Polymer Resin**

- [0044]** The polymer resin may comprise a thermoplastic polymer. In some examples, the polymer resin comprises a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid. The alkylene monomer may be ethylene or propylene. In one example, the polymer resin comprises a copolymer of ethylene and acrylic acid or methacrylic acid. In one example, the polymer resin comprises a copolymer of ethylene and methacrylic acid. The acrylic acid and/or methacrylic acid content of the copolymer may be 5 to 20 weight % based on the total weight of the copolymer. In one example, the polymer resin comprises a copolymer of ethylene and methacrylic acid, wherein the methacrylic acid content is 5 to 15 weight %, for instance, 10 weight %. A suitable copolymer is sold under the tradename Nucrel®599 by Dupont®.

- [0045]** The polymer resin may include (i) a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid as well as (ii) an ionomer. The polymer resin may comprise 50 to 95 weight % of the copolymer (i) and 5 to 50 weight % of the ionomer (ii) based on the total weight of the polymer resin. In one example, the polymer resin may comprise 70 to 90 weight % of the copolymer (i) and 10 to 30 weight % of the ionomer (ii) based on the total weight of the polymer resin. In one example, the polymer resin may comprise 75 to 85 weight % of the copolymer (i) and 15 to 25 weight % of the ionomer (ii) based on the total weight of the polymer resin. In one example, the polymer resin may comprise 80 to 85 weight % of the copolymer (i) and 15 to 20 weight % of the ionomer (ii) based on the total weight of the polymer resin.

- [0046]** The ionomer may be a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid with at least a portion of the acrylic acid and/or methacrylic acid groups neutralised by metal ions. The alkylene monomer may be ethylene or propylene. In one example, the ionomer may be a copolymer of ethylene and acrylic acid or methacrylic acid. In one example, the ionomer may be a copolymer of

ethylene and acrylic acid. Examples of metal ions include sodium, calcium, magnesium and zinc. In one example, 50 to 100% of the methacrylic acid and/or acrylic acid groups may be neutralised by metal ions. In one example, the ionomer may be a copolymer of ethylene and acrylic acid, wherein 50 to 100% of the acrylic acid groups are neutralised by metal ions. In one example, the ionomer may be a copolymer of ethylene and acrylic acid, wherein 80 to 100% of the acrylic acid groups are neutralised by metal ions. Suitable ionomers include those sold under the tradename AClyn® by Honeywell®. Examples include AClyn®201, AClyn®285 and AClyn®295.

[0047] By using an ionomer in the coating, the particle conductivity of the coated conductive metallic pigment particles can be increased. As discussed above, this can have a positive influence on optical density, for example, optical density stability. Furthermore, the polar domains within the ionomer may help the coating to wet the surface of the conductive metallic pigment particles, prevent agglomeration and improve dispersion of the particles in the ink composition.

[0048] Where an ionomer is used in the polymer resin, the nature and concentration of the ionomer may be adjusted to provide the coated conductive metallic pigment particles with e.g. the desired conductivity. The particle conductivity of the coated conductive metallic pigment particles may be at least 100 pmho/cm, for example, at least 110 pmho/cm or at least 130 pmho/cm. In one example, the particle conductivity may be at least 150 pmho/cm, for instance, at least 160 pmho/cm or at least 180 pmho/cm. In another example, the particle conductivity may be at least 200 pmho/cm.

[0049] In some examples, the polymer resin may include a polymer selected from ethylene or propylene acrylic acid co-polymers; ethylene or propylene methacrylic acid co-polymers; ethylene vinyl acetate co-polymers; co-polymers of ethylene or propylene (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%); co-polymers of ethylene (e.g. 80 wt% to 99.9 wt%), acrylic or methacrylic acid (e.g. 0.1 wt% to 20.0 wt%) and alkyl (e.g. C1 to C5) ester of methacrylic or acrylic acid (e.g. 0.1 wt% to 20 wt%); co-polymers of ethylene or propylene (e.g. 70 wt% to 99.9 wt%) and maleic anhydride (e.g. 0.1 wt% to 30 wt%); polyethylene; polystyrene; isotactic polypropylene (crystalline); co-polymers of ethylene ethylene ethyl acrylate; polyesters; polyvinyl toluene; polyamides; styrene/butadiene co-polymers; epoxy resins; acrylic resins (e.g. co-polymer of acrylic or methacrylic acid and at least one alkyl ester of acrylic or methacrylic acid wherein alkyl may have from 1 to about 20 carbon atoms, such as methyl methacrylate (e.g. 50% to 90%)/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.

[0050] The resin may comprise a polymer having acidic side groups. Examples of the polymer having acidic side groups will now be described. 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.

[0051] 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 70 g/10 minutes, in some examples about 60 g/10 minutes or less, 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 80 g/10 minutes or less, in some examples 70 g/10 minutes or less, in some examples 70 g/10 minutes or less, in some examples 60 g/10 minutes or less.

[0052] 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.

[0053] 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 sides groups can be selected from resins such as co-polymers 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 co-polymers 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 co-polymer 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 co-polymer, in some examples from 10 wt% to about 20 wt% of the co-polymer.

- 10 **[0054]** 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 10 mg KOH/g to 110 mg KOH/g, in some examples 20 mg KOH/g to 110 mg KOH/g, in some examples 30 mg KOH/g to 110 mg KOH/g, in some
15 examples 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.

- [0055]** 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 10 mg KOH/g to 110 mg KOH/g, in some
20 examples 20 mg KOH/g to 110 mg KOH/g, in some examples 30 mg KOH/g to 110 mg KOH/g, in some examples 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.

- 25 **[0056]** 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
30 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
35 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.

[0057] 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 co-polymer 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.

[0058] In any of the examples 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.

[0059] 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), and example of the second polymer is Nucrel 699 (from DuPont), and an example of the third polymer is AC-5120 or AC-5180 (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.

- 10 **[0060]** If the resin comprises a single type of polymer, the polymer (excluding any other components of the electrophotographic 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 electrophotographic 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.

- 25 **[0061]** 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.

[0062] 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 may be a thermoplastic polymer. The polymer having ester side groups may further comprise acidic side groups. The polymer having ester side groups may be a co-polymer of a monomer having ester side groups and a monomer having acidic side groups. The polymer may be a co-polymer 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.

[0063] The polymer having ester side groups may be a co-polymer 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 co-polymer 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 co-polymer, in some examples 5% to 40% by weight, in some examples 5% to 20% by weight of the co-polymer, in some examples 5% to 15% by weight of the co-polymer. The second monomer may constitute 1% to 50 % by weight of the co-polymer, in some examples 5% to 40% by weight of the co-polymer, in some examples 5% to 20% by weight of the co-polymer, in some examples 5% to 15% by weight of the co-polymer. The first monomer can constitute 5% to 40 % by weight of the co-polymer, the second monomer constitutes 5% to 40% by weight of the co-polymer, and with the third monomer constituting the remaining weight of the co-polymer. In some examples, the first monomer constitutes 5% to 15% by weight of the co-polymer, the second monomer constitutes 5% to 15% by weight of the co-polymer, with the third monomer constituting the remaining weight of the co-polymer. In some examples, the first monomer constitutes 8% to 12% by weight of the co-polymer, the second monomer

constitutes 8% to 12% by weight of the co-polymer, with the third monomer constituting the remaining weight of the co-polymer. In some examples, the first monomer constitutes about 10% by weight of the co-polymer, the second monomer constitutes about 10% by weight of the co-polymer, and with the third monomer constituting the remaining weight of the co-polymer. The polymer may be selected from the Bynel® class of monomer, including Bynel 2022 and Bynel 2002, which are available from DuPont®.

[0064] 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.

[0065] 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.

[0066] 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.

[0067] The polymer, polymers, co-polymer or co-polymers of the resin can in some examples 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, Bynell 2020 and Bynell 2022, (sold by E. I. du PONT)), the AC family of toners (e.g. AC-5120, AC-5180, AC-540, AC-580 (sold by Honeywell)), the Aclyn family of toners (e.g. Aclyn 201, Aclyn 246, Aclyn 285, and Aclyn 295), and the Lotader family of toners (e.g. Lotader 2210, Lotader, 3430, and Lotader 8200 (sold by Arkema)).

