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54 POLYMERS FOR INKJET INK COMPOSITIONS

57 Disclosed herein are polymers, which can be incorporated in pigment dispersions and inkjet ink compositions, comprising first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof. The polymers can have a portion of the second monomers functionalized with at least one organic group having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid. Additionally and/or alternatively, the at least one polymer can be crosslinked via the second monomers. Dispersions and inkjet ink compositions comprising such polymers can also further comprise at least one pigment and a liquid vehicle. Also disclosed are methods of making such polymers.

Title: POLYMERS FOR INKJET INK COMPOSITIONS

Field of the invention

5 [0001] Disclosed herein are polymers comprising ethylenically unsaturated hydrophobic monomers and maleic anhydride and/or maleic acid (or salts, esters, imides, and amides thereof) monomers, as well as compositions comprising such monomers, which can be useful in inkjet ink applications.

10

Background

[0002] In inkjet printing of pigment-based inks, individual ink droplets are deposited on a substrate with the aim of quickly forming pigment aggregates on the substrate. This process can be challenging for plain 15 papers and coated papers including those with low solute salts such as calcium and magnesium salts. Slow pigment aggregation can lead to average or below average image quality as indicated by low optical density, bad mottle, *etc.*

[0003] Other challenges include maintaining the stability of such 20 pigment-based dispersions. Accordingly, there is a need to develop new pigment-based inkjet ink compositions to address these challenges.

Summary

[0004] One embodiment provides a polymer comprising:
25 first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof,

wherein at least one a portion of the second monomers is functionalized with at least one organic group having a calcium index value greater than a 30 calcium index value of phenylphosphonic acid.

[0005] Another embodiment provides a composition comprising:

at least one pigment;
a liquid vehicle; and
at least one polymer comprising first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof,
5 wherein a portion of the second monomers are functionalized with at least one organic group having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid.

10 [0006] Another embodiment provides a composition comprising:
at least one pigment;
a liquid vehicle; and
at least one polymer encapsulating the at least one pigment wherein the at least one polymer comprises first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, wherein the ethylenically unsaturated hydrophobic monomers comprise the formula $\text{CH}_2=\text{CR}^1\text{R}^2$, where R^1 and R^2 are independently selected from H, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_5\text{-C}_{20}$ aryl, and $\text{C}_6\text{-C}_{20}$ alkaryl,
15 and the carbon atoms of R^1 and R^2 can be optionally substituted with at least one heteroatom selected from O, N, and S, and
20 wherein the at least one polymer is crosslinked via the second monomers.

[0007] Another embodiment provides a method of making a polymer (e.g., a polymer capable of binding a divalent metal ion, such as a calcium and/or magnesium binding polymer) comprising:
25 (a) combining:
(i) at least one polymer comprising first monomers selected from ethylenically unsaturated hydrophobic monomers, and second

monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, and

5 (ii) at least one reagent comprising an amino group and at least one organic group having a calcium index value greater than a calcium index value of phenylphosphonic acid; and

5 (b) forming the polymer.

[0008] Another embodiment provides a method of making a polymer comprising,

10 (a) combining:

10 (i) at least one polymer comprising first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, wherein the ethylenically unsaturated hydrophobic monomers comprise the formula $\text{CH}_2=\text{CR}^1\text{R}^2$, where R^1 and R^2 are independently selected from H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, and C₆-C₂₀ alkaryl, and the carbon atoms of R^1 and R^2 can be optionally substituted with at least one heteroatom selected from O, N, and S, and

15 (ii) at least one crosslinking agent selected from epoxy-containing compounds; and

20 (b) forming the polymer.

Detailed description

[0009] Disclosed herein are compositions comprising:

25 at least one pigment;

25 a liquid vehicle; and

25 at least one polymer that is crosslinked and/or capable of binding calcium and/or other divalent metals.

[0010] In one embodiment, the at least one polymer is capable of binding 30 calcium and/or other divalent metals. In one embodiment, the at least one

polymer comprises first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, wherein a portion of the second monomers is functionalized with at least one 5 organic group having a calcium index value greater than or equal to a calcium index value of phenyl phosphonic acid. In one embodiment, the least one organic group has a calcium index value greater than or equal to a calcium index value of 1,2,3-benzene tricarboxylic acid.

10 [0011] Another embodiment provides a composition comprising:

at least one pigment;
a liquid vehicle; and

15 at least one polymer encapsulating the at least one pigment wherein the at least one polymer comprises first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, wherein the ethylenically unsaturated hydrophobic monomers comprise the formula $\text{CH}_2=\text{CR}^1\text{R}^2$, where R^1 and R^2 are independently selected from H, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_5\text{-C}_{20}$ aryl, and $\text{C}_6\text{-C}_{20}$ alkaryl, and the carbon atoms of R^1 and R^2 can be optionally substituted with at 20 least one heteroatom selected from O, N, and S, and

wherein the at least one polymer is crosslinked via the second monomers.

25 [0012] In one embodiment, a composition comprising the at least one polymer encapsulating the pigment exhibits enhanced stability relative to a composition comprising a self-dispersed pigment and/or a composition comprising a pigment and a polymeric dispersant having the same monomers, where the polymeric dispersant is not crosslinked.

30 [0013] In one embodiment, an “ethylenically unsaturated” monomer contains a polymerizable $\text{C}=\text{C}$ group. Exemplary ethylenically unsaturated hydrophobic monomers include acrylate and methacrylate acid groups, vinyl

groups, and allyl groups. In one embodiment, the ethylenically unsaturated hydrophobic monomers have the formula $\text{CH}_2=\text{CR}^1\text{R}^2$, wherein R^1 and R^2 are independently selected from H, C₁-C₂₀ alkyl (e.g., C₁-C₁₂ or C₁-C₆ alkyl), C₅-C₂₀ aryl (e.g., C₅-C₁₂ aryl, C₆-C₁₂ aryl, C₅-C₁₀ aryl, C₆-C₁₀ aryl), C₆-C₂₀ aralkyl (aryl-substituted alkyl, e.g., C₆-C₁₂ aralkyl, C₆-C₁₀ aralkyl), and C₆-C₂₀ alkaryl (alkyl-substituted aryl, e.g., C₆-C₁₂ alkaryl, C₆-C₁₀ alkaryl). R^1 and R^2 can be linear or branched. In one embodiment, the carbon atoms of R^1 and R^2 can be optionally substituted with at least one heteroatom selected from O, N, and S. In one embodiment, R^1 and R^2 are independently selected from H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, C₆-C₂₀ aralkyl, and C₆-C₂₀ alkaryl. In another embodiment, R^1 and R^2 are independently selected from H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, and C₆-C₂₀ alkaryl. In yet another embodiment, R^1 and R^2 are independently selected from H, C₅-C₂₀ aryl, and C₆-C₂₀ alkaryl.

[0014] In one embodiment, the ethylenically unsaturated hydrophobic monomers are selected from those containing vinyl groups, e.g., α -olefins. Exemplary monomers containing vinyl groups include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 2-methyl-1-butene, 3,3-dimethyl-1-pentene, 2-methyl-1-heptene, 4,4-dimethyl-1-heptene, 3,3-dimethyl-1-hexene, 4-methyl-1-pentene, isobutylene, di-isobutylene, styrene, α -methyl styrene, and vinyl toluene and mixtures thereof.

[0015] In one embodiment, the ethylenically unsaturated hydrophobic monomers are selected from ethylenically unsaturated esters, e.g., ethylenically unsaturated esters of an aliphatic acid wherein the acid moiety has 3-8 carbon atoms, e.g., 3-6 carbon atoms, and the ester moiety has 1-8, e.g., 1-6 or 1-4 carbon atoms. Exemplary ethylenically unsaturated esters include vinyl acetate, allyl acetate, methyl methacrylate, ethyl acrylate, *n*-butyl acrylate, *n*-butyl methacrylate, *n*-octyl acrylate, benzyl acrylate, acrylonitrile, and, acrylamide. In one embodiment, the first monomers can

comprise two or more different ethylenically unsaturated hydrophobic monomers.

[0016] In one embodiment, the ethylenically unsaturated hydrophobic monomers are selected from styrene, α -methyl styrene, ethylene, propylene, 5 1-butylene, isobutylene, butadiene, methyl vinyl ether. In one embodiment, the ethylenically unsaturated hydrophobic monomers are selected from styrene and α -methyl styrene.

[0017] In one embodiment, the second monomers are selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof.

10 For example, the second monomers can comprise maleic anhydride, or maleic acid, or a mixture of maleic anhydride and maleic acid (and/or salts, esters, imides, and amides thereof). The second monomers can be unsubstituted (other than the portion functionalized with the at least one organic group). Alternatively, the second monomers can be substituted, e.g., 15 with at least one group selected from C₁-C₆ alkyl and halide. Exemplary substituted second monomers include methylmaleic anhydride, dimethylmaleic anhydride, fluoromaleic anhydride, and methylethyl maleic anhydride.

[0018] In one embodiment, the second monomers are present in the at 20 least one polymer in an amount ranging from 10 to 60 mol% relative to the at least one polymer, e.g., an amount ranging from 10 to 50 mol%, from 10 to 40 mol%, from 10 to 35 mol%, from 20 to 60 mol%, from 20 to 50 mol%, from 20 to 40 mol%, from 20% to 35 mol% relative to the at least one polymer. In one embodiment, the at least one polymer comprises the first monomers in 25 an amount ranging from 40 to 90 mol%, from 50 to 90 mol%, 40 to 80 mol%, or from 50 to 80 mol%. In another embodiment, the at least one polymer comprises the first monomers in an amount ranging from 67 to 80 mol% and second monomers in an amount ranging from 20 to 33 mol% relative to the at least one polymer. The at least one polymer can be a random copolymer 30 or alternating copolymer.

[0019] In one embodiment, the first monomers are selected from styrene. In one embodiment, the at least one polymer is selected from styrene-maleic anhydride (SMA) polymers in which a portion of the maleic anhydride monomers are functionalized with the at least one organic group. In one embodiment, the styrene-maleic anhydride polymer can be prepared by the polymerization of styrene or a styrenic monomer and maleic anhydride or derivatives thereof. For example, the styrene-maleic anhydride polymer may be a copolymer of styrene and maleic anhydride. In one embodiment, some or all of the maleic anhydride monomers are hydrolyzed to maleic acid, resulting in a polymer comprising styrene, maleic anhydride, and maleic acid (and salts thereof) monomers. Additional monomers, such as acrylate and methacrylates, may also be present. In one embodiment, the additional monomers are present in low levels. For example, the styrene-maleic anhydride polymers can be a polymer of styrene, maleic anhydride, and an additional monomer having a mole ratio of polymerized styrene and maleic anhydride to other polymerized monomer that is greater than 1/1, such as greater than 5/1, greater than 10/1, and greater than 20/1. Such polymers can be prepared using any method known in the art, including polymerization using a continuous monomer feed as well as using a one-pot polymerization process. In one embodiment, the styrene-maleic anhydride polymer is prepared with a continuous monomer feed method.

[0020] Other examples of styrene-maleic anhydride polymers include functionalized styrene-maleic anhydride polymers (in addition to the portion functionalized with the at least one organic group), which are polymers prepared by the polymerization of styrene and maleic anhydride monomers that have been further reacted, for example, with alcohols to form ester groups or with amines to form amide or imide groups. Specific examples of functionalized styrene-maleic anhydride polymers include polymers comprising styrene monomers and monomers of the half ester or amide of polymerized maleic anhydride (thus comprising monomers comprising

formulas such as $-(\text{CH}(\text{COOH})-\text{CH}(\text{COOR})-$ or $-(\text{CH}(\text{COOH})-\text{CH}(\text{CONR}_2)-$, wherein R is selected from C₁-C₂₀ alkyl, aralkyl, alkaryl, and aryl groups, *e.g.*, selected from C₆-C₁₈, alkyl, aralkyl, and aryl groups. Partially functionalized styrene-maleic anhydride polymers
5 can also be used, in which some, but not all of the polymerized maleic anhydride monomers have been functionalized. Examples of these polymers include styrene-maleic anhydride-maleic acid ester polymers and styrene-maleic anhydride-maleic acid amide polymers. In addition, polymers comprising monomers of polymerized styrene and monomers of the imide of
10 polymerized maleic anhydride may also be used.

[0021] In one embodiment, a portion of the second monomers is functionalized with at least one organic group having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid. In one embodiment, the at least one organic group is capable of binding
15 calcium and/or other divalent metals. In one embodiment, the binding capability of divalent metals can be quantified via calcium index values, as described in U.S. Pat. No. 8,858,695, the disclosure of which is incorporated herein by reference. “Calcium index value” refers to a measure of the ability of an organic group to coordinate or bind calcium ions in solution. The
20 higher the calcium index value, the more strongly or effectively the group can coordinate calcium ions. Calcium index values can also be used to indicate binding capability of other divalent metal ions, *e.g.*, magnesium.