[0068] In an example, the resin constitutes about 5 to 90 %, in some examples about 5 to 70 %, by weight of any of the solids of the electrostatic ink composition. In another example, the resin constitutes about 10 to 60 % by weight of any of the solids of the electrostatic ink composition. In another example, the resin constitutes about 15 to 40 % by weight of any of the solids of the electrostatic ink composition. In another example, the resin constitutes about 60 to 95 % by weight, in some examples from 70 to 90 % by weight, in some examples 75 to 85 % by weight of the solids of the electrostatic ink composition.

[0069] The weight ratio of polymer resin to conductive metallic pigment particles may be 1:2 to 5:1, for example, 1:1 to 4:1 or 1.5: 1 to 3:1, for instance, 2:1.

Carrier Liquid

[0070] In some examples, the methods described produce coated pigment particles which are formed in and/or dispersed in a carrier liquid. Before application to the print substrate in the electrostatic printing process, the composition may be an electrostatic ink composition, which may be in dry form, for example in the form of flowable pigment particles coated with the thermoplastic resin. Alternatively, before application to the print substrate in the electrostatic printing process, the electrostatic ink composition may be in liquid form; and may comprise a carrier liquid in which is suspended conductive metallic pigment particles coated with the thermoplastic resin.

[0071] Generally, the carrier liquid acts as a reaction solvent in preparing the coated pigment particles, and can also act as a dispersing medium for the other components in the resulting electrostatic ink composition. In one example, the carrier liquid is a liquid which does not dissolve the polymer resin at room temperature. In one example, the carrier liquid is a liquid which dissolves the polymer resin at elevated temperatures. For example, the polymer resin may be soluble in the carrier liquid when heated to a temperature of at least 80 °C, for example 90 °C, for example 100 °C, for example 110 °C, for example 120 °C. For example, the carrier liquid can comprise or be a hydrocarbon, silicone oil, vegetable oil, etc. The carrier liquid can include, but is not limited to, an insulating, non-polar, non-aqueous liquid that can be used as a medium for toner particles. The carrier liquid can include compounds that have a resistivity in excess of about 10⁹

ohm-cm. The carrier liquid may have a dielectric constant below about 5, in some examples below about 3. The carrier liquid can include, but is not limited to, hydrocarbons. The hydrocarbon can include, but is not limited to, an aliphatic hydrocarbon, an isomerized aliphatic hydrocarbon, branched chain aliphatic hydrocarbons, aromatic hydrocarbons, and combinations thereof. Examples of the carrier liquids include, but are not limited to, aliphatic hydrocarbons, isoparaffinic compounds, paraffinic compounds, dearomatized hydrocarbon compounds, and the like. In particular, the carrier liquids can include, but are not limited to, 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™).

[0072] In the example in which the carrier liquid is acting as a solvent during preparation of the liquid electrophotographic ink composition comprising coated conductive metallic pigment particles, the carrier liquid can constitute about 20% to 99.5% by weight of the composition, in some examples 50% to 99.5% by weight of the composition in the step of coating the particles. In the example in which the carrier liquid is acting as a solvent during preparation of coated pigment particles, the carrier liquid may constitute about 40 to 90 % by weight of the composition in the step of coating the particles. In the example in which the carrier liquid is acting as a solvent during preparation of coated pigment particles, the carrier liquid may constitute about 60% to 80% by weight of the composition in the step of coating the particles. In the example in which the carrier liquid is acting as a solvent during preparation of coated pigment particles, the carrier liquid may constitute about 90% to 99.5% by weight of the composition, in some examples 95% to 99% by weight of the composition in the step of coating the particles.

[0073] Before printing, the carrier liquid can constitute about 20% to 99.5% by weight of the electrostatic ink composition, in some examples 50% to 99.5% by weight of the electrostatic ink composition. Before printing, the carrier liquid may constitute about 40 to 90 % by weight of the electrostatic ink composition. Before printing, the carrier liquid may constitute about 60% to 80% by weight of the electrostatic ink composition. Before printing,

the carrier liquid may constitute about 90% to 99.5% by weight of the electrostatic ink composition, in some examples 95% to 99% by weight of the electrostatic ink composition.

[0074] The ink, when printed on the print substrate, may be substantially free from carrier liquid. In an electrostatic printing process and/or afterwards, the carrier liquid may be removed, e.g. by an electrophoresis processes during printing and/or evaporation, such that substantially just solids are transferred to the print substrate. Substantially free from carrier liquid may indicate that the ink printed on the print substrate contains less than 5 wt% carrier liquid, in some examples, less than 2 wt% carrier liquid, in some examples less than 1 wt% carrier liquid, in some examples less than 0.5 wt% carrier liquid. In some examples, the ink printed on the print substrate is free from carrier liquid.

Charge Director

[0075] The liquid electrophotographic composition and/or the ink composition printed on the print substrate can comprise a charge director. The method as described here may involve adding a charge director at any stage. A charge director can be added to an electrostatic composition to impart a charge of a desired polarity and/or maintain sufficient electrostatic charge on the particles of an electrostatic ink composition. The charge director may comprise ionic compounds, including, but not limited to, 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 aluminium 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 (e.g. see WO 2007/130069). The charge director can impart a negative charge or a positive charge on the resin-coated conductive metallic pigment particles of an electrostatic ink composition.

[0076] The charge director can comprise a sulfosuccinate moiety of the general formula $[R_a-O-C(O)CH_2CH(SO_3^-)C(O)-O-R_b]$, where each of R_a and R_b is an alkyl group. In some examples, the charge director comprises nanoparticles of a simple salt and 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 $[R_a-O-C(O)CH_2CH(SO_3^-)C(O)-O-R_b]$, where each of R_a and R_b is an

alkyl group, or other charge directors as found in WO2007130069, which is incorporated herein by reference in its entirety. As described in WO2007130069, the sulfosuccinate salt of the general formula MA_n is an example of a micelle forming salt. The charge director may be substantially free or free of an acid of the general formula HA, where A is as described above. The charge director may comprise micelles of said sulfosuccinate salt enclosing at least some of the nanoparticles. The charge director may comprise at least some nanoparticles having a size of 200 nm or less, in some examples 2 nm or more. As described in WO2007130069, 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 ions constructing the simple salts are all hydrophilic. The simple salt may comprise a cation selected from Mg, Ca, Ba, NH_4 , tert-butyl ammonium, Li^+ , and Al^{+3} , or from any sub-group thereof. The simple salt may comprise an anion selected from SO_4^{2-} , PO_3^{3-} , NO_3^- , HPO_4^{2-} , CO_3^{2-} , acetate, trifluoroacetate (TFA), Cl^- , Br^- , 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 , $Al_2(SO_4)_3$, $Al(NO_3)_3$, $Ca_3(PO_4)_2$, $BaSO_4$, $BaHPO_4$, $Ba_2(PO_4)_3$, $CaSO_4$, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, 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. The charge director may further comprise basic barium petronate (BBP).

[0077] In the formula $[R_a-O-C(O)CH_2CH(SO_3^-)C(O)-O-R_b]$, in some examples, each of R_a and R_b is an aliphatic alkyl group. In some examples, each of R_a and R_b independently is a C_{6-25} 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_a and R_b are the same. In some examples, at least one of R_a and R_b is $C_{13}H_{27}$. In some examples, M is Na, K, Cs, Ca, or Ba. The formula $[R_a-O-C(O)CH_2CH(SO_3^-)C(O)-O-R_b]$ and/or the formula MA_n may be as defined in any part of WO2007130069.

[0078] The charge director may comprise (i) soya lecithin, (ii) a barium sulfonate salt, such as basic barium petronate (BPP), and (iii) an isopropyl amine sulfonate salt. Basic barium petronate is a barium sulfonate salt of a 21-26 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.

[0079] In some examples, the charge director constitutes about 0.001% to 20%, in some examples 0.01 to 20% by weight, in some examples 0.01 to 10% by weight, in some examples 0.01 to 1% by weight of the solids of the electrostatic ink composition. In some examples, the charge director constitutes about 0.001 to 0.15 % by weight of the solids of the electrostatic ink composition. In some examples, the charge director constitutes 0.001

to 0.15 %, in some examples 0.001 to 0.02 % by weight of the solids of the electrostatic ink composition.

Charge Adjuvant

[0080] The liquid electrophotographic ink composition and/or ink composition printed on the print substrate can include a charge adjuvant. A charge adjuvant may be present with a charge director, and may be different to the charge director, and act to increase and/or stabilise the charge on particles, e.g. resin-containing particles, of an electrostatic composition. The charge adjuvant can include, but is not limited to, 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, Cu 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 co-polymers of 2-ethylhexyl methacrylate-co-methacrylic acid calcium, and ammonium salts, co-polymers of an alkyl acrylamidoglycolate alkyl ether (e.g. methyl acrylamidoglycolate methyl ether-co-vinyl acetate), and hydroxy bis(3,5-di-tert-butyl salicylic) aluminate monohydrate. In some examples, the charge adjuvant is aluminium di and/or tristearate and/or aluminium di and/or tripalmitate. In one example, the charge adjuvant is aluminium tri-stearate.

[0081] The charge adjuvant may be present in an amount of about 0.1 to 5, about 0.5 to 4, and about 1 to 3 % weight of the solids of the electrostatic ink composition.

[0082] The charge adjuvant may be included in the electrophotographic ink composition in any suitable method. For example, the charge adjuvant may be ground with the ink or coated conductive metallic pigment particles to allow the charge adjuvant to associate with the particles' surface. This may cause the charge adjuvant to agglomerate onto the polymer resin precipitated on the conductive metallic pigment particles so as to form a coating that includes both the polymer resin and the polymer resin. In one example, where the the polymer resin comprises (i) a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, and (ii) an ionomer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, wherein at least a portion of the acrylic acid and/or methacrylic acid groups neutralised with metal ions, a charge adjuvant may be ground with the ink or coated conductive metallic pigment

particles. Alternatively or additionally, where the charge adjuvant is included in the coating that is formed on the conductive metallic pigment particles, additional charge adjuvant may be ground with the ink or coated conductive metallic pigment particles to allow the charge adjuvant to associate with the particles' surface.

- 5 **[0083]** In one example, the coating that is formed on the conductive metallic pigment particles by precipitation includes a charge adjuvant. The charge adjuvant may be included in the coating during the coating process. For example, the charge adjuvant may be ground or otherwise incorporated with the polymer resin the carrier liquid. In some examples, the charge adjuvant may be ground with the polymer resin in the carrier liquid to
10 form a paste. The resulting mixture may be heated before addition of the conductive metallic pigment particles. The mixture may then be cooled to allow a coating to be formed on the metallic pigment particles. The coating may be formed by polymer resin and charge adjuvant precipitating onto the surface of the metallic pigment particles. In one example, this precipitation step results in a polymer matrix being coated onto the metallic
15 pigment particles. The polymer matrix may contain particles of the charge adjuvant dispersed throughout. If the coated conductive metallic pigment particles are re-heated and then re-precipitated, the re-precipitated coating may also include a polymer matrix comprising charge adjuvant dispersed throughout.
- [0084]** The weight of charge adjuvant present in the ink solids as a percentage of the
20 weight of polymer resin may be 2.5% to 10%, for example, 2.5% to 7.5%. In one example, the weight of charge adjuvant present in the ink solids as a percentage of the weight of polymer resin may be 5% to 12%, for example, 5% to 8%.

Other Additives

- [0085]** The electrophotographic ink composition may include an additive or a plurality of
25 additives. The additive or plurality of additives may be added at any stage of the method. The additive or plurality of additives may be selected from a wax, a surfactant, biocides, organic solvents, viscosity modifiers, materials for pH adjustment, sequestering agents, preservatives, compatibility additives, emulsifiers and the like. The wax may be an incompatible wax. As used herein, "incompatible wax" may refer to a wax that is
30 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.

- [0086]** In some examples a surfactant is present in the any portion of the carrier liquid
35 before, during and/or after effecting precipitation of the resin. In some examples a

surfactant is present in the electrostatic ink composition or the composition resulting from the method, which may be an electrostatic ink composition. A surfactant has been found to promote encapsulation of the conductive metallic pigment particles by the resin, which has been found to promote the print properties of resin-coated metallic pigment particles.

5 Surfactants comprising an acidic group have been found to be particularly effective. Accordingly, in some examples, the surfactant comprises an acidic group. In some examples, the surfactant is or comprises a polyhydroxy fatty acid, which may be a saturated or unsaturated fatty acid. The polyhydroxy fatty acid may be a C₈ to C₂₆ polyhydroxy fatty acid, in some examples a C₁₂ to C₂₀ polyhydroxy fatty acid, in some
10 examples a C₁₆ to C₂₀ polyhydroxy fatty acid. In some examples, the polyhydroxy fatty acid is a polyhydroxystearic acid. In some examples, the polyhydroxy fatty acid is poly(12-hydroxystearic acid) stearate. In some examples, the surfactant is or comprises Solsperse® 3000, available from Lubrizol. The polyhydroxy fatty acid may have a molecular weight of at least 300 Daltons, in some examples at least 1000 Daltons, in some
15 examples 300 to 24000 Daltons, in some examples 1000 to 24000 Daltons.

[0087] In some examples, the surfactant may be selected from anionic surfactant, cationic surfactant, amphoteric surfactant, non-ionic surfactant, polymeric surfactant, oligomeric surfactant, crosslinking surfactant, or combinations thereof.

[0088] The anionic surfactant may be or comprise sulfosuccinic acid and derivatives thereof such as, for instance, alkyl sulfosuccinates (e.g., GEROPON® SBFA-30 and GEROPON® SSO-75, both of which are manufactured by Rhodia, Boulogne-Billancourt, France) and docusate sodium.

[0089] The cationic surfactant may be selected from quaternary amine polymers, protonated amine polymers, and polymers containing aluminum (such as those that are
25 available from Lubrizol Corp., Wickliffe, Ohio). Further examples of cationic surfactants include SOLSPERSE® 2155, 9000, 13650, 13940, and 19000 (Lubrizol Corp.) and other like cationic surfactants.

[0090] The amphoteric surfactant may be selected from surfactants that contain compounds having protonizable groups and/or ionizable acid groups. An example of a
30 suitable amphoteric surfactant includes lecithin.

[0091] The non-ionic surfactant may be selected from oil-soluble polyesters, polyamines, polyacrylates, polymethacrylates (such as, e.g., SOLSPERSE® 3000 (Lubrizol Corp.), SOLSPERSE® 21000 (Lubrizol Corp.), or the like.

[0092] The oligomeric surfactant may be selected from low average molecular weight (i.e.,
35 less than 1000) non-ionic surfactants.

[0093] The cross-linking surfactant may be selected from polymers or oligomers containing two or more carbon double bonds (C=C) and/or free amine groups such as, e.g., polyamines, crosslinkable polyurethanes, and divinyl benzene.

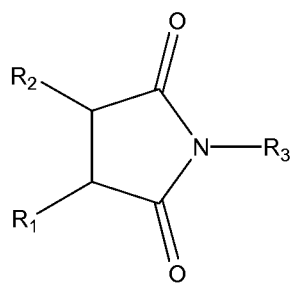
5 [0094] Other suitable surfacants include OS#13309AP, OS#13309AQ, 14179BL, and 45479AB from Lubrizol Corp, which are surfacants based on polyisobutylene succinic acid with polyethyleneimines. These surfacants are combination polymers that are cationic in nature.

10 [0095] In some examples, the surfactant is selected from a fatty acid sarcosine and a fatty acid sarcosinate. In some examples, the fatty acid in the fatty acid sarcosine and/or fatty acid sarcosinate is selected from a C₈ to C₂₆ fatty acid, in some examples a C₁₂ to C₂₀ fatty acid, in some examples a C₁₆ to C₂₀ fatty acid. The fatty acid may be saturated or unsaturated. In some examples, the fatty acid in the fatty acid sarcosine and/or fatty acid sarcosinate is selected from lauroyl, cocoyl, myristoyl, oleoyl, and stearyl. Suitable surfactants may be available from Crodasinic®, for example Crodasinic L, C, M, O, S or SM.