[0022] Calcium index values can be determined by any method known in the art. For example, the calcium index value may be measured with a
25 method in which the amount of calcium coordinated by a compound in a standard solution containing soluble calcium ions and a color indicator is measured using UV-Vis spectroscopy. Alternatively, for compounds having a strong color, the calcium index value may be measured using an NMR method.

[0023] In one embodiment, “calcium index value,” is according to the methods (described in U.S. Pat. No. 8,858,695, *e.g.*, Method A or Method B at col. 29, line 45 to col. 31, line 37, the disclosure of which is incorporated herein by reference. For either method used, a compound was chosen that 5 corresponds to a desired organic group to be tested. In the test compound, the at least one organic group can be bonded to any residue so long as the atoms responsible for binding calcium ions are separated from the residue by at least two bonds. The residue can comprise or consist of hydrogen, a C₁-C₁₀ alkyl (substituted or unsubstituted), or C₄-C₁₈ aryl (substituted or 10 unsubstituted), *e.g.*, the compound to be tested can comprise the organic group bonded to hydrogen, a C₁-C₁₀ alkyl (substituted or unsubstituted), or C₄-C₁₈ aryl (substituted or unsubstituted). For example, for a 15 3,4,5-tricarboxyphenyl functional group and salts thereof, 1,2,3-benzene tricarboxylic acid can be chosen. In this example, the residue is hydrogen and the oxygen atoms of the carboxylic acids are at least two bonds away from the hydrogen residue.

[0024] In one embodiment, reference to the calcium index value means that the value is greater than or equal to that of a reference material. In one embodiment, the reference is phenylphosphonic acid. Thus, the at least one 20 organic group, has a calcium index value that is greater than or equal to the calcium index value of phenyl phosphonic acid. In another embodiment, the reference is 1,2,3-benzene tricarboxylic acid. In one embodiment, the calcium index value is greater than or equal to 2.53, *e.g.*, greater than or equal to 2.8, greater than or equal to 3.0, or greater than or equal to 3.2, as 25 determined using UV-Vis spectroscopy (or method A), as described in more detail below.

[0025] **Method A.** For this method, a series of solutions were prepared at pH 9 that contained 0.087 mM Congo Red indicator, 5 mM cesium chloride, 1 wt% MW350 polyethylene glycol methyl ether, and calcium 30 chloride in concentrations ranging from 0 to 7 mM (0.2, 0.5, 1, 2, 3, 4, 4.5, 5,

6, and 7 mM). The UV-Vis spectra of these solutions were recorded within 1 hour of their preparation using a UV-2501PC. These spectra were used to create a calibration curve relating the absorbance at 520 nm to the calcium concentration.

5 [0026] Test solutions were then prepared at pH 9 that contained 0.087 mM Congo Red indicator, 1 wt% MW350 polyethylene glycol methyl ether, 5mM calcium chloride, and the cesium salt of the compound of interest such that the ion concentration at pH 9 was 5 mM. The uncomplexed calcium concentration was determined by comparison with the calibration curve.

10 The calcium index value was then calculated as $\log_{10}((0.005 - \text{uncomplexed calcium}) / (\text{uncomplexed calcium})^2)$. Measurements were made in duplicate and averaged.

[0027] **Method B.** For compounds that develop a high level of color and are therefore difficult to use in Method A, a second method was developed.

15 For this method, an aqueous solution that was 0.01 M in $^{43}\text{CaCl}_2$, 0.01 M in NaCl, 10 % D₂O and at pH 8 or 9 was prepared from $^{43}\text{CaCO}_3$, HCl/D₂O, NaOH/D₂O, D₂O and water. The pH was chosen to ionize the compound under investigation and to dissolve the compound. A portion of the solution weighing about 0.65 g was added to a 5 mm NMR tube and weighed to the

20 nearest 0.001 g. The chemical shift of the unbound ^{43}Ca was measured using a Bruker Avance II spectrometer with a proton resonance frequency at 400.13 MHz. A 0.2-1.0 M solution of the compound (ligand) under investigation was added in successive increments. After each addition, the ^{43}Ca chemical shift was measured, and δ , the difference between the

25 chemical shift of the sample and that of unbound calcium was calculated. The successive increments were planned such that the L_o/Ca_o ratio was 0.25, 0.5, 1, 2, 3, 4, 6 and 8 where L_o is the total concentration of complexed, protonated and free anions from the ligand and Ca_o is the total concentration of calcium in all species present. The calcium index value

(NMR) was calculated as $\log_{10}(X)$ where X was determined by fitting the parameters X and δ_m in the equation:

$$\delta = \frac{\delta_m}{2} \left\{ [1 + (L_0 / Ca_0) + (1 + H^+ / K_a) / (XCa_0)] - \sqrt{[1 + (L_0 / Ca_0) + (1 + H^+ / K_a) / (XCa_0)]^2 - 4(L_0 / Ca_0)} \right\}$$

so that the RMS difference between the data and the predicted chemical

5 shifts from the equation are minimized where:

δ is the difference in the ^{43}Ca chemical shift of the sample *vs.* that of free aqueous $^{43}\text{Ca}^{2+}$;

δ_m is the calculated difference in the ^{43}Ca chemical shift at infinite L/Ca *vs* that of free $^{43}\text{Ca}^{2+}$;

10 L_0 is the total concentration of complexed, protonated and free anions from the ligand;

Ca_0 is the total concentration of calcium in all species present;

X is a fitting parameter; and

K_a is the proton dissociation constant for the ligand LH.

15 [0028] Without wishing to be bound by any theory, the presently claimed polymer dispersant can lead to improved printing performance as a result of an interaction or binding with calcium salts and/or other divalent metal salts (e.g., magnesium) present in or on the substrate. The divalent metal salts can be a coating on the substrate or subsequently added, such as by 20 printing with a fixer fluid containing metal salts. The initially stable dispersions can rapidly destabilize when in contact with a substrate.

Alternatively, or in addition, destabilization may result from a change in pH on contact with the substrate, which may be advantageous for polymer dispersants comprising the attached functional groups described above. It is 25 believed that the rapid destabilization after printing, caused either by a change in pH, interaction with calcium and/or other divalent metal salts, or mixtures thereof, results in printed images with good overall properties, such as optical density, edge acuity, and/or intercolor bleed.

[0029] In one embodiment, the portion of the second monomers

30 functionalized with the at least one organic group is expressed as mol% of

the total amount of second monomers (sum of functionalized and non-functionalized second monomers). In one embodiment, the portion of the second monomers functionalized with the at least one organic group is at least 3 mol%, *e.g.*, at least 5 mol%, at least 7 mol%, or at least 10 mol%

5 relative to the total amount of second monomers. In one embodiment, the portion of the second monomers functionalized with the at least one organic group is at most 75 mol% of the total second monomers, *e.g.*, at most 60 mol%, at most 50 mol%, or at most 40 mol% of the total amount of second monomers. In one embodiment, the portion of the second monomers

10 functionalized with the at least one organic group ranges from 3 mol% to 75 mol%, *e.g.*, from 5 mol% to 75 mol%, from 3 mol% to 60 mol%, from 5 mol% to 60 mol%, from 3 mol% to 50 mol%, from 5 mol% to 50 mol%, from 3 mol% to 40 mol%, or from 5 mol% to 40 mol% of the total amount of second monomers.

15 [0030] In one embodiment, a portion of the second monomers are functionalized with the at least one organic group via a number of reactions known in the art, *e.g.*, reactions with carboxylic acids and/or anhydrides. In one embodiment, alcohols or amines containing the at least one organic group can react with the maleic anhydride or acid, optionally in the

20 presence of a base where needed. In one embodiment, a primary amine containing the at least one organic group can react with the maleic anhydride or acid in the presence of a base to form an amide group that bonds the at least one organic group to the polymer.

[0031] In one embodiment, the at least one organic group comprises at

25 least one group selected from carboxylic acids, sulfonic acids, phosphonic acids, hydroxyls, amines, and esters, amides, and salts, and esters thereof.

[0032] In one embodiment, the at least one organic group is selected from one or more of:

- at least one phosphonic acid group (e.g., at least two phosphonic acid groups), partial esters thereof, and salts thereof, such as a germinal bisphosphonic acid group, partial esters thereof, and salts thereof;
- at least one heterocyclic group comprising at least one OH group (e.g., at least two OH groups) and salts thereof;
- at least one phosphonic acid group or a salt thereof and at least one second ionic, ionizable, or basic group vicinal or geminal to the phosphonic acid group, and salts thereof;
- an aryl or alkyl polyacid group comprising at least three carboxylic acids;
- a heteroaryl group comprising at least one carboxylic acid group, and salts thereof;
- an aryl group comprising at least one nitroso group and at least one OH group, and salts thereof; and
- an azoarene group comprising at least one OH group, at least one NH₂ group, or at least one OH group and at least one NH₂ group and has the formula Ar¹-N=N-Ar², wherein Ar¹ and Ar², which can be the same or different, are an arylene group or an aryl group and at least one of Ar¹ or Ar² is an arylene group.

20 [0033] In one embodiment, the at least one organic group comprises at least two phosphonic acid groups, esters thereof, or salts thereof.

[0034] In one embodiment, the at least one organic group may comprise at least one geminal bisphosphonic acid group, partial esters thereof, and salts thereof, that is, the at least one organic group may comprise at least two phosphonic acid groups, partial esters thereof, and salts thereof that are directly bonded to the same carbon atom. Such a group may also be referred to as a 1,1-diphosphonic acid group, partial ester thereof, or salt thereof. Thus, for example, the at least one organic group may comprise a group comprising the formula -CQ(PO₃H₂)₂, partial esters thereof, and salts thereof. Q is bonded to the geminal position and may be H, R, OR, SR, or

NR₂ wherein R, which can be the same or different, is H, a C₁-C₁₈ saturated or unsaturated, branched or unbranched alkyl group, a C₁-C₁₈ saturated or unsaturated, branched or unbranched acyl group, an aralkyl group, an alkaryl group, or an aryl group. For example, Q may be H, R, OR, SR, or

5 NR₂, wherein R, which can be the same or different, is H, a C₁-C₆ alkyl group, or an aryl group. In one embodiment, Q is H, OH, or NH₂.

Furthermore, the at least one organic group may comprise a group comprising the formula -(CH₂)_n-CQ(PO₃H₂)₂, partial esters thereof, and salts thereof, wherein Q is as described above and n is 0 to 9, such as 1 to 9,

10 0 to 3, or 1 to 3. In one embodiment, n is either 0 or 1. Also, the at least one organic group may comprise a group comprising the formula

-Y-(CH₂)_n-CQ(PO₃H₂)₂, partial esters thereof, and salts thereof, wherein Q and n are as described above and Y is an arylene, heteroarylene, alkylene, vinylidene, alkarylene, aralkylene, cyclic, or heterocyclic group. In one

15 embodiment, Y is an arylene group, such as a phenylene, naphthalene, or biphenylene group, which may be further substituted with any group, such as one or more alkyl groups or aryl groups. When Y is an alkylene group, examples include, but are not limited to, substituted or unsubstituted alkylene groups, which may be branched or unbranched and can be

20 substituted with one or more groups, such as aromatic groups. Examples include, but are not limited to, C₁-C₁₂ groups like methylene, ethylene, propylene, or butylene, groups.

[0035] Y may be further substituted with one or more groups selected from, but not limited to, R', OR', COR', COOR', OCOR', carboxylates, halogens, CN, NR'₂, SO₃H, sulfonates, sulfates, NR'(COR'), CONR'₂, imides, NO₂, phosphates, phosphonates, N=NR', SOR', NR'SO₂R', and SO₂NR'₂, wherein R' which can be the same or different, is independently hydrogen, branched or unbranched C₁-C₂₀ substituted or unsubstituted, saturated or unsaturated hydrocarbons, *e.g.*, alkyl, alkenyl, alkynyl, substituted or

unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted alkaryl, or substituted or unsubstituted aralkyl.

[0036] In one embodiment, the at least one organic group may comprise a group comprising the formula $-Y-Sp-(CH_2)_n-CQ(PO_3H_2)_2$, partial esters

5 thereof, or salt thereof, wherein Y, Q, and n are as described above. Sp is a spacer group, which, as used herein, is a link between two groups. Sp can be a bond or a chemical group. Examples of chemical groups include, but are not limited to, $-CO_2-$, $-O_2C-$, $-CO-$, $-OSO_2-$, $-SO_3-$, $-SO_2-$, $-SO_2C_2H_4O-$, $-SO_2C_2H_4S-$, $-SO_2C_2H_4NR"-$, $-O-$, $-S-$, $-NR"-$, $-NR"CO-$, $-CONR"-$,
10 $-NR"CO_2-$, $-O_2CNR"-$, $-NR"CONR"-$, $-N(COR")CO-$, $-CON(COR")-$,
 $-NR"COCH(CH_2CO_2R")-$ and cyclic imides therefrom,
 $-NR"COCH_2CH(CO_2R")-$ and cyclic imides therefrom,
 $-CH(CH_2CO_2R")CONR"-$ and cyclic imides therefrom,
 $-CH(CO_2R")CH_2CONR"-$ and cyclic imides therefrom (including phthalimide
15 and maleimides of these), sulfonamide groups (including $-SO_2NR"-$ and
 $-NR"SO_2-$ groups), arylene groups, alkylene groups and the like. R", which
can be the same or different, represents hydrogen or an organic group such
as a substituted or unsubstituted aryl or alkyl group. As shown by the
structure above, a group comprising at least two phosphonic acid groups and
20 salts thereof is bonded to Y through the spacer group Sp. In one
embodiment, Sp is $-CO_2-$, $-O_2C-$, $-O-$, $-NR"CO-$, or $-CONR"-$,
 $-SO_2NR"-$, $-SO_2CH_2CH_2NR"-$, $-SO_2CH_2CH_2O-$, or $-SO_2CH_2CH_2S-$,
wherein R" is H or a C₁-C₆ alkyl group.

[0037] In addition, the at least one organic group may comprise at least

25 one group comprising the formula $-CR=C(PO_3H_2)_2$, partial esters thereof, and salts thereof. R can be H, a C₁-C₁₈ saturated or unsaturated, branched or unbranched alkyl group, a C₁-C₁₈ saturated or unsaturated, branched or unbranched acyl group, an aralkyl group, an alkaryl group, or an aryl group. In one embodiment, R is H, a C₁-C₆ alkyl group, or an aryl group.

[0038] In one embodiment, the at least one organic group may comprise more than two phosphonic acid groups, partial esters thereof, and salts thereof and may, for example comprise more than one type of group (such as two or more) in which each type of group comprises at least two phosphonic acid groups, partial esters thereof, and salts thereof. For example, the at least one organic group may comprise a group comprising the formula $-Y-[CQ(PO_3H_2)_2]p$, partial esters thereof, or salt thereof. Y and Q are as described above. In one embodiment, Y is an arylene, heteroarylene, alkylene, alkarylene, or aralkylene group. In this formula, p is 1 to 4, e.g., p is 2.

[0039] In one embodiment, the at least one organic group may comprise at least one vicinal bisphosphonic acid group, partial ester thereof, and salts thereof, meaning that these groups are adjacent to each other. Thus, the at least one organic group may comprise two phosphonic acid groups, partial esters thereof, and salts thereof bonded to adjacent or neighboring carbon atoms. Such groups are also sometimes referred to as 1,2-diphosphonic acid groups, partial esters thereof, and salts thereof. The group comprising the two phosphonic acid groups, partial esters thereof, and salts thereof may be an aromatic group or an alkyl group, and therefore the vicinal bisphosphonic acid group may be a vicinal alkyl or a vicinal aryl diphosphonic acid group, partial ester thereof, and salts thereof. For example, the at least one organic group may be a group comprising the formula $-C_6H_3-(PO_3H_2)_2$, partial esters thereof, and salts thereof, wherein the acid, ester, or salt groups are in positions ortho to each other.

[0040] In one embodiment, the at least one organic group comprises at least one phosphonic acid group or a salt thereof and at least one second ionic, ionizable, or basic group vicinal or geminal to the phosphonic acid group, and salts thereof.

[0041] In one embodiment, the at least one organic group is selected from $-C(OH)(PO_3H_2)_2$, $-CH_2C(OH)(PO_3H_2)_2$, $-CH_2CH_2C(OH)(PO_3H_2)_2$,

$-\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{OH})(\text{PO}_3\text{H}_2)_2$, $-\text{CH}(\text{PO}_3\text{H}_2)_2$, $-\text{CH}_2\text{CH}(\text{PO}_3\text{H}_2)_2$, partial esters thereof, and salts thereof.

[0042] In one embodiment, the at least one organic group comprises at least one heterocyclic group (e.g., a heteroaryl group) comprising at least one OH group, e.g., at least two OH groups, and salts thereof. The heterocyclic group can be a nitrogen-containing heteroaryl group, such as a pyridinyl group or a quinolinyl group, and the at least one organic group is a hydroxy pyridinyl group or a hydroxy quinolinyl group. The hydroxy group can be positioned on the heteroaryl group such that it is geometrically close to the heteroatom, such as ortho to the heteroatom. Such a group may be in the salt form. For example, the at least one organic group may comprise a 2-hydroxy pyridinyl group or a 2-hydroxy-quinolinyl group, as well as an 8-hydroxy-quinolinyl group and salts thereof. Other isomers or tautomers will also be known to one skilled in the art. In one embodiment, the at least one organic group comprises an 8-hydroxy-quinolinyl group. In addition, the at least one organic group may further comprise additional organic groups, including those described above for Y. For example, electron withdrawing groups, such as chloro or nitro groups, may be included in order to lower the pK_a of the OH group. In one embodiment, the organic group may comprise at least one heterocyclic group (e.g., a heteroaryl group) comprising at least one OH group, and salts thereof.

[0043] In one embodiment, the at least one organic group may also comprise at least one heteroaryl group comprising at least two OH groups. When there are two OH groups, the OH groups can be in positions ortho to each other on the heteroaryl group. When there are more than two OH groups, at least two of the OH groups are in positions ortho to each other on the heteroaryl group. For example, the at least one organic group may be a dihydroxy-pyridinyl group, such as a 2,3-dihydroxy-pyridinyl group (which can also be referred to as a 3-hydroxy-2-pyridonyl group), a 3,4-dihydroxy-pyridinyl group (which can also be referred to as a

3-hydroxy-4-pyridonyl group), a 2,3-dihydroxy-quinolinyl group (which can also be referred to as 3-hydroxy-2-quinolonyl group), or a 3,4-dihydroxy-quinolinyl group (which can also be referred to as a 3-hydroxy-4 quinolonyl group). Other isomers and tautomers will also be 5 known to one skilled in the art.

[0044] In one embodiment, the at least one organic group comprises at least one phosphonic acid group, a partial ester thereof, and salts thereof and at least one second ionic, ionizable group, or basic group. The second group is not a phosphonic acid group or salt thereof. In one embodiment, the 10 second ionic or ionizable group is a carboxylic acid group, a sulfonic acid group, or a salt thereof. In one embodiment, the basic group is a Lewis base, such as an OH group (a hydroxyl group) or an amino group. In one embodiment, these two groups are geminal to each other, by which is meant, are directly bonded to the same carbon atom. Thus, for example, when the 15 second ionic or ionizable group is a carboxylic acid group or salt thereof, the at least one organic group may comprise a group having the formula $-CQ(PO_3H_2)(CO_2H)$ and salts thereof. Q, which is bonded to the geminal position, may be any of those described above. In one embodiment, Q is H. In addition, the at least one organic group may comprise a group having the 20 formula $-(CH_2)_n-CQ(PO_3H_2)(CO_2H)$ and salts thereof, wherein n is 0 to 9, *e.g.*, 0 to 3. Furthermore, the at least one organic group may comprise a group having the formula $-Y-(CH_2)_n-CQ(PO_3H_2)(CO_2H)$ or salt thereof, wherein Y is as described above. In one embodiment, Y is an arylene group. Also, the at least one organic group may comprise a group having the 25 formula $-Y-Sp-(CH_2)_n-CQ(PO_3H_2)(CO_2H)$ or salt thereof, wherein Y and Sp, which is a spacer group, are as described above. In one embodiment, Y is an arylene group.

[0045] In one embodiment, the at least one organic group may comprise at least one phosphonic acid group, a partial ester thereof, and salts thereof 30 and at least one hydroxy group or salt thereof, such as a group having the

formula $-Y-(PO_3H_2)(OH)$ and salts thereof, wherein Y is as described above. In one embodiment, Y is an arylene group and the phosphonic acid group and hydroxy group are in positions ortho to each other. When these groups are geminal, the at least one organic group may comprise at least one group having the formula $-CR(PO_3H_2)(OH)$ and/or salts thereof, wherein R is H or a C₁-C₆ alkyl group. In one embodiment, R is H. Also, the at least one organic group may comprise at least one group having the formula $-(CH_2)_n-CR(PO_3H_2)(OH)$ and salts thereof, wherein n is 0 to 9, e.g., 0 to 3. Furthermore, the at least one organic group may comprise a group having the formulas $-Y-(CH_2)_n-CR(PO_3H_2)(OH)$ and salts thereof or $-Y-Sp-(CH_2)_n-CR(PO_3H_2)(OH)$ and salts thereof, wherein Y and Sp are as described above.

[0046] In one embodiment, the at least one organic group comprises an aryl or alkyl polyacid group having at least three carboxylic acids. In one embodiment, at least two of the carboxylic acid groups are vicinal, meaning that they are bonded to adjacent atoms (e.g., adjacent carbon atoms). For example, the at least one organic group is an aryl polyacid group having at least three carboxylic acids, such as 1,2,3- or 1,2,4-tricarboxylic acid, a 1,2,3,4- or 1,2,4,5-tetra carboxylic acid group.

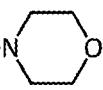
[0047] In one embodiment, the at least one organic group comprises a heteroaryl group having at least one carboxylic acid group or salt thereof. The heteroaryl group may be any of those known in the art. In one embodiment, the heteroaryl group is a nitrogen containing heteroaryl group, such as a pyridinyl group, a pyrimidinyl group, a pyrrolyl group, a quinolinyl group, or a pyrazinyl group. In one embodiment, the at least one organic group comprises two carboxylic acid groups and salts thereof. These acid groups may be anywhere on the heteroaryl ring. In one embodiment, the acid groups can be either ortho or meta to each other. Furthermore, when the heteroaryl group contains at least one nitrogen atom, the two acid groups can be both adjacent to (that is, ortho to) the nitrogen atom. Thus,

for example, the heteroaryl group may be a 2,6-pyridinyl-dicarboxylic acid group.

[0048] In one embodiment, the at least one organic group comprises an aryl group having at least one nitroso group and at least one OH group, or a salt thereof. The two groups may be located anywhere on the aryl group. In one embodiment, the aryl group is a phenyl group and the nitroso and OH groups are in positions ortho to each other. The aryl group may further comprise other substituents, such as alkyl groups, halogen groups, ether groups and the like, including electron withdrawing groups, such as chloro and nitro groups, capable of lowering the pK_a of the at least one organic group, regardless of which tautomeric form it is in. For example, the at least one organic group can be a nitrosophenolic group, such as a group having the formula $-C_6H_3(OH)(NO)$ or a group having the formula $-C_6H_2Z(OH)(NO)$, wherein Z is an electron withdrawing group such as 15 chloro or nitro.

[0049] In one embodiment, the at least one organic group comprises an azoarene group. For example, the at least one organic group may comprise a group having the formula $Ar^1-N=N-Ar^2$, wherein Ar^1 and Ar^2 , which can be the same or different, are an arylene group, such as a phenylene or a 20 naphthylene group, or an aryl group, such as a phenyl group or a naphthyl group, and at least one of Ar^1 or Ar^2 is an arylene group. For this embodiment, the azoarene group has at least one or at least two OH groups, at least one or at least two NH_2 groups, or at least one OH group and at least one NH_2 group. Thus, for example, the azoarene group may have the 25 formula $-(HO)Ar^1-N=N-Ar^2(OH)$ (a *bis*-hydroxy azoarene group), $-(H_2N)Ar^1-N=N-Ar^2(NH_2)$ (a *bis*-amino azoarene group), or $-(HO)Ar^1-N=N-Ar^2(NH_2)$ or $-(H_2N)Ar^1-N=N-Ar^2(OH)$ (an amino-hydroxy azoarene group). Other combinations may also be possible. In one embodiment, the OH and/or NH_2 groups are located at positions ortho to the 30 azo group (the $N=N$ group). For example, the at least one organic group may

be a group having the structure $-(HO)C_6H_3-N=N-C_6H_3(OH)$. Also, electron withdrawing groups, such as chloro or nitro groups, may be included on the aryl and/or arylene groups. For example, the at least one organic group is a group having the structure $-(HO)C_6H_3-N=N-C_6H_3Z(OH)$, wherein Z is an electron withdrawing group such as chloro or nitro.