15 [0096] Surfactants typically comprise a head group and a tail group, with the head group and tail group typically of different polarity, e.g. the head group being polar and the tail group being relatively non-polar compared to the head group. The surfactant may comprise an acidic head group, e.g. a head group comprising a carboxylic acid. The surfactant may comprise a basic head group. The basic head group may comprise an amine group, which may be selected from a primary amine group and a secondary amine group. The basic head group may comprise a plurality of amine groups, which may each independently be selected from a primary amine group and a secondary amine group.

20 [0097] In some examples, the surfactant comprises a succinimide. The succinimide may be linked, e.g. via a hydrocarbon-containing linker group, to an amine group. In some examples, the surfactant comprises a polyisobutylene succinimide having a head group comprising an amine.

[0098] In some examples, the surfactant is of formula (I)



formula (I)

wherein R_1 , R_2 and R_3 are selected from an amine-containing head group, a hydrocarbon
5 tail group and hydrogen,

wherein at least one of R_1 , R_2 and R_3 comprises a hydrocarbon tail group,

at least one of R_1 , R_2 and R_3 comprises an amine-containing head group. In some examples,
 R_1 and R_2 are selected from a hydrocarbon tail group and hydrogen, with at least one of R_1
and R_2 comprising a hydrocarbon tail group, and R_3 comprises an amine-containing head
10 group. The hydrocarbon tail group may comprise or be a hydrocarbon group, which may be
branched or straight chain and may be unsubstituted. The hydrocarbon tail group may
comprise or be a hydrocarbon group containing a polyalkylene, which may be selected from
a polyethylene, polypropylene, polybutylene. In some examples, the hydrocarbon tail group
may contain a polyisobutylene. The hydrocarbon tail group may contain from 10 to 100
15 carbons, in some examples from 10 to 50 carbons, in some examples from 10 to 30 carbons.
The hydrocarbon tail group may be of the formula (II)

P-L-

formula (II),

20 wherein P is or comprises polyisobutylene and L is selected from a single bond, $(CH_2)_n$,
wherein n is from 0 to 5, in some examples 1 to 5, -O- and -NH-. In some examples, the
amine-containing head group comprises or is a hydrocarbon group having an amine group
attached to one of the carbons of the hydrocarbon group. In some examples, the amine-
containing head group is of the formula (III)

25

$(CH_2)_m[(CH_2)_oNH(CH_2)_p]_q(CH_2)_rNH_2$ formula (III),

wherein m is at least 1, in some examples 1 to 5, q is 0 to 10, o is 0, 1 or 2, p is 1 or 2, r is
0 to 10; in some examples, m is 1, o is 1, p is 1 and q is from 0 to 10, in some examples

from 1 to 5, and in some examples r is 1 to 5; in some examples m is 1, q is 0 to 10, in some examples 1 to 10, in some examples 1 to 5, o is 1, p is 1, r is 1.

[0099] In some examples, the surfactant is of formula (I), wherein R_1 is of formula (II), R_2 is H and R_3 is of formula (III). In some examples, the surfactant is of formula (I), wherein R_1 is of formula (II), wherein L is $-\text{CH}_2-$, R_2 is H and R_3 is of formula (III), wherein m is 1, q is 0 to 10, in some examples 1 to 10, in some examples 1 to 5, o is 1, p is 1 and r is 1. In some examples, the surfactant is or comprises Lubrizol ® 6406.

Method of producing the liquid electrophotographic ink composition

[00100] The method of producing a conductive liquid electrophotographic ink composition involves heating a polymer resin in a carrier liquid to dissolve the polymer resin. The pigment particles may then be added to the carrier liquid and the resulting composition cooled to effect precipitation of the resin around the pigment particles. Precipitation of the resin around the pigment particles may help to encapsulate the pigment particles.

[00101] In some examples, the polymer resin may be insoluble in the carrier liquid at room temperature but soluble in the carrier liquid at elevated temperatures, for example at a temperature of at least 50 °C, for example at a temperature of at least 60 °C, for example at a temperature of at least 70 °C, for example at a temperature of at least 80 °C, for example at a temperature of at least 90 °C, for example at a temperature of at least 100 °C, for example at a temperature of at least 110 °C, for example at a temperature of at least 120 °C. The dispersion of the polymer resin in the carrier liquid may be heated to any of the above stated temperatures for sufficient time until the polymer resin has dissolved. Dissolution may be confirmed by the carrier liquid appearing clear and homogenous. In some examples, the dispersion of polymer resin in the carrier liquid may be mixed at a rate of less than 500 rpm, for example less than 400 rpm, for example less than 300 rpm, for example less than 200 rpm until dissolution is complete. In some examples, heating a dispersion of polymer resin in carrier liquid may cause the polymer resin to swell with carrier liquid. In some examples, the dispersion of polymer resin in carrier liquid may be heated to swell the polymer resin. Swelling of the polymer resin may allow better encapsulation of the conductive pigment particle. In some examples, the polymer resin may be heated in a solvating carrier liquid to swell and solvate the polymer resin. The swollen and solvated polymer resin may then be removed from the solvating carrier liquid and re-dispersed in a new portion of carrier liquid.

[00102] In some examples, a charge adjuvant may also be added to the carrier liquid and the polymer resin. The charge adjuvant may be incorporated (e.g. by grinding) with the polymer resin, for example, to form a paste. This may help to disperse the charge adjuvant

in the polymer. By dispersing the charge adjuvant in the polymer prior to, for example, the addition of the conductive metallic pigment particles, a mixture of the polymer and the charge adjuvant may be precipitated onto the particles. In some examples, the mixture is deposited as a polymer matrix within which particles of charge adjuvant is dispersed. The concentration and/or nature of the charge adjuvant may be varied to provide the coated conductive metallic pigment particles with the desired particle conductivity. For instance, the particle conductivity may be at least 100 pmho/cm, for instance, at least 110 pmho/cm or at least 130 pmho/cm. In one example, the particle conductivity may be at least 150 pmho/cm, for instance, at least 160 pmho/cm or at least 180 pmho/cm. In another example, the particle conductivity may be at least 200 pmho/cm.

[00103] The conductive metallic pigment particles are added to the carrier liquid. In some examples, the conductive metallic pigment particles may be added to the carrier liquid as a single addition. In some examples, the conductive metallic pigment particles may be added to the carrier liquid in a portion-wise manner, over a period of time. In some examples, the conductive metallic pigment particles may be added to the carrier liquid over a period of at least 10 minutes, for example at least 20 minutes, for example at least 30 minutes.

[00104] In some examples, the conductive metallic pigment particles may be added to the carrier liquid before any heating occurs, for example at room temperature. In some examples, the conductive metallic pigment particles may be added to the carrier liquid while the carrier liquid is being heated.

[00105] In some examples, the conductive metallic pigment particles may be added to the carrier liquid after it has been heated and the polymer resin has dissolved. In some examples, the conductive metallic pigment particles to be coated may be added to the carrier liquid before any cooling occurs, for example at the temperature at which dissolution of the polymer resin in the carrier liquid was carried out. In some examples, the carrier liquid may be cooled to an intermediate temperature before the pigment particles are suspended in the carrier liquid. The intermediate temperature may be any temperature above the cloud point of the solution comprising the carrier liquid and the dissolved polymer resin.

[00106] In some examples, the cloud point of any given carrier liquid-polymer resin system can be readily determined by heating and slowly cooling the solution. The cloud point may be the temperature at which dissolved solids begin to precipitate, giving a phase separation and a cloudy or turbid appearance. In some examples, the solution comprising the carrier liquid and the dissolved polymer resin may be cooled to at least 2 °C, for example at least 3°C, for example at least 4°C, for example at least 5°C, for example at

least 6°C, for example at least 7°C, for example at least 8°C, for example at least 9°C, for example at least 10°C above the cloud point before the pigment is added. In some examples, the solution comprising the carrier liquid and the dissolved polymer resin may be cooled to at least 15 °C, for example at least 20 or 30 °C above the cloud point before pigment is added.