[0050] In one embodiment, at least a portion of the second monomers are functionalized with at least one organic group (or at least a second portion of the second monomers functionalized with at least one second organic group, for polymers containing at least one organic group having the desired calcium index values) comprising the formula $-A-N(R^3)(R^4)$, wherein R^3 and R^4 are independently selected from H, C₁-C₁₀ alkyl, C₄-C₁₈ aryl, C₄-C₁₈ heteroaryl, and C₃-C₂₀ heterocycloalkyl, and A is selected from C₁-C₁₀ alkylene, C₃-C₂₀ cycloalkylene, C₃-C₂₀ heterocycloalkylene (wherein at least one ring atom of the cycloalkylene is a heteroatom selected from O, N, and S), arylene, heteroarylene (wherein at least one ring atom of the heteroarylene is a heteroatom selected from O, N, and S), and C₂-C₂₀ ether. In another embodiment, at least a portion of the second monomers are functionalized with at least one organic group (or at least a second portion of the second monomers functionalized with at least one second organic group, for polymers containing at least one organic group having the desired calcium index values) comprising the formula selected from -CH₂CH₂-N(CH₃)₂, -CH₂CH₂CH₂-N(CH₃)₂, -CH(CH₃)CH₂-N(CH₃)₂, -CH₂CH₂CH₂CH₂-N(CH₃)₂, -CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂-NHCH₂CH₂OH, -CH₂CH₂CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂-NHCH₂CH₂OH, -CH₂CH₂-N(CH₂CH₂OH)₂, and $-(CH_2)_3-N$ . In yet another embodiment, at least a second portion of the second monomers are functionalized with at least one organic group (or at least a second portion of the second monomers functionalized with at least one second organic group,

for polymers containing at least one organic group having the desired calcium index values) comprising the formula -A-N⁺(R³)(R⁴)(R⁵), wherein R³, R⁴, and R⁵ are independently selected from H, C₁-C₁₀ alkyl, C₄-C₁₈ aryl, C₄-C₁₈ heteroaryl, and C₃-C₂₀ heterocycloalkyl, and A is selected from C₁-C₁₀ alkylene, C₃-C₂₀ cycloalkylene, C₃-C₂₀ heterocycloalkylene, arylene, heteroarylene, and C₂-C₂₀ ether. In any of these embodiments, the at least one organic group is bonded to that portion of the second monomers via amide, imide, and ester linkages, *e.g.*, via amide linkages and ester linkages.

[0051] In one embodiment, the at least one polymer can act as a polymer dispersant to disperse a pigment in a liquid medium (*e.g.*, an aqueous medium). The dispersing can be performed with methods known in the art, *e.g.*, mixing (*e.g.*, with high shear mixer), sonication, milling (*e.g.*, with media or ball mill), *etc.* In one embodiment, crosslinking is performed by adding crosslinking agents to the polymer-dispersed pigment.

[0052] In one embodiment, the composition comprises a pigment that is a polymer-dispersed pigment comprising the at least one polymer adsorbed to or encapsulating the pigment (*e.g.*, a polymer-encapsulated pigment). In another embodiment, the at least one polymer is crosslinked via the second monomers. For example, polymer-encapsulated pigments can comprise polymer-dispersed pigments in which the at least one polymer is crosslinked with various crosslinking agents. The pigment can be any pigment described herein, *e.g.*, a non-modified, or otherwise untreated pigment, or a modified (self-dispersed) pigment.

[0053] In one embodiment, the at least one polymer is crosslinked via at least one linkage selected from amide, ester, ether, and thioether linkages. For example, crosslinking agents such as multifunctional reagents (*e.g.*, difunctional, trifunctional, *etc.*) containing two or more epoxy, thiol, and amine groups, and mixtures thereof can be used to form linkages. In one embodiment, the second monomers (*e.g.*, comprising maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, *etc.*) of at least

two different polymers can react with the crosslinking agents. In one embodiment, the cross-linking agents are selected from epoxy-containing compounds, *e.g.*, di- or tri-epoxy-based compounds, such as trimethylolpropane polyglycidyl ether. In another embodiment, the cross-linking agent is selected from aminoethanethiol.

5 [0054] In one embodiment, the at least one polymer is crosslinked through carboxylate-containing groups of the second monomer, *e.g.*, anhydrides, carboxylic acids and salts, esters, imides, and amides thereof, or carboxylic acids and salts thereof. In one embodiment, the at least one 10 polymer, if containing anhydrides, carboxylic acids and salts, esters, imides, and amides thereof, can be hydrolyzed to generate carboxylic acid or carboxylate, which can be reacted with the crosslinking agent. Hydrolysis can be performed to generate the carboxylic acid or carboxylate either prior to concurrent with addition of the crosslinking agent.

15 [0055] In another embodiment, the at least one polymer is crosslinked through at least 10 % of the carboxylate-containing groups of the second monomer, *e.g.*, 10 % to 50 %, 10 % to 40 %, or 10 % to 30 % of the carboxylate-containing groups of the second monomer. In one embodiment, the number of carboxylate-containing groups targeted for crosslinking 20 ("% CO₂ targeted") can be determined by the amount of crosslinking agent added.

25 [0056] In one embodiment, the at least one polymer, which is crosslinked, has an acid number ("AN(xlink)") of less than 325. In one embodiment, the acid number of the at least one polymer is defined as a theoretical value in relation to the acid number of the starting polymer ("AN(SP)") and the percentage of carboxylate-containing targeted for crosslinking ("% CO₂ targeted") according to the following equation:

$$\text{AN(xlink)} = \text{AN(SP)} - (\% \text{ CO}_2 \text{ targeted}) \times \text{AN(SP)}$$

30 [0057] In one embodiment, the at least one polymer has an acid number AN(xlink) less than 300, less than 275, less than 250, or less than 200. In

another embodiment, the at least one polymer AN(xlink) has an acid number ranging from 50 to 325, *e.g.*, an acid number ranging from 50 to 300, from 50 to 275, from 50 to 250, from 50 to 225, from 50 to 200, from 75 to 325, from 75 to 300, from 75 to 275, from 75 to 250, from 75 to 225, from 75 to 200, from 90 to 325, from 90 to 300, from 90 to 275, from 90 to 250, from 90 to 225, or from 90 to 200.

[0058] In one embodiment, the at least one polymer is present in an amount ranging from 0.1 % to 25 % by weight, *e.g.*, from 0.1 % to 20 % by weight, from 0.2 % to 25 % by weight, from 0.2 % to 20 % by weight, from 0.5 % to 25 % by weight, or from 0.5 % to 20 % by weight relative to the total weight of the inkjet ink composition.

[0059] In one embodiment, the at least one polymer has a weight average molecular weight (M_w) of at least 1000, *e.g.*, at least 2000 or at least 3000 (for the uncrosslinked polymer). In another embodiment, the M_w is less than or equal to 200 000, *e.g.*, less than 150 000, less than 100 000, or less than 70 000. In one embodiment, the M_w ranges from 1000 to 200 000, *e.g.*, from 1000 to 150 000, from 1000 to 100 000, from 1000 to 70 000, from 2000 to 200 000, from 2000 to 150 000, from 2000 to 100 000, from 2000 to 70 000, from 3000 to 200 000, from 3000 to 150 000, from 3000 to 100 000, or from 3000 to 70 000.

[0060] Another embodiment provides a method of making a polymer (*e.g.*, a polymer capable of binding a divalent metal ion, such as a calcium and/or magnesium binding polymer) comprising:

(a) combining:
25 (i) at least one polymer comprising first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, and

(ii) at least one reagent comprising an amino group and at least one organic group having a calcium index value greater than a calcium index value of phenylphosphonic acid; and

(b) forming the polymer.

5 [0061] In one embodiment, the combining is performed in the presence of at least one base selected from NH₄OH, NaOH, and KOH. In one embodiment, the at least one reagent comprises an amino group selected from a primary amine.

10 [0062] Another embodiment provides a method of making a polymer comprising,

(a) combining:

(i) at least one polymer comprising first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof, wherein the ethylenically unsaturated hydrophobic monomers comprise the formula CH₂=CR¹R², where R¹ and R² are independently selected from H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, and C₆-C₂₀ alkaryl, and the carbon atoms of R¹ and R² can be optionally substituted with at least one heteroatom selected from O, N, and S, and

15 (ii) at least one crosslinking agent selected from epoxy-containing compounds; and

(b) forming the polymer.

20 [0063] In one embodiment, any of the methods described herein further comprises combining the polymer with at least one crosslinking agent, *e.g.*, selected from epoxy-containing compounds such as the di- or tri-epoxy-based compounds disclosed herein. In one embodiment, the method comprises combining the polymer with the at least one crosslinking agent and boric acid. In one embodiment, wherein prior to or simultaneous with the 25 combining the at least one polymer with at least one crosslinking agent, the

method further comprises hydrolyzing the at least one polymer. Hydrolysis can be performed by any method known in the art. In one embodiment, hydrolysis generates carboxylic acid or carboxylate groups that can be further reacted with the at least one crosslinking agent.

5 **Pigments**

[0064] In one embodiment, the inkjet ink composition comprises at least one pigment, which can be unmodified or modified. The pigments are solid materials generally in the form of a particulate or in a form readily formed into a particulate, such as a pressed cake. In one embodiment, the modified 10 pigment has attached at least one moiety, *e.g.*, acid groups (and partial salts, partial esters, salts, and esters thereof), and organic groups. In another embodiment, the modified pigment is an oxidized pigment, which can further comprise attached moieties. In one embodiment, the modified pigment is self-dispersible such that an external dispersant is not required 15 for dispersing the pigment (self-dispersed pigments).

[0065] In one embodiment where the pigment is unmodified, the at least one polymer can further function as a dispersant. In one embodiment where the pigment is modified, the at least one polymer can further function as an additive. In either embodiment, the polymer can improve one or more 20 printing performance properties, such as O.D., mottle, and durability.

[0066] The unmodified pigment can be any type of pigment conventionally used by those skilled in the art, such as black pigments and other colored pigments including blue, black, brown, cyan, green, white, violet, magenta, red, orange, or yellow pigments. Mixtures of different 25 pigments can also be used. Representative examples of black pigments include various carbon blacks (Pigment Black 7) such as channel blacks, furnace blacks, gas blacks, and lamp blacks, and include, for example, carbon blacks sold as Regal®, Black Pearls®, Elftex®, Monarch®, Mogul®, and Vulcan® carbon blacks available from Cabot Corporation (such as Black 30 Pearls® 2000, Black Pearls® 1400, Black Pearls® 1300, Black Pearls® 1100,

Black Pearls® 1000, Black Pearls® 900, Black Pearls® 880, Black Pearls® 800, Black Pearls® 700, Black Pearls® 570, Black Pearls® L, Elftex® 8, Monarch® 1400, Monarch® 1300, Monarch® 1100, Monarch® 1000, Monarch® 900, Monarch® 880, Monarch® 800, Monarch® 700, Regal® 660, Mogul® L, Regal® 330, Regal® 400, Vulcan® P). Carbon blacks available from other suppliers can be used. Suitable classes of colored pigments include, for example, anthraquinones, phthalocyanine blues, phthalocyanine greens, diazos, monoazos, pyranthrone, perylenes, heterocyclic yellows, quinacridones, quinolonoquinolones, and (thio)indigoids. Such pigments are commercially available in either powder or press cake form from a number of sources including, BASF Corporation, Engelhard Corporation, Sun Chemical Corporation, Clariant, and Dianippon Ink and Chemicals (DIC). Examples of other suitable colored pigments are described in the Colour Index, 3rd edition (The Society of Dyers and Colourists, 1982). In one embodiment, the pigment is a cyan pigment, such as Pigment Blue 15, Pigment Blue 15:3, Pigment Blue 15:4, or Pigment Blue 60, a magenta pigment, such as Pigment Red 122, Pigment Red 177, Pigment Red 185, Pigment Red 202, or Pigment Violet 19, a yellow pigment, such as Pigment Yellow 74, Pigment Yellow 128, Pigment Yellow 139, Pigment Yellow 155, Pigment Yellow 180, Pigment Yellow 185, Pigment Yellow 218, Pigment Yellow 220, or Pigment Yellow 221, an orange pigment, such as Pigment Orange 168, a green pigment, such as Pigment Green 7 or Pigment Green 36, or black pigment, such as carbon black.

[0067] In one embodiment, the pigment is a high structure carbon black, e.g., a carbon black having the following properties:

OAN \geq 170 mL/100 g; and

a ratio of STSA/BET ranging from 0.7 to 1.

[0068] In one embodiment, the ratio of STSA/BET ranges from 0.8 to 1, e.g., from 0.9 to 1. In one embodiment, the carbon black has an STSA ranging from 160 to 220 m²/g. In another embodiment, the carbon black has

a BET surface area of at least 150 m²/g, *e.g.*, at least 170 m²/g, at least 190 m²/g ranging from 190 to 275 m²/g. In another embodiment, the carbon black has a compressed OAN (COAN) of at least 120 mL/100 g, *e.g.*, a COAN of at least 130 mL/100 g. OAN and COAN can be determined according to 5 ASTM-D2414. Surface area measurements can be determined according to ASTM-D6556. Additional details on such carbon black can be found in U.S. Pat. No. 9,388,300, the disclosure of which is incorporated herein by reference.