[00107] In some examples, the conductive metallic pigment particles may be added to the carrier liquid with high shear mixing. The high shear process may involve stirring the mixture, for example at a high speed, for example a speed of at least 1000 RPM, in some examples at least 2000 RPM, in some examples at least 5000 RPM, in some examples at least 10,000 RPM, in some examples at least 15,000 RPM, in some examples at least 20,000 RPM. The stirring may be carried out for a period of at least 30 seconds, in some examples at least 1 minute, in some examples at least 2 minutes. In some examples, the stirring may be carried out at least 1,000 RPM for at least 2 minutes, in some examples at least 2,000 RPM for at least 2 minutes. In one example, high shear mixing takes places at a speed of 3000rpm for, for example, at least 20, for instance, 30 minutes. The weight ratio of pigment dispersion to carrier liquid may be 1:1.

[00108] In some examples, the pigment particles are mixed into the carrier liquid at a speed of 12 000 RPM or less, for example 11 000 RPM or less, for example 10 000 RPM or less, for example 9000 RPM or less to ensure complete dispersion before the precipitation of the polymer resin is effected. In other examples, the pigment particles are mixed into the carrier liquid at a speed of 100 RPM or less, for example 90 RPM or less, for example 80 rpm or RPM, for example 70 RPM or less, for example 60 RPM or less, for example 50 RPM or less to ensure complete dispersion before the precipitation of the polymer resin is effected. In some examples, following dispersion of the pigment particles at a low speed, the rate of mixing may be increased to less than 100 RPM, for example less than 90 RPM, for example less than 80 RPM, for example 70 RPM or less. In some examples, following dispersion of the pigment particles, the rate of mixing may be lowered to less than 500 RPM, for example less than 400 RPM, for example less than 300 RPM, for example less than 200 RPM, for example 100 RPM or less, for example less than 90 RPM, for example less than 80 RPM, for example less than 70 RPM, for example less than 60 RPM, for example 50 RPM or less while the first precipitation is effected.

[00109] In some examples, the conductive metallic pigment particles can be dispersed in a first portion of a carrier liquid which is later combined with a second portion of the carrier liquid containing the polymer resin. In some examples, the first and second portions of the carrier liquid are identical in nature. In some examples, the carrier liquid, the first portion thereof and the second portion thereof all comprise or consist of an iso-paraffinic carrier

liquid. In some examples, the first and second portions of the carrier liquid are different solvents, but are miscible with one another and are both suitable carrier liquids for electrostatic printing.

5 **[00110]** In some examples, the conductive metallic pigment particles are dispersed in the first portion of the carrier liquid with high shear mixing. The high shear process may involve stirring the mixture, for example at a high speed, for example a speed of at least 1000 RPM, in some examples at least 2000 RPM, in some examples at least 5000 RPM, in some examples at least 10,000 RPM, in some examples at least 15,000 RPM, in some examples at least 20,000 RPM. The stirring may be carried out for a period of at least 30
10 seconds, in some examples at least 1 minute, in some examples at least 2 minutes. In some examples, the stirring may be carried out at least 1,000 RPM for at least 2 minutes, in some examples at least 2,000 RPM for at least 2 minutes.

[00111] In some examples, once the pigment particles are fully dispersed, the system is cooled until precipitation of the resin from solution (and onto the pigment particles) is
15 complete. For example, the system may be cooled through the cloud point of the solution to effect precipitation of the polymer resin from solution. In some examples, cooling comprises cooling at a rate of at least or about 20 °C/hour. The cooling rate may be adjusted as required. Example cooling rates include 40 °C/hour or 60 °C/hour. Such cooling rates can be achieved through the use of heat exchangers and suitable
20 refrigerants. In some examples, the temperature of the carrier liquid is lowered further through a controlled cooling process at a given rate. For example, the temperature of the carrier liquid may be lowered at a rate of less than 7 °C per hour, for example less than 6 °C per hour, for example less than 5 °C per hour, for example less than 4 °C per hour, for example 3 °C per hour.

25 **[00112]** In some examples, once the solution has cooled to below the cloud point temperature and the polymer resin has precipitated, the system may then be reheated to above the cloud point of the solution, for example to at least 5 °C above the cloud point of the solution, for example at least 10 °C above the cloud point of the solution, at least 15 °C above the cloud point temperature of the solution, at least 20 °C above the cloud point
30 temperature of the solution. Heating may, in certain examples, be 30 °C or up to 50 °C above the cloud point depending on the nature of the precipitation stage in question. The reheating of the solution to above the cloud point followed by a second precipitation is thought to improve the final encapsulation of the conductive metallic pigment particle by the polymer resin.

35 **[00113]** The second precipitation may be effected by controlling the cooling of the system such that solubility of the resin in the carrier liquid is reduced and precipitation of the resin

occurs. In some examples, the system may be cooled until precipitation of the resin from solution (and onto the pigment particles). For example, the system may be cooled through the cloud point of the solution to effect precipitation of the polymer resin from solution. In some examples, the system may be cooled at a rate of 20 °C/hour. In some examples, the temperature of the carrier liquid is lowered through a controlled cooling process at a given rate. For example, the temperature of the carrier liquid may be lowered at a rate of less than 7 °C per hour, for example less than 6 °C per hour, for example less than 5 °C per hour, for example less than 4 °C per hour, for example 3 °C per hour.

[00114] In some examples, the second precipitation may be effected through controlled cooling through the cloud point of the polymer resin-carrier liquid system. For example, the controlled cooling at a rate of less than 7 °C/hour, for example a rate of 3 °C/hour, may be carried out beginning at a temperature of 5 °C above the cloud point of the solution and continued until a temperature of at least 5 °C below the cloud point of the solution. In some examples, once the temperature has been lowered in a controlled manner to at least 5 °C below the cloud point of the solution, the system is then cooled at an uncontrolled rate to room temperature. In some examples, the second precipitation is effected through cooling at an uncontrolled rate (for example at a rate of 20 °C/hour) to at least 5 °C below the cloud point of the solution, followed by controlled cooling at a slower cooling rate, for example at a rate of less than 7 °C per hour, for example less than 6 °C per hour, for example less than 5 °C per hour, for example less than 4 °C per hour, for example 3 °C per hour until precipitation of the resin and concomitant encapsulation of the conductive metallic pigment particle is complete.

[00115] In some examples, following the second precipitation of the resin from the carrier liquid, the composition comprising polymer resin-coated conductive metallic pigment particles in carrier liquid may be subjected to a high shear treatment. The high shear process may involve stirring the mixture, for example at a high speed, for example a speed of at least 1000 RPM, in some examples at least 5000 RPM, in some examples at least 5000 RPM, in some examples at least 10,000 RPM, in some examples at least 15,000 RPM, in some examples at least 20,000. The stirring may be carried out for a period of at least 30 seconds, in some examples at least 1 minute in some examples at least 2 minutes. In some examples, the stirring may be carried out at least 10,000 RPM for at least 2 minutes, in some examples at least 20,000 RPM for at least 2 minutes.

[00116] In some examples, the composition comprising polymer resin-coated conductive metallic pigment particles in carrier liquid obtained from the method is suitable for use as a printing composition without further treatment, in particular without a grinding treatment. In some examples, the composition comprising polymer resin-coated conductive metallic

pigment particles in carrier liquid obtained from the method is diluted with additional carrier liquid to a required pigment loading, for example at least 15 wt.%, for example at least 20 wt.%, at least 25 wt.%, at least 30 wt.% based on the total solids of the composition.

Liquid Electrophotographic Printing

5 **[00117]** The liquid electrostatic composition described in the present disclosure may be used in an electrophotographic printing method. The printing method may comprise forming a latent electrostatic image on a surface; contacting the surface with the electrostatic ink composition, such that at least some of the particles adhere to the surface to form a developed toner image on the surface, and transferring the toner image to a print
10 substrate, in some examples, via an intermediate transfer member.

[00118] The surface on which the latent electrostatic image is formed may be on a rotating member, e.g. in the form of a cylinder. The surface on which the latent electrostatic image is formed may form part of a photo imaging plate (PIP). The intermediate transfer member may be a rotating flexible member, which may be heated, e.g. to a temperature of from 80
15 to 130 °C. The print substrate may be or comprise a cellulosic print substrate such as paper. The cellulosic print substrate may be or comprise an uncoated cellulosic print substrate, i.e. absent of a coating of a polymeric material. The print substrate may be an acrylic print substrate, in some examples a coated acrylic print substrate, e.g. coated with a styrene-butadiene co-polymer.

20

Examples

[00119] The following illustrates examples of the methods and related aspects described herein. Thus, these examples should not be considered as limitations of the present
25 disclosure, but are merely in place to teach how to make examples of compositions of the present disclosure. As such, a representative number of compositions and their method of manufacture are disclosed herein.

Materials

[00120] Resins: Nucrel ® 599 is an ethylene-methacrylic acid copolymer available from
30 DuPont.

[00121] Pigments: Silver dollar 12541 pigment is available from Schleck (Germany). This contains 80% aluminium metal by weight.

[00122] Solvent: Isopar-L is available from Exxon-Mobil.

Comparative Example A

[00123] The resin was dissolved in the solvent at 28% solids w/w at 120 degrees C.

[00124] Once the resin had dissolved (confirmed by the appearance of a clear solution), the mixture was cooled to within 20 to 30 degrees C of the cloud point. The pigment
5 particles were then added to the vessel at 50% solids w/w, followed by high shear mixing to break any pigment agglomerates in the solution.

[00125] When the solution reached 15 degrees C above the cloud point, the cooling rate was reduced to 10 degrees per hour until the temperature reached 5 degrees below the cloud point. The rate of cooling in the vicinity of the cloud point can determine the
10 precipitation rate and the size of the ink particles.

[00126] At the cloud point, precipitation of the resin begins to occur around the pigment particles. After slow cooling of the temperature 5 degrees below the cloud point, cooling can be carried out more rapidly without affecting particle size.

[00127] The reaction mixture was then re-precipitated by heating again to about 20 to 30
15 degrees C above the cloud point and cooled as described above to re-precipitate the resin on the pigment particles.

The resulting composition contained coated pigment particles dispersed in the liquid carrier (solvent). Comparative Example B

[00128] Comparative Example A was repeated except that the resin was a blend of 95
20 weight % Nucrel ® 599 and 5 weight % AC-5120, an ethylene acrylic acid copolymer resin available from Honeywell.

Example 1

[00129] Comparative Example A was repeated except that the composition produced was ground with aluminium tristearate (VCA). The charge adjuvant was employed in an
25 amount of 7.5 weight % based on the weight of the resin.

Example 2

[00130] In this example, the resin was dissolved in solvent at a concentration of 42 weight %. The mixture was heated until the resin dissolved. Once dissolved, the solution was cooled at a rate of 30 degrees C per minute until the temperature reached 42 degrees C.
30 At this temperature, additional solvent was used to dilute the solution to 25% NVS.

[00131] The resulting paste was ground with 7.5 weight % aluminium tri- stearate (VCA). The mixture was ground in an attritor at 35 degrees C for 30 hours to provide a mixture with a NVS content of 25%.

[00132] The ground paste was concentrated by evaporation of solvent to maintain the resin content at 28 weight % .

[00133] The pigment particles were then added to the paste and precipitation performed as described in relation to Comparative Example A above.

5 Example 3 - Particle Conductivity

[00134] The Particle Conductivities of Comparative Examples A and B, and Examples 1 and 2 were determined by placing the composition between 2 parallel electrodes and applying an electric field between the electrodes. The electrodes were of a known area and were spaced 1 mm apart.

10 [00135] Two measurements are carried out:

[00136] Low field conductivity: Bias voltage – 10V, ~1 sec (no ink development)

[00137] The low field conductivity was measured at the following conditions:

- Electrical field amplitude: 5 – 15 V/mm
- Frequency: 5 – 15 Hz
- 15 • Temperature: 23 +/- 2 C

[00138] High field conductivity: Bias voltage - 1500V, 8 sec (ink is developed)

[00139] High field conductivity was measured under the following conditions:

- Electrical field pulse:

Shape: Rectangular

20 Height: 1500 V/mm

Duration: 8 sec

Rise time: 1 ms or less

Ripple: 10 V/mm or less

- Sampling frequency: 1000 per second
- 25 • Temperature: 23 +/- 2 C

[00140] When using high voltage (1500 V), the ink particles become charged under the electric field and are developed on one of the electrodes (the positive pole) The current is monitored during the 8 second period and conductance calculated using Ohm's law:

[00141] Conductance= $1/R=I/V$ (current/voltage)

[00142] Conductivity is the conductance normalized to the distance between the electrodes and to the electrodes area :

[00143] Conductivity = Conductance·(distance between electrodes)/(electrode area) with units pmho/cm (p for pico, 10^{-12} , mho is conductivity units, 1/ohm and cm is distance)

- 5 **[00144]** The low field conductivity relates to the conductivity of the liquid. From the high field conductivity, it is possible to determine the maximal conductivity during the measurement bias voltage=1500V.

[00145] The particle conductivity was calculated as the difference between the high field conductivity and low field conductivity.

- 10 **[00146]** Comparative Example A: 110 pmho/cm

[00147] Comparative Example B: 50 pmho/cm

[00148] Example 1: 160

[00149] Example 2: 250

Example 4 - Effect of Ageing on Optical Density

- 15 **[00150]** The compositions of Comparative Examples A and B, and Examples 1 and 2 were printed onto a paper substrate using an electrophotographic printer. The optical densities were measured of images taken after 1, 5000, 10000, 15000 and 20000 print impressions (NB 1kimps = 1000 impressions). The applied printing voltages remained unchanged over the course of the impressions.

- 20 **[00151]** The optical density (OD) was measured using a spectrometer at an angel of 45 degrees. Optical Density (OD) is given by the equation

$$OD = - \text{Log} \left(\frac{\text{Reflected Light}}{\text{Incident Light}} \right)$$

- 25 **[00152]** Figure 1 shows how the optical densities of the images change as the number of print impressions increase. It can be seen that, as the particle conductivity of the particles in the composition increase, so optical density stability increases. The composition of Example 2 exhibits the best optical density stability and the composition of Comparative Example B, the worse.

- 30 **[00153]** Figure 2 plots long-term optical density stability (LODs)of the compositions against particle conductivities of Comparative Examples A, B and Example 2. In this example, the long-term optical density stability is determined by:

[00154] $[\text{OD}_{\text{start}} - \text{OD}_{\text{end}}]/[\text{OD}_{\text{start}}]$

[00155] For the first 20000 impressions, OD_{start} is the optical density of the first image and OD_{end} is the optical density of the 20000th image.

[00156] For the 10000th to 20000th impressions, OD_{start} is the optical density of the
5 10,000th image and OD_{end} is the optical density of the 20000th image.

[00157] It can be seen that LODs improves with particle conductivity.

Example 5 – Effect on particle agglomeration

[00158] In this example, the properties of the compositions in the ink tank of a printer were determined after 0, 5000, 10000, 15000 and 20000 print impression. Figure 3 shows how
10 the content of non-volatile solids (NVS%) of the compositions varied. It can be seen that Comparative Example B exhibited a significant increase in NVS%, showing that the particles in this composition had a greater tendency to agglomerate with time. In contrast, the compositions of Examples 1 and 2 exhibited lower increases in NVS%.

Example 6

[00159] Comparative Example A was repeated except that the following resin blend was employed: 83% Nucrel 599 and 17% AClyn® 285 (Honeywell®). AClyn®285 is an ionomer formed from a copolymer of ethylene and acrylic acid (based on AC5120, Honeywell® in which 80% of the acrylic acid groups are replaced with sodium ions. Also, the re-precipitation step was carried out twice rather than once as described in relation to
20 Comparative Example A.

[00160] The particle conductivity of the composition was determined to be 165 pmho/cm. The increased particle conductivity can provide the composition with improved optical density stability.

Example 7

[00161] Example 6 was repeated except that the following resin blend was employed: 83% Nucrel 599 and 17% AClyn® 201 (Honeywell®). AClyn®201 is an ionomer formed from a copolymer of ethylene and acrylic acid (based on AC5120, Honeywell® in which 50% of the acrylic acid groups are replaced with calcium ions.

[00162] The particle conductivity of the composition was determined to be 130 pmho/cm.
30 The increased particle conductivity can provide the composition with improved optical density stability.