[0069] In one embodiment, the self-dispersed pigment is an oxidized 10 carbon black. In one embodiment, “oxidized carbon blacks” are carbon black pigments generally having a pH < 7.0 that feature surface-bound ionic or ionizable groups such as one or more of alcohols (phenols, naphthols), lactones, carbonyls, carboxyls (*e.g.*, carboxylic acids), anhydrides, ethers, and quinones. The extent of oxidation of carbon black can determine the 15 surface concentration of these groups. In one embodiment, the oxidized carbon black is obtained by oxidizing an unmodified carbon black, *e.g.*, pigments selected from channel blacks, furnace blacks, gas blacks, and lamp blacks. Exemplary unmodified carbon blacks include those commercially available from Cabot Corporation as Regal®, Black Pearls®, Elftex®, 20 Monarch®, Mogul®, and Vulcan®, such as Black Pearls® 1100, Black Pearls® 900, Black Pearls® 880, Black Pearls® 800, Black Pearls® 700, Black Pearls® 570, Elftex® 8, Monarch® 900, Monarch® 880, Monarch® 800, Monarch® 700, Regal® 660, and Regal® 330. Exemplary oxidizing agents for carbon blacks 25 include oxygen gas, ozone, peroxides such as hydrogen peroxide, persulfates such as sodium and potassium persulfate, hypohalites such as sodium hypochlorite, nitric acid, and transition metal-containing oxidants such as permanganate salts, osmium tetroxide, chromium oxides, ceric ammonium nitrates, and mixtures thereof (*e.g.*, mixtures of gaseous oxidants such as oxygen and ozone).

[0070] In another embodiment, the oxidized carbon black is obtained from commercial sources, such as Black Pearls® 1400, Black Pearls® 1300, Black Pearls® 1000, Black Pearls® L, Monarch® 1000, Mogul® L, and Regal® 400, available commercially from Cabot Corporation.

5 [0071] In one embodiment, the pigment has attached at least one organic group where an “attached” organic group can be distinguished from an adsorbed group in that a soxhlet extraction for several hours (*e.g.*, at least 4, 6, 8, 12, or 24 hours) will not remove the attached group from the pigment. In another embodiment, the organic group is attached to the pigment if the

10 organic group cannot be removed after repeated washing with a solvent or solvent mixture that can dissolve the starting organic treating material but cannot disperse the treated pigment. In yet another embodiment, “attached” refers to a bond such as a covalent bond, *e.g.*, a pigment bonded or covalently bonded to a nucleophile or organic group.

15 [0072] The arylene, heteroarylene, and alkylene can be unsubstituted or substituted. Exemplary arylenes include phenylene, naphthylene, and biphenylene, and exemplary heteroarylenes include phenylene, naphthylene, and biphenylene having a ring carbon substituted with one or more oxygen or nitrogen atoms. In one embodiment, the arylene is a C₅-C₂₀ arylene. Heteroarylenes can be an arylene as defined herein which one or more ring carbon atoms is replaced with a heteroatom, *e.g.*, N, O, and S. The heteroatom can be bonded to other groups in addition to being a ring atom. Alkylenes may be branched or unbranched. The alkylene may be a C₁-C₁₂ alkylene such as methylene, ethylene, propylene, or butylene.

20 [0073] In one embodiment, the pigment (carbon black or colored pigment) is modified with at least one organic group via a diazonium treatment as detailed, for instance, in the following patents: U.S. Patent Nos. 5,554,739; 5,630,868; 5,672,198; 5,707,432; 5,851,280; 5,885,335; 5,895,522; 5,900,029; 5,922,118; 6,042,643; 6,506,245, 6,534,569; 6,641,653, 25 7,223,302, 6,398,858 and 6,494,943 (high shear conditions) 6,372,820;

6,368,239; 6,350,519; 6,337,358; 6,103,380; 7,173,078; 7,056,962; 6,942,724; 6,929,889; 6,911,073; 6,478,863; 6,472,471; WO 2011/143533; and 8,858,695, the disclosures of which are incorporated herein by reference. In one embodiment, the attachment is provided via a diazonium reaction where the 5 at least one organic group has a diazonium salt substituent. In another embodiment, the direct attachment can be formed by using the diazonium and stable free radical methods described, for instance, in U.S. Patent Nos. 6,068,688; 6,337,358; 6,368,239; 6,551,393; 6,852,158, the disclosures of which are incorporated herein by reference, which makes use of reacting at 10 least one radical with at least one particle, wherein a radical is generated from the interaction of at least one transition metal compound with at least one organo-halide compound in the presence of one or more particles capable of radical capture, and the like. In yet another embodiment, the pigment (carbon black or colored pigment) can be modified (e.g., to attach organic 15 groups) by using the methods of U.S. Pat. Nos. 5,837,045, 6,660,075 and WO 2009/048564 (reaction with organic compounds containing a C--C double bond or triple bond activated by at least one substituent) or U.S. Pub. No. 2004/0171725, 6,664,312, 6,831,194 (reaction with anhydride component), 6,936,097, U.S. Pub. Nos. 2001/0036994, 2003/0101901 20 (reaction with organic groups having $-N=N-N-$ group), Canadian Patent No. 2,351,162, European Patent No. 1394221, and PCT Publication Nos. WO 01/51566 (reaction between at least one electrophile and at least one nucleophile), WO 04/63289, WO 2010/141071 (reaction with H_2N-A-Y where A is a heteroatom), and WO 99/23174, the disclosures of which are 25 incorporated herein by reference.

[0074] In one embodiment, the dispersion can be formulated to provide an amount of pigment such that the final amount in the inkjet ink composition is effective to provide the desired image quality (for example, optical density) without detrimentally affecting the performance of the 30 inkjet ink. In one embodiment, the colorant (e.g., a pigment) is present in an

amount ranging from 1 % to 15 % by weight, *e.g.*, from 1 % to 10 % by weight, relative to the total weight of the composition, *e.g.*, an amount ranging from 2 % to 10 % by weight, from 3 % to 10 % by weight, from 2 % to 7 % by weight, or from 3 % to 7 % by weight, relative to the total weight of 5 the composition.

Dispersions and Inkjet Ink Compositions

[0075] In one embodiment, the dispersion is an aqueous dispersion such as an inkjet ink composition, *e.g.*, comprising a liquid vehicle. In one embodiment, the dispersion or inkjet ink composition comprises at least 10 40 % water, *e.g.*, at least 45 % water or at least 50 % water.

[0076] In one embodiment, the dispersion or inkjet ink composition comprises at least one organic solvent present in an amount ranging from 1 % to 50 % relative to the total weight of the inkjet ink composition, or present in other amounts as disclosed herein. In one embodiment, the 15 organic solvent is soluble or miscible in water. In another embodiment, the organic solvent is chemically stable to aqueous hydrolysis conditions (*e.g.*, reaction with water under heat aging conditions, including, for example, the hydrolysis of esters and lactones). In one embodiment, the organic solvent has a dielectric constant below that of water, such as a dielectric constant 20 ranging from about 10 to about 78 at 20 °C. Examples of suitable organic solvents include low molecular-weight glycols (such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, triethylene glycol monomethyl or monoethyl ether, diethylene glycol 25 monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, and tetraethylene glycol monobutyl ether); alcohols (such as ethanol, propanol, *iso*-propyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol, and *tert*-butyl alcohol, 2-propyn-1-ol (propargyl alcohol), 2-buten-1-ol, 3-buten-2-ol, 3-butyn-2-ol, and cyclopropanol); diols containing from about 2 30 to about 40 carbon atoms (such as 1,3-pentanediol, 1,4-butanediol,

1,5-pentanediol, 1,4-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 2,6-hexanediol, neopentylglycol (2,2-dimethyl-1,3-propanediol), 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2,6-hexanetriol, and poly(ethylene-co-propylene) glycol, as well as their 5 reaction products with alkylene oxides, including ethylene oxides, including ethylene oxide and propylene oxide); triols containing from about 3 to about 40 carbon atoms (such as glycerine (glycerol), trimethylolethane, trimethylolpropane, 1,3,5-pantanetriol, 1,2,6-hexanetriol, and the like as well as their reaction products with alkylene oxides, including ethylene 10 oxide, propylene oxide, and mixtures thereof); polyols (such as pentaerythritol); amides (such as dimethyl formaldehyde and dimethyl acetamide); ketones or ketoalcohols (such as acetone and diacetone alcohol); ethers (such as tetrahydrofuran and dioxane); lactams (such as 2-pyrrolidone, *N*-methyl-2-pyrrolidone, and ϵ -caprolactam); ureas or urea 15 derivatives (such as di-(2-hydroxyethyl)-5,5,-dimethyl hydantoin (dantacol) and 1,3-dimethyl-2-imidazolidinone); inner salts (such as betaine); and hydroxyamide derivatives (such as acetylethanolamine, acetylpropanolamine, propylcarboxyethanolamine, and propylcarboxy 20 propanolamine, as well as their reaction products with alkylene oxides). Additional examples include saccharides (such as maltitol, sorbitol, gluconolactone and maltose); sulfoxide derivatives (symmetric and 25 asymmetric) containing from about 2 to about 40 carbon atoms (such as dimethylsulfoxide, methylethylsulfoxide, and alkylphenyl sulfoxides); and sulfone derivatives (symmetric and asymmetric) containing from about 2 to about 40 carbon atoms (such as dimethylsulfone, methylethylsulfone, sulfolane (tetramethylenesulfone, a cyclic sulfone), dialkyl sulfones, alkyl phenyl sulfones, dimethylsulfone, methylethylsulfone, diethylsulfone, ethylpropylsulfone, methylphenylsulfone, methylsulfolane, and 30 dimethylsulfolane). The organic solvent can comprise mixtures of organic solvents.

[0077] The amount of the solvent can be varied depending on a variety of factors, including the properties of the solvent (solubility and/or dielectric constant), the type of colorant, and the desired performance of the resulting inkjet ink composition. The solvent may be used in amounts ranging from

5 1 % to 40 % by weight based on the total weight of the inkjet ink composition, including amounts ranging from 1 % to 30 %, or amounts ranging from 1 % to 20 %. In another embodiment, the amount of the solvent is greater than or equal to about 2 % by weight based on the total weight of the aqueous dispersion or inkjet ink composition, including

10 greater than or equal to about 5 % and greater than or equal to about 10 % by weight.

[0078] In one embodiment, an ink composition (e.g., an inkjet ink composition) comprises at least one surfactant, e.g., when the pigment is not self-dispersible. The at least one surfactant can enhance the colloidal stability of the composition or change the interaction of the ink with either the printing substrate, such as printing paper, or with the ink printhead. Various anionic, cationic and nonionic dispersing agents can be used in conjunction with the ink composition of the present invention, and these may be used neat or as a water solution. In one embodiment, the surfactant is present in an amount ranging from 0.05 % to 5 %, e.g., an amount ranging from 0.1 % to 5 %, or from 0.5 % to 2 %, by weight relative to the total weight of the inkjet ink composition.

[0079] Representative examples of anionic dispersants or surfactants include, but are not limited to, higher fatty acid salts, higher alkylidicarboxylates, sulfuric acid ester salts of higher alcohols, higher alkyl-sulfonates, alkylbenzenesulfonates, alkynaphthalene sulfonates, naphthalene sulfonates (Na, K, Li, Ca, etc.), formalin polycondensates, condensates between higher fatty acids and amino acids, dialkylsulfosuccinic acid ester salts, alkylsulfosuccinates, naphthenates, alkylether carboxylates, acylated peptides, α -olefin sulfonates,

N-acrylmethyl taurine, alkylether sulfonates, secondary higher alcohol ethoxysulfates, polyoxyethylene alkylphenylether sulfates, monoglycylsulfates, alkylether phosphates and alkyl phosphates, alkyl phosphonates and bisphosphonates, included hydroxylated or aminated derivatives. For example, polymers and copolymers of styrene sulfonate salts, unsubstituted and substituted naphthalene sulfonate salts (e.g. alkyl or alkoxy substituted naphthalene derivatives), aldehyde derivatives (such as unsubstituted alkyl aldehyde derivatives including formaldehyde, acetaldehyde, propylaldehyde, and the like), maleic acid salts, and mixtures thereof may be used as the anionic dispersing aids. Salts include, for example, Na^+ , Li^+ , K^+ , Cs^+ , Rb^+ , and substituted and unsubstituted ammonium cations. Representative examples of cationic surfactants include aliphatic amines, quaternary ammonium salts, sulfonium salts, phosphonium salts and the like.

[0080] Representative examples of nonionic dispersants or surfactants that can be used in ink jet inks of the present invention include fluorine derivatives, silicone derivatives, acrylic acid copolymers, polyoxyethylene alkyl ether, polyoxyethylene alkylphenyl ether, polyoxyethylene secondary alcohol ether, polyoxyethylene styrol ether, ethoxylated acetylenic diols, polyoxyethylene lanolin derivatives, ethylene oxide derivatives of alkylphenol formalin condensates, polyoxyethylene polyoxypropylene block polymers, fatty acid esters of polyoxyethylene polyoxypropylene alkylether polyoxyethylene compounds, ethylene glycol fatty acid esters of polyethylene oxide condensation type, fatty acid monoglycerides, fatty acid esters of polyglycerol, fatty acid esters of propylene glycol, cane sugar fatty acid esters, fatty acid alkanol amides, polyoxyethylene fatty acid amides and polyoxyethylene alkylamine oxides. For example, ethoxylated monoalkyl or dialkyl phenols may be used. These nonionic surfactants or dispersants can be used alone or in combination with the aforementioned anionic and cationic dispersants.