[00163] While the compositions, methods and related aspects have been described with reference to certain examples, those skilled in the art will appreciate that various

modifications, changes, omissions, and substitutions can be made without departing from the spirit of the disclosure. It is intended, therefore, that the invention be limited by the scope of the following claims. The features of any dependent claim may be combined with the features of any of the other dependent claims or any and/or any of the independent

5 claims.

Claims

1. A method for producing a conductive liquid electrophotographic ink composition,
5 the method comprising:
 heating a polymer resin in a carrier liquid to dissolve the polymer resin;
 adding conductive metallic pigment particles to the carrier liquid;
 cooling the carrier liquid to effect precipitation of the polymer resin from the carrier
liquid, such that a coating comprising the resin is formed on the conductive metallic
10 pigment particles;
 wherein:
 I) the polymer resin comprises (i) a copolymer of an alkylene monomer and a
monomer selected from acrylic acid and methacrylic acid, and (ii) an ionomer of an
alkylene monomer and a monomer selected from acrylic acid and methacrylic acid,
15 wherein at least a portion of the acrylic acid and/or methacrylic acid groups are
neutralised with metal ions; and/or
 II) a charge adjuvant is included in the coating that is formed on the
conductive metallic pigment particles.
- 20 2. A method as claimed in claim 1, which further comprises reheating the coated
conductive metallic pigment particles in the carrier liquid, and cooling the carrier liquid to
effect precipitation of the polymer resin from the carrier liquid such that a coating
comprising the resin is re-formed on the conductive metallic pigment particles.
3. A method as claimed in claim 1, wherein the charge adjuvant is included in the
25 coating by including both charge adjuvant and polymer resin in the carrier liquid, such that
cooling the carrier liquid effects precipitation of the charge adjuvant and polymer resin onto
the conductive metallic pigment particles.
4. A method as claimed in claim 1, wherein the charge adjuvant is agglomerated onto
the resin that is precipitated on the conductive metallic pigment particles to form the
30 coating.
5. A method as claimed in claim 1, wherein, in the ionomer (ii), 50 to 100% of the
acrylic acid and/or methacrylic acid groups are neutralised with metal ions.
6. A method as claimed in claim 5, wherein the metal ions are selected from sodium,
calcium, magnesium and zinc.

7. A method as claimed in claim 1, wherein the polymer resin comprises 70 to 95% by weight of copolymer (i) and 5 to 30% by weight of ionomer (ii) based on the total weight of the polymer resin.
8. A method as claimed in claim 1, wherein the conductive metallic particles are
5 metallic aluminium particles.
9. A method as claimed in claim 1, wherein the coated conductive metallic particles have a particle conductivity of at least 120 pmho/cm.
10. A method according to claim 1, wherein cooling the carrier liquid to effect precipitation of the polymer resin comprises cooling to below the cloud point of the solution.
- 10 11. A method according to claim 2, wherein the coated conductive metallic pigment particles in the carrier liquid are reheated to above the cloud point of the solution, and then subsequently cooled to below the cloud point.
12. A liquid electrophotographic ink composition comprising coated conductive metallic pigment particles dispersed in a carrier liquid,
15 wherein the coated conductive metallic pigment particles are coated with a coating comprising particles of charge adjuvant dispersed within a polymer resin matrix; and/or wherein the coated conductive metallic pigment particles are coated with a coating comprising a polymer resin, wherein the polymer resin comprises (i) a copolymer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, and (ii)
20 an ionomer of an alkylene monomer and a monomer selected from acrylic acid and methacrylic acid, wherein the acrylic acid and/or methacrylic acid groups neutralised with metal ions.
13. A composition as claimed in claim 12, wherein the conductive metallic pigment
25 particles are formed of metallic aluminium.
14. A composition as claimed in claim 12, wherein the coated conductive metallic pigment particles have a particle conductivity of at least 120 pmho/cm.
15. A composition as claimed in claim 14, wherein the polymer resin comprises 70 to 95% by weight of copolymer (i) and 5 to 30% by weight of ionomer (ii) based on the total
30 weight of the polymer resin, and wherein 50 to 100% of the acrylic acid and/or methacrylic acid groups of the ionomer (ii) are neutralised with metal ions.