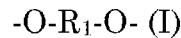
[0081] In one embodiment, the inkjet ink composition comprises the polymers disclosed herein as a first polymer and further comprises a second polymer that is a polymeric dispersant, *e.g.*, a natural polymer or a synthetic polymer dispersant. Specific examples of natural polymer dispersants 5 include proteins such as glue, gelatin, casein and albumin; natural rubbers such as gum arabic and tragacanth gum; glucosides such as saponin; alginic acid, and alginic acid derivatives such as propyleneglycol alginate, triethanolamine alginate, and ammonium alginate; and cellulose derivatives such as methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose 10 and ethylhydroxy cellulose. Specific examples of polymeric dispersants, including synthetic polymeric dispersants, include polyvinyl alcohols, polyvinylpyrrolidones, acrylic or methacrylic resins (often written as "(meth)acrylic") such as poly(meth)acrylic acid, acrylic acid-(meth)acrylonitrile copolymers, potassium 15 (meth)acrylate-(meth)acrylonitrile copolymers, vinyl acetate-(meth)acrylate ester copolymers and (meth)acrylic acid-(meth)acrylate ester copolymers; styrene-acrylic or methacrylic resins such as styrene-(meth)acrylic acid copolymers, styrene-(meth)acrylic acid-(meth)acrylate ester copolymers, styrene- α -methylstyrene-(meth)acrylic acid copolymers, 20 styrene- α -methylstyrene-(meth)acrylic acid-(meth)acrylate ester copolymers; vinyl naphthalene-acrylic or methacrylic acid copolymers; vinyl naphthalene-maleic acid copolymers; and vinyl acetate copolymers such as vinyl acetate-ethylene copolymer, vinyl acetate-fatty acid vinyl ethylene copolymers, vinyl acetate-maleate ester copolymers, vinyl acetate-crotonic acid copolymer and vinyl acetate-acrylic acid copolymer; and salts thereof. 25

[0082] In one embodiment, the inkjet ink composition has a viscosity ranging from 1-25 cP. It is understood that viscosity can be adjusted by a variety of methods. In one embodiment, polymeric binders can be used in conjunction with the inkjet ink composition disclosed herein to adjust the 30 viscosity of the composition and/or provide other desirable properties, such

as durability (e.g., at least one durability polymer). Suitable polymeric binders include, but are not limited to, water soluble polymers and copolymers such as gum arabic, polyacrylate salts, polymethacrylate salts, polyvinyl alcohols (Elvanol® polyvinyl alcohol from DuPont, Selvol™ from 5 Sekisui Specialty Chemicals), hydroxypropylenecellulose, hydroxyethylcellulose, polyvinylpyrrolidinone (such as Luvitec®, polyvinylpyrrolidinone and Kollidon® polyvinylpyrrolidinone from BASF), polyvinylether, starch, polysaccharides, polyethyleneimines with or without being derivatized with ethylene oxide and propylene oxide; the Jeffamine® 10 polyetheramines (Huntsman); and the like. Additional examples of water-soluble polymer compounds include various dispersants or surfactants described above, including, for example, styrene-acrylic acid copolymers (such as Joncryl® resins from BASF), styrene-acrylic acid-alkyl acrylate terpolymers, styrene-methacrylic acid copolymers (such as Joncryl® resins 15 from BASF), styrene-maleic acid-alkyl acrylate terpolymers, styrene-methacrylic acid-alkyl acrylate terpolymers, styrene-maleic acid half ester copolymers, vinyl naphthalene-acrylic acid copolymers, alginic acid, polyacrylic acids or their salts and their derivatives. In addition, the binder may be added or present in dispersion or latex form. For example, 20 the polymeric binder may be a latex of acrylate or methacrylate copolymers (such as NeoCryl® resins from Koninklijke DSM N.V., the AC and AS polymers from Alberdingk-Boley) or may be a water dispersible polyurethane (such as ABU polymers from Alberdingk-Boley) or polyester (such as Eastman AQ™ polymers from Eastman Chemical). Polymers, such 25 as those listed above, and variations and related materials that can be used for binders in inkjet inks are included in the Ethacryl® dispersants from Lyondell Chemical Company, the Joncryl® resins from BASF, the NeoCryl® resins from Koninklijke DSM N.V., and the AC and AS polymers Alberdingk-Boley.

[0083] In one embodiment, the polymeric binders are selected from polyurethanes. Exemplary polyurethanes include those that comprise at least one polyether and at least one diisocyanate. In one embodiment, the at least one polyether comprises a monomer having the formula (I):

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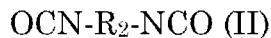


wherein R_1 can be substituted or unsubstituted and is selected from $\text{C}_1\text{-C}_{10}$ alkylene, $\text{C}_3\text{-C}_{20}$ cycloalkylene, $\text{C}_3\text{-C}_{20}$ heterocycloalkylene (at least one ring atom being a heteroatom selected from O, N, and S), $\text{C}_5\text{-C}_{20}$ arylene, $\text{C}_3\text{-C}_{20}$ heteroarylene (at least one ring atom being a heteroatom selected from O,

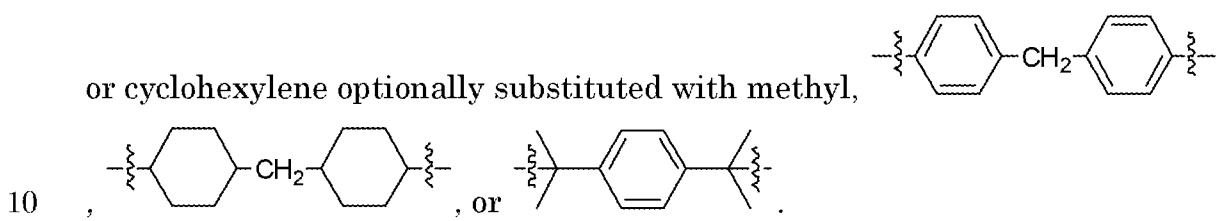
10 N, and S), $\text{C}_6\text{-C}_{20}$ alkylarylene, a polyether moiety, and combinations thereof. In one embodiment, R_1 is unsubstituted. In one embodiment, R_1 is substituted with at least one substituent selected from $\text{C}_1\text{-C}_{10}$ alkyl and $\text{C}_5\text{-C}_{20}$ aryl groups. In one embodiment, R_1 is selected from a polyether moiety, *e.g.*, polyethylene glycol moiety, a polypropylene glycol moiety, a

15 polytetramethyleneoxide moiety, and combinations thereof. In one embodiment, the at least one polyether is formed from a diol monomer, *e.g.*, via polymerization of diol monomers. Exemplary diol monomers include $\text{C}_1\text{-C}_{10}$ alkylene diols such as propylene glycol, polytetramethyleneoxide diol, 1,6-hexanediol, 1,5-pentanediol, and 2-butyl-2-ethylpropyl diol. In another 20 embodiment, the diol monomer comprises the monomer of formula (I), *e.g.*, the diol monomer is a $\text{C}_1\text{-C}_{10}$ polyalkylene glycol, a polyether glycol, or any other diols consistent with formula (I). In one embodiment, the at least one polyether is polypropylene glycol, such as polypropylene glycols having a 25 number average molecular weight ranging from 400 g/mol to 6000 g/mol. In one embodiment, the at least one polyether is present in an amount ranging from 30 % to 95 % by weight relative to the polyurethane.

[0084] In one embodiment, the at least one diisocyanate has the formula (II):

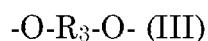


wherein R₂ can be substituted or unsubstituted and is selected from C₁-C₁₀ alkylene, C₃-C₂₀ cycloalkylene, C₃-C₂₀ heterocycloalkylene (at least one ring atom being a heteroatom selected from O, N, and S), C₅-C₂₀ arylene, C₃-C₂₀ heteroarylene (at least one ring atom being a heteroatom selected from O, N, and S), and combinations thereof. In one embodiment, R₂ is unsubstituted. In one embodiment, R₂ is substituted with at least one substituent selected from C₁-C₁₀ alkyl and C₅-C₂₀ aryl groups. For example, R₂ can be hexamethylene or phenylene optionally substituted with methyl, or cyclohexylene optionally substituted with methyl,



[0085] In one embodiment, the at least one diisocyanate is selected from toluene diisocyanates such as toluene 2,4-diisocyanate (2,4-TDI) and toluene 2,6-diisocyanate (2,6-TDI), hexamethylene diisocyanate (HDI), 4,4'-methylene diphenyl diisocyanate (4,4'-MDI), 2,4'-methylene diphenyl diisocyanate (2,4'-MDI), 2,2'-methylene diphenyl diisocyanate (2,2'-MDI), methylene bis(4-cyclohexyl diisocyanate) (HDMI), *m*-tetramethylxylene diisocyanate (*m*-TMXDI), and isophorone diisocyanate (IPDI). In one embodiment, the diisocyanate is selected from toluene diisocyanates (e.g., toluene 2,4-diisocyanate, toluene 2,6-diisocyanate), isophorone diisocyanate, and combinations thereof. In one embodiment, the at least one diisocyanate is present in an amount ranging from 3 % to 50 % by weight, relative to the polyurethane.

[0086] In one embodiment, in addition to the at least one polyether and the at least one diisocyanate, the at least one polyurethane further comprises a monomer containing at least one hydrophilic group. In one embodiment, the monomer containing at least one hydrophilic group has the formula (III):



wherein R₃ comprises the at least one hydrophilic group bonded to a moiety, which can be substituted or unsubstituted, selected from C₁-C₁₀ alkylene, C₃-C₂₀ cycloalkylene, C₃-C₂₀ heterocycloalkylene (at least one ring atom being a heteroatom selected from O, N, and S), C₅-C₂₀ arylene, C₃-C₂₀ heteroarylene (at least one ring atom being a heteroatom selected from O, N, and S), C₆-C₂₀ alkylarylene. In one embodiment, a “hydrophilic group” is capable of hydrogen bonding with water. In one embodiment, the at least one hydrophilic group is selected from hydroxyls, carboxylic acids, sulfonic acids, phosphonic acids, polyethers (e.g., a polyethylene glycol, polypropylene glycol, etc.), and salts and ethers thereof. In one embodiment, the at least one hydrophilic group is selected from carboxylic acids, and salts and ethers thereof. In one embodiment, the R₃ moiety is unsubstituted. In another embodiment, the R₃ moiety is substituted with at least one substituent selected from C₁-C₁₀ alkyl and C₅-C₂₀ aryl groups. One exemplary monomers of formula (III) is dimethylolpropionic acid (DMPA).

[0087] In one embodiment, the molar ratio between the at least one diisocyanate and a polyol or diol-based monomer in the polyurethane ranges from 0.5:1 to 3:1. In another embodiment, the at least one polyurethane is characterized by an NCO/OH ratio, which is the ratio of the molar amount of isocyanate groups / molar amount of the hydroxyl groups from all diol monomers, e.g., the at least one polyether alone, or if present, the sum of the at least one polyether and the monomer containing at least one hydrophilic group. In one embodiment, the NCO/OH ratio ranges from 0.85 to 1.15, e.g., from 0.85 to 1.1, from 0.9 to 1.15, or from 0.9 to 1.1.

[0088] In one embodiment, the at least one polyurethane has an acid number corresponding to the amount of monomer containing at least one hydrophilic group, e.g., a carboxylic acid group, or any hydrophilic group disclosed herein. For example, the acid number (AN(PU)) of the at least one polyurethane can be calculated from the following equation:

AN(PU) = (no. mol of monomer containing hydrophilic group \times 56.1 mgKOH \times 1000) / (the total mass (g) of monomers

[0089] In one embodiment, the at least one polyurethane has an acid number ranging from 10 to 100 mg KOH/g polyurethane, *e.g.*, from 10 to 80, from 10 to 70, from 10 to 60, from 10 to 50, from 10 to 40, from 10 to 35, from 15 to 100, from 15 to 80, from 15 to 70, from 15 to 60, from 15 to 50, from 15 to 40, from 15 to 35, from 20 to 100, from 20 to 80, from 20 to 70, from 20 to 60, from 20 to 50, from 20 to 40, or ranging from 20 to 35 mg KOH/g polyurethane.

10 [0090] In one embodiment, the inkjet ink further comprises at least one water-soluble compound having a hydroxyl number of at least 80, wherein the at least one water-soluble compound is selected from ethoxylated C₃-C₂₀ polyols, such as ethoxylated triols, ethoxylated tetraols, ethoxylated pentaols, and ethoxylated hexaols. In one embodiment, the ethoxylated C₃-C₂₀ polyols are selected from ethoxylated glycerol, ethoxylated pentaerythritol, ethoxylated trimethylolpropane, ethoxylated glucoside, and ethoxylated glucose. In another embodiment, the at least one water-soluble compound is selected from polyols having three or more hydroxyl groups (*e.g.*, xylitol and sorbitol), and polyether polyols. The at least one water-soluble compound can be present in an amount ranging from 1 % to by 60 % weight, relative to the total weight of the inkjet ink composition.

15 [0091] Exemplary rheological additives to adjust the viscosity of an inkjet ink composition include, but are not limited to, alkali swellable emulsions (such as Rheovis® AS rheology-control additive from BASF), hydrophobically modified alkali swellable emulsions (such as Rheovis® HS rheology-control additive from BASF), hydrophobically modified polyurethanes (such as Rheovis® PU rheology-control additive from BASF), and hydrophobically modified polyethers (such as Rheovis® PE rheology-control additive from BASF).

[0092] In one embodiment, the inkjet ink compositions may further comprise dyes to modify color balance and adjust optical density.

Exemplary dyes include food dyes, FD&C dyes, acid dyes, direct dyes, reactive dyes, derivatives of phthalocyanine sulfonic acids, including copper phthalocyanine derivatives, sodium salts, ammonium salts, potassium salts, and lithium salts.

[0093] In one embodiment, the inkjet ink composition comprises one or more polymers selected from polymeric dispersants and polymeric binders, as disclosed herein, in an amount ranging from 0.1 % to 20 % by weight

10 relative to the total weight of the composition, *e.g.*, an amount ranging from 0.1 % to 10 %, from 0.1 % to 5 %, from 0.2 % to 20 %, from 0.2 % to 10 %, from 0.2 % to 5 %, from 0.5 % to 20 %, from 0.5 % to 10 %, or from 0.5 % to 5 % by weight relative to the total weight of the composition.

[0094] In one embodiment, in addition to the surfactant, the inkjet ink

15 compositions can further comprise one or more suitable additives to impart a number of desired properties while maintaining the stability of the compositions. Other additives are well known in the art and include humectants, biocides and fungicides, pH control agents, drying accelerators, penetrants, and the like. The amount of a particular additive will vary
20 depending on a variety of factors but are generally present in an amount ranging between 0.01 % and 40 % based on the weight of the inkjet ink composition. In one embodiment, the at least one additive is present in an amount ranging from 0.05 % to 5 %, *e.g.*, an amount ranging from 0.1 % to 5 %, or an amount ranging from 0.5 % to 2 %, by weight relative to the total
25 weight of the inkjet ink composition

[0095] Humectants and water soluble organic compounds other than the at least one organic solvent may also be added to the inkjet ink composition of the present invention, *e.g.*, for the purpose of preventing clogging of the nozzle as well as for providing paper penetration (penetrants), improved

30 drying (drying accelerators), and anti-cockling properties. In one

embodiment, the humectant and/or water soluble compound is present in an amount ranging from 0.1 % to 50 %, *e.g.*, an amount ranging from 1 % to 50 %, from 0.1 % to 30 %, from 1 % to 30 %, from 0.1 % to 10 %, or from 1 % to 10 %.

5 [0096] Specific examples of humectants and other water soluble compounds that may be used include low molecular-weight glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol and dipropylene glycol; diols containing from about 2 to about 40 carbon atoms, such as 1,3-pentanediol, 1,4-butanediol, 1,5-pentanediol,

10 1,4-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 2,6-hexanediol, neopentylglycol (2,2-dimethyl-1,3-propanediol), 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2,6-hexanetriol, poly(ethylene-co-propylene) glycol, and the like, as well as their reaction products with alkylene oxides, including ethylene oxide, including ethylene oxide and propylene oxide; triol derivatives containing from about 3 to about 15 40 carbon atoms, including glycerine, trimethylolpropane, 1,3,5-pentanetriol, 1,2,6-hexanetriol, and the like as well as their reaction products with alkylene oxides, including ethylene oxide, propylene oxide, and mixtures thereof; neopentylglycol, (2,2-dimethyl-1,3-propanediol), and the like, as well as their reaction products with alkylene oxides, including 20 ethylene oxide and propylene oxide in any desirable molar ratio to form materials with a wide range of molecular weights; thiodiglycol; pentaerythritol and lower alcohols such as ethanol, propanol, *iso*-propyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol, and *tert*-butyl alcohol,

25 2-propyn-1-ol (propargyl alcohol), 2-buten-1-ol, 3-buten-2-ol, 3-butyn-2-ol, and cyclopropanol; amides such as dimethyl formaldehyde and dimethyl acetamide; ketones or ketoalcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; cellosolves such as ethylene glycol monomethyl ether and ethylene glycol monoethyl ether, triethylene glycol monomethyl (or monoethyl) ether; carbitols such as diethylene glycol

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monomethyl ether, diethylene glycol monoethyl ether, and diethylene glycol monobutyl ether; lactams such as 2-pyrrolidone, *N*-methyl-2-pyrrolidone and ϵ -caprolactam; urea and urea derivatives; inner salts such as betaine, and the like; thio (sulfur) derivatives of the aforementioned materials

5 including 1-butanethiol; *t*-butanethiol 1-methyl-1-propanethiol, 2-methyl-1-propanethiol; 2-methyl-2-propanethiol; thiocyclopropanol, thioethyleneglycol, thiodiethyleneglycol, trithio- or dithio-diethyleneglycol, and the like; hydroxyamide derivatives, including acetylethanolamine, acetylpropanolamine, propylcarboxyethanolamine, propylcarboxy

10 propanolamine, and the like; reaction products of the aforementioned materials with alkylene oxides; and mixtures thereof. Additional examples include saccharides such as maltitol, sorbitol, gluconolactone and maltose; polyhydric alcohols such as trimethylol propane and trimethylol ethane; *N*-methyl-2-pyrrolidone; 1,3-dimethyl-2-imidazolidinone; sulfoxide

15 derivatives containing from about 2 to about 40 carbon atoms, including dialkylsulfides (symmetric and asymmetric sulfoxides) such as dimethylsulfoxide, methylethylsulfoxide, alkylphenyl sulfoxides, and the like; and sulfone derivatives (symmetric and asymmetric sulfones) containing from about 2 to about 40 carbon atoms, such as dimethylsulfone,

20 methylethylsulfone, sulfolane (tetramethylenesulfone, a cyclic sulfone), dialkyl sulfones, alkyl phenyl sulfones, dimethylsulfone, methylethylsulfone, diethylsulfone, ethylpropylsulfone, methylphenylsulfone, methylsulfolane, dimethylsulfolane, and the like. Such materials may be used alone or in combination.

25 [0097] Biocides and/or fungicides may also be added to the aqueous dispersions or inkjet ink composition disclosed herein. Biocides are important in preventing bacterial growth since bacteria are often larger than ink nozzles and can cause clogging as well as other printing problems. Examples of useful biocides include, but are not limited to, benzoate or

30 sorbate salts, and isothiazolinones. In one embodiment, the biocides and/or

fungicides are present in an amount ranging from 0.05 % to 5 % by weight, 0.05 % to 2 % by weight, 0.1 % to 5 % by weight, or 0.1 % to 2 % by weight, relative to the total weight of the composition.

[0098] The at least one polymer may be prepared using conventional 5 polymerization techniques. Alpha olefin maleic anhydride copolymers, *e.g.*, may be prepared by any of a number of conventional polymerization processes including those as set forth in U.S. Reissue Pat. No. Re. 28,475 and U.S. Pat. Nos. 3,553,117, 3,560,455, 3,560, 456, 3,560,457, 3,488,311, 4,522, 992, 4,358,573, 4,871,823, 4,859,752, and 5, 336,727, the disclosures 10 of which are incorporated herein by reference. The at least one polymer can be prepared, for example, in neat alkenes at 160 °C; in solvents such as the aromatic hydrocarbons that dissolve the monomers but precipitate the polymers (precipitation polymerization or suspension polymerization); or in solvents such as the ketones that dissolve both the reactants and the 15 polymers (solution polymerization). In one embodiment, temperature for solution polymerization ranges from 60-80 °C. The radical initiators are usually AIBN or benzoyl peroxide.

EXAMPLES

20 **Definitions**

NaAL = sodium alendronate.

NaOH = sodium hydroxide.

SMA 2000 = a low molecular weight styrene-maleic anhydride copolymer with an approximately 2:1 molar ratio of styrene and maleic anhydride

25 (SMA® 2000 polymer, from Total Petrochemicals & Refining USA, Inc.).

SMA 3000 = a low molecular weight styrene-maleic anhydride copolymer with an approximately 3:1 molar ratio of styrene and maleic anhydride (SMA® 3000 polymer, from Total Petrochemicals & Refining USA, Inc.)

SMA EF40 = a low molecular weight styrene-maleic anhydride copolymer with an approximately 4:1 molar ratio of styrene and maleic anhydride (SMA® EF40 polymer, from Total Petrochemicals & Refining USA, Inc.).

Joncrys 683 = a styrene-acrylic resin (Joncrys® 683 resin from BASF) .

5 Acid ion-exchange resin = Purolite® C107E ion-exchange resin (from Purolite).

TMPTGE = Trimethylolpropane triglycidyl ether from Sigma Aldrich.

SURFYNOL 465 = SURFYNOL® 465 surfactant, a non-ionic surfactant from Air Products.

10 TEGMBE = triethylene glycol monobutyl ether.

XIRAN® SZ25010 resin is a low molecular weight styrene-maleic anhydride copolymer with 25 % maleic anhydride content, from Polyscope Polymers, BV.

15 XIRAN® SZ15010 resin is a low molecular weight styrene-maleic anhydride copolymer with 15 % maleic anhydride content from Polyscope Polymers, BV.

DMAPA = 3-(dimethylamino)-1-propylamine.

Polymer Examples

[0099] The Polymer-A to Polymer-D Examples describe the synthesis of a 20 polymer having first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, wherein a portion of the second monomers are functionalized with at least one organic group having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid. The Polymer-E 25 and Polymer-G Examples describe the synthesis of a comparative polymer having first monomers selected from ethylenically unsaturated hydrophobic monomers, and second monomers selected from maleic anhydride, wherein none of the second monomers is functionalized with at least one organic group having a calcium index value greater than or equal to a calcium index 30 value of phenylphosphonic acid. The Polymer-H Example describes the

synthesis of a comparative polymer having monomers selected from ethylenically unsaturated hydrophobic and hydrophilic monomers, wherein none of monomers is selected from maleic anhydride, maleic acid, or salts, esters, imides, and amides thereof.

5 **Polymer-A**

[0100] To a 1 liter cylindrical reactor equipped with a temperature monitor, a stirrer, and a condenser, were added 100 g of SMA EF40 polymer powder and 320 g of deionized (DI) water. A NaAL solution was prepared by dissolving sodium alendronate trihydrate (31.6 g) in the mixture of 122 g DI water and 58.4 g of 40 wt% NaOH solution. The NaAL solution was added to the reactor under stirring. The resultant mixture was heated at 90 °C for 11 h. During this time, the initial milky slurry gradually became clear and homogeneous. After cooling to room temperature, the solution was transferred to a stainless steel beaker, where its pH was adjusted by stirring the solution in the presence of an acid resin from an initial value of 11-12 until the pH was 8.5-10. Suction filtration through a glass frit to remove the ion exchange beads afforded a clear, colorless liquid. ^{31}P NMR was used to determine the amount of bisphosphonate groups that were attached to the polymer. A final solution of Polymer-A was obtained: 19.2 % solid, pH = 9.60, and 13 % of initially charged NaAL were covalently bonded to the polymer. For Polymer-A, the portion of the second monomers, which have been functionalized with bisphosphonate groups (having a calcium index value greater than a calcium index value of phenylphosphonic acid), is 13 mol% of the total second monomers.

25 **Polymer-B**

[0101] To a 1 liter cylindrical reactor equipped with a temperature monitor, a stirrer, and a condenser, were added 100 g of SMA EF40 polymer powder and 360 g of DI water. A NaAL solution was prepared by dissolving sodium alendronate trihydrate (56.9 g) in the mixture of 126 g DI water and 74 g of 40 wt% NaOH solution. The NaAL solution was added to the reactor

under stirring. The resultant mixture was heated at 90 °C for 11 h. During this time, the initial milky slurry gradually became clear and homogeneous. After cooling to room temperature, the solution was transferred to a stainless steel beaker, where its pH was adjusted by stirring the solution in 5 the presence of an acid resin from an initial value of 11-12 until the pH was 8.5-10. Suction filtration through a glass frit to remove the ion exchange beads afforded a clear, colorless liquid. ^{31}P NMR was used to determine the amount of bisphosphonate groups that were attached to the polymer. A final solution of Polymer-B was obtained: 17.6 % solid, pH = 9.75, and 11 % of 10 initially charged NaAL were covalently bonded to the polymer. For Polymer-B, the portion of the second monomers, which have been functionalized with bisphosphonate groups (having a calcium index value greater than a calcium index value of phenylphosphonic acid), is 11 mol% of the total second monomers.