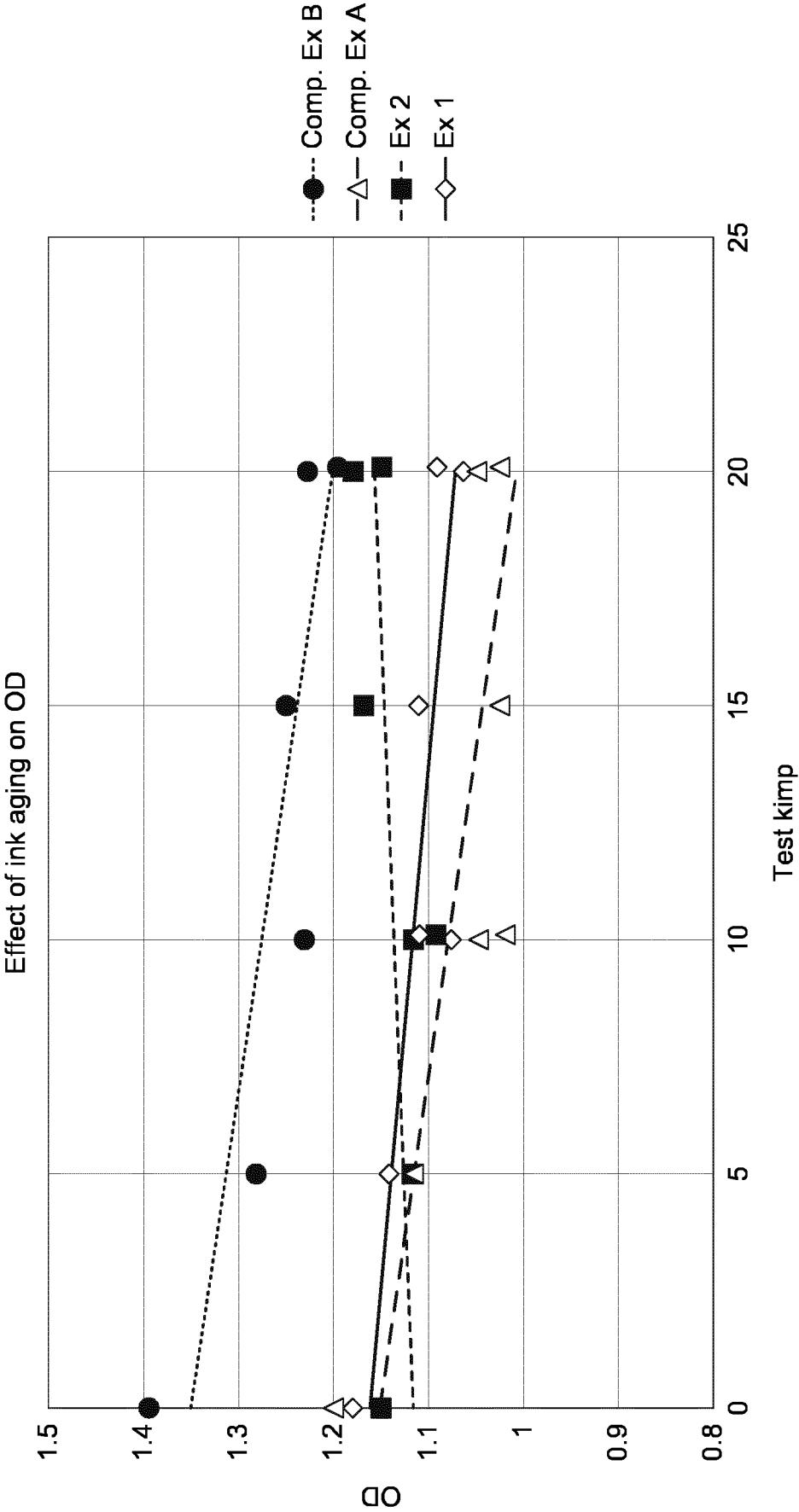


FIG. 1

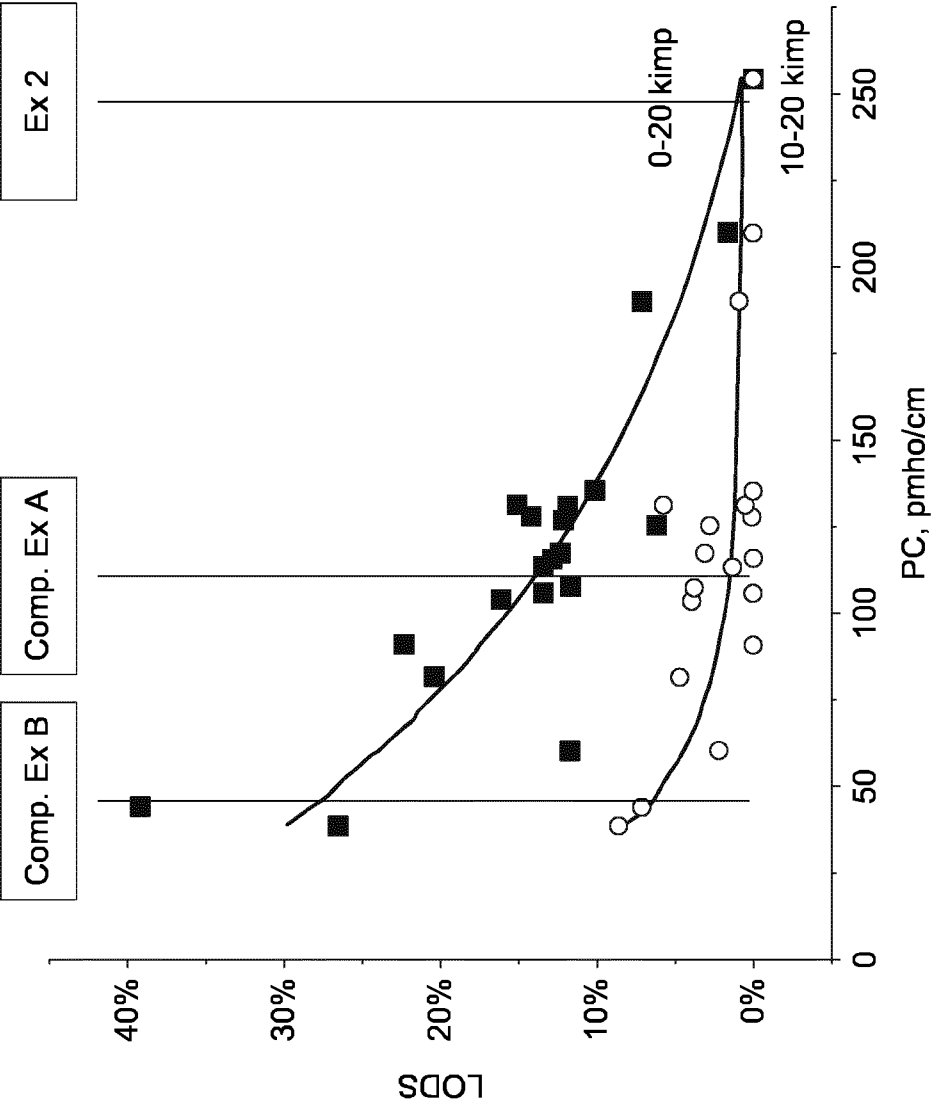


FIG. 2

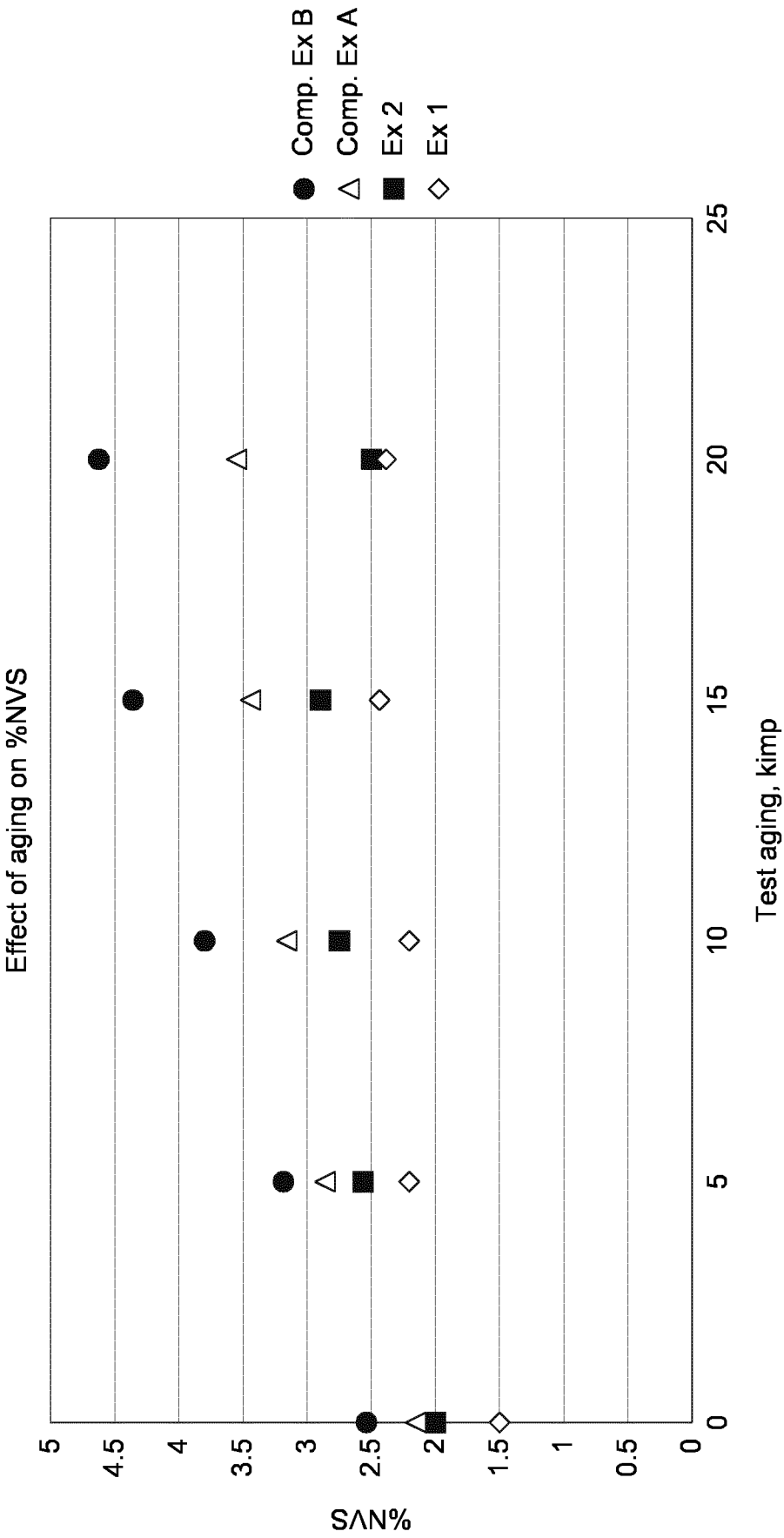


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/070966

A. CLASSIFICATION OF SUBJECT MATTER

INV. G03G9/12 G03G9/13 G03G9/135
ADD.

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

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/175826 A1 (MOR ILANIT [IL] ET AL) 25 June 2015 (2015-06-25) paragraph [0084] claims 1-15 paragraph [0027] paragraph [0094] paragraph [0096] paragraph [0036] paragraph [0040] paragraph [0044] paragraph [0046] paragraph [0022]	1-15
X	US 2016/216629 A1 (GRINWALD YARON [IL] ET AL) 28 July 2016 (2016-07-28) paragraph [0026] paragraph [0064] paragraph [0065]	12,14
A		1-11,13, 15
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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"&" document member of the same patent family

Date of the actual completion of the international search

25 October 2017

Date of mailing of the international search report

07/11/2017

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Authorized officer

Weiss, Felix

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/070966

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/342279 A1 (CHUN DORIS [US] ET AL)	12-14
A	20 November 2014 (2014-11-20) claims 1-15 paragraph [0022] -----	1-11,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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		WO 2013103346 A1	11-07-2013