15 **Polymer-C**

[0102] To a 1 liter cylindrical reactor equipped with a temperature monitor, a stirrer, and a condenser, were added 80 g of SMA 3000 polymer powder and 200 g of DI water. A NaAL solution was prepared by dissolving sodium alendronate trihydrate (31.7 g) in the mixture of 122 g DI water and 20 29.3 g of 40 wt% NaOH solution. The NaAL solution was added to the reactor under stirring. The resultant mixture was heated at 80 °C for 11 h. During this time, the initial milky slurry gradually became clear and homogeneous. After cooling to room temperature, the solution was transferred to a stainless steel beaker, where its pH was adjusted by 25 stirring the solution in the presence of an acid resin from an initial value of 11-12 until the pH was 8.5-10. Suction filtration through a glass frit to remove the ion exchange beads afforded a clear, colorless liquid. ICP analysis method was used to determine the amount of bisphosphonate groups that were attached to the polymer, wherein a small portion of 30 polymer solution was first dialyzed against deionized water by using a

dialysis tube with an appropriate molecular weight cut off (*i.e.*, MWCO) (e.g., Spectro/Por® Dialysis Membrane, MWCO 2 kD). A final solution of Polymer-C was obtained: 12.7 % solid, pH = 9.62, and 11 % of initially charged NaAL were covalently bonded to the polymer. For Polymer-C, the 5 portion of the second monomers, which have been functionalized with bisphosphonate groups (having a calcium index value greater than a calcium index value of phenylphosphonic acid), is 11 mol% of the total second monomers.

Polymer-D

10 [0103] To a 1 liter cylindrical reactor equipped with a temperature monitor, a stirrer, and a condenser, were added 80 g of SMA 2000 polymer powder and 200 g of DI water. A NaAL solution was prepared by dissolving sodium alendronate trihydrate (42.5 g) in the mixture of 164 g DI water and 78.4 g of 40 wt% NaOH solution. The NaAL solution was added to the 15 reactor under stirring. The resultant mixture was heated at 80 °C for 8 h. During this time, the initial milky slurry gradually became clear and homogeneous. After cooling to room temperature, the solution was transferred to a stainless steel beaker, where its pH was adjusted by stirring the solution in the presence of an acid resin from an initial value of 20 11-12 until the pH was 8.5-10. Suction filtration through a glass frit to remove the ion exchange beads afforded a clear, colorless liquid. ICP analysis method was used to determine the amount of bisphosphonate groups that were attached to the polymer, wherein a small portion of polymer solution was first dialyzed against deionized water by using a 25 dialysis tube with an appropriate molecular weight cut off (*i.e.*, MWCO) (e.g., Spectro/Por® Dialysis Membrane, MWCO 2 kD). A final solution of Polymer-D was obtained: 14.7 % solid, pH = 9.58, and 22 % of initially charged NaAL were covalently bonded to the polymer. For Polymer-D, the portion of the second monomers, which have been functionalized with 30 bisphosphonate groups (having a calcium index value greater than a

calcium index value of phenylphosphonic acid), is 22 mol% of the total second monomers.

Polymer-E

[0104] Polymer-E was an aqueous solution of sodium salt of SMA 2000, 5 which can be prepared via hydrolysis in the presence of NaOH solution. A final solution of Polymer-E was: 28.7 % solid and pH 9.83.

Polymer-F

[0105] Polymer-F was an aqueous solution of sodium salt of SMA 3000, 10 which can be prepared via hydrolysis in the presence of NaOH solution. A final solution of Polymer-F was: 17.2 % solid and pH 9.75.

Polymer-G

[0106] Polymer-G was an aqueous solution of sodium salt of SMA EF40, 15 which can be prepared via hydrolysis in the presence of NaOH solution and a small amount of Polymer-F (used as hydrolysis aid), wherein the amount of SMA 3000 added was 5.3 wt% of SMA EF40. A final solution of Polymer-G was: 20.9 % solid and pH 9.90.

Polymer-H

[0107] Polymer-H was an aqueous solution of sodium salt of Joncryl 683, 20 which can be prepared by neutralizing Joncryl 683 polymer with NaOH solution. A final solution of Polymer-H was: 22.6 % solid and pH 8.84.

Polymer-I

[0108] To a 1 liter cylindrical reactor equipped with a temperature monitor, an overhead stirrer and a condenser, were added 285 g of XIRAN[®] SZ25010 resin powder (acid number, AN(SP) = 285) and 1044 g of DI water. 25 To the mixing slurry of polymer and water, 137.5 g of 40 wt% NaOH solution was added. The resultant mixture was heated at 95 °C for 10 h. During this time, the initial milky slurry gradually became clear and homogeneous, as the polymer was completely hydrolyzed resulting in a 22.1 % solids solution of pH 10.1.

Polymer J

[0109] To a 1 liter cylindrical reactor equipped with a temperature monitor, an overhead stirrer, and a condenser, were added 285 g of XIRAN® SZ15010 resin granules (acid number, AN(SP) = 156) and 1169 g of DI water. To the mixing slurry of polymer and water, 75.3 g of 40 wt% NaOH solution was added. The resultant mixture was heated at 95 °C for 10 h. During this time, the initial milky slurry gradually became clear and homogeneous, as the polymer was completely hydrolyzed resulting in a 19.8 % solids solution of pH 10.4.

10 **Polymer-K**

[0110] To a 0.5 L cylindrical reactor equipped with a temperature monitor, a stirrer, and a condenser, were added 30 g of SMA 3000 polymer powder, 0.91 mL of 3-(dimethylamino)-1-propylamine (DMAPA) from Sigma Aldrich, and 180 g of DI water. A NaAL solution was prepared by dissolving 15 sodium alendronate trihydrate (2.6 g) in the mixture of 20 g DI water and 4.4 g of 40 wt% NaOH solution. The NaAL solution was added to the reactor under stirring. The resultant mixture was heated at 90 °C for 2 h. An additional 13.6 g of 40 wt% NaOH solution was added and the mixture was heated at 90 °C for 6 h. During this time, the initial milky slurry gradually 20 became clear and homogeneous. A final solution of Polymer-K was obtained: 15.8 % solid, pH = 8.59. ^{31}P NMR was used to determine the amount of bisphosphonate groups that were attached to the polymer, and ^1H NMR was used to determine the amount of dimethylamino groups that were attached to the polymer. For Polymer-K, the portion of the second monomers, which 25 have been functionalized with bisphosphonate groups (having a calcium index value greater than a calcium index value of phenylphosphonic acid), is 3.3 mol% of the total second monomers. The portion of the second monomers, which have been functionalized with dimethyl amino groups (organic group having the formula -A-N(R³)(R⁴)), is 8.5 mol% of the total 30 second monomers.

Polymer-L

[0111] To a 0.5 L cylindrical reactor equipped with a temperature monitor, a stirrer, and a condenser, were added 30 g of SMA® EF40 polymer powder, 0.56 g of 3-(dimethylamino)-1-propylamine (DMAPA) from Sigma 5 Aldrich, and 130 g of DI water. After mixing, 0.5 g of 40 wt% NaOH solution was added and the resultant mixture was heated at 94 °C for 2 h. An additional 10.6 g of 40 wt% NaOH solution was added and the mixture was heated at 94 °C for 8 h. During this time, the initial milky slurry gradually became clear and homogeneous. A final solution of Polymer-L was obtained: 10 14.1 % solid, pH = 8.59. ^1H NMR was used to determine the amount of dimethylamino groups that were attached to the polymer. For Polymer-L the portion of the second monomers, which have been functionalized with dimethyl amino groups (organic group having the formula -A-N(R³)(R⁴)), is 8.4 mol% of the total second monomers.

Pigment Dispersion Examples

[0112] Pigment dispersion Examples PigDisp-1-5 are aqueous yellow pigment dispersions, which are stabilized by polymers. Pigment dispersion Examples PigDisp-6-9 are aqueous cyan pigment dispersions, which are stabilized by polymers. Pigment dispersion Examples PigDisp-10-21 are 20 aqueous magenta pigment dispersions, which are stabilized by polymers. Pigment dispersion Examples PigDisp-22-24 are aqueous black pigment dispersions, which are stabilized by polymers. The pigment dispersions are prepared as follows.

PigDisp-1 and PigDisp-2

[0113] Polymer-G (560 g of solution, 20.9 % solids in water) was combined with 724 g of DI water and 272 g of Pigment Yellow 74 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 7 h to afford a low viscosity, yellow dispersion. A small portion of this dispersion 30 (approximately 50 g) was centrifuged at 2500 G for 20 minutes, and then

decanted to isolate the product. A final solution of Polymer-G-dispersed yellow pigment, PigDisp-1, was obtained and had 15.5 % solid and a mean particle size of 198 nm (determined by using a Microtrac® Particle Size Analyzer).

5 [0114] To the remaining dispersion (2014 g of solution, 18.2 % solid content) were added 5.87 g of TMPTGE, 3.6 g of boric acid, and 190 g of DI water. The resultant mixture was heated at 65 °C for 4 h. After cooling to room temperature, the solution was diluted to 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After that, the solution was
10 purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-2: 16.5 % solid and a mean particle size of 162 nm (determined by using a Microtrac® Particle Size Analyzer)

PigDisp-3

15 [0115] Polymer-A (829 g of solution, 19.2 % solids in water) was combined with 917 g of DI water and 370 g of Pigment Yellow 74 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 7 h to afford a low viscosity, yellow dispersion. The solution was then diluted to 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After that, the solution
20 was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-3: 18.5 % solid and a mean particle size of 170 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-4

25 [0116] Polymer-A (112 g of solution, 19.2 % solids in water) was combined with 124 g of DI water and 50 g of Pigment Yellow 74 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 1 h to afford a low viscosity, yellow dispersion. To the dispersion were added 1.21 g of TMPTGE (% CO₂ targeted = 15 %), 0.74 g of boric acid, and 144 g of DI
30 water. The resultant mixture was heated at 65 °C for 4 h. After cooling to

room temperature, the solution was centrifuged at 2500 G for 20 minutes. After centrifugation, the solution, first diluted to 12 % solid, was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-4: 20.1 % solid and a mean particle size of 177

5 nm (determined by using a Microtrac[®] Particle Size Analyzer).

PigDisp-5

[0117] PigDisp-5 is Pro-JetTM APD1000 yellow colorant, an aqueous pigment yellow dispersion and commercially available from FUJIFILM Imaging Colorants, Inc. This dispersion is stabilized by using polyacrylates

10 dispersants.

Evaluation of PigDisp 1-5

[0118] Dispersion Examples PigDisp-1-4 were evaluated by performing settling experiments, where these dispersions were left undisturbed on the bench over a period of time at room temperature. Their settling performance

15 was ranked based on the following criteria:

Poor = Dispersion separates into two layers in \leq 4 days, where the top layer contained little or reduced amount of pigment, while the pigment concentration in the bottom level is much higher than its initial concentration;

20 Good = Dispersion remains uniform (*i.e.*, little or no layer separation) for 5 days or longer.

Table 1

Dispersion	Polymer	Crosslinking	Settling Performance
PigDisp-1	Polymer-G	No	Poor
PigDisp-2	Polymer-G	Yes	Poor
PigDisp-3	Polymer-A	No	Good
PigDisp-4	Polymer-A	Yes	Good

[0119] Table 1 showed that for both un-crosslinked and crosslinked samples, pigment dispersions, which are stabilized by Polymer-A, exhibited better settling performance than those dispersions stabilized by Polymer-G. The main difference between Polymer-A and Polymer-G is that Polymer-A is 5 a functionalized SMA EF40 polymer, where bisphosphonate groups are attached to polymer, while Polymer-G does not contain any such functional groups. The calcium index value of phenylphosphonic acid is 2.53, which was measured by using Method A as described in U.S. Pat. No. 8,858,695, at col. 29, line 45 to col. 30, line 44, including a list of calcium index values for 10 various compounds in Table 5A, the disclosure of which is incorporated herein by reference. Based on the previous measurement of $-\text{CH}_2(\text{PO}_3^{2-})_2$ (Table 5A of U.S. Pat. No. 8,858,695), the calcium index value for bisphosphonate group was determined to be about 3.45.

[0120] To take into account the ability of the polymer to bind polyvalent 15 metal ions, *e.g.*, magnesium and calcium, taking into account the functional group and hydrophobicity, among other factors, a magnesium sensitivity test was developed. The Mg-sensitivity test was conducted by (1) adding one drop (*ca.* 0.05 g) of the dispersion Examples PigDisp-3-5 (as is) into a series of 10-15 mL MgCl_2 solutions with varied levels of molar concentrations: 1.0 20 mM, 2.0 mM, 3.0 mM, and 5.0 mM; (2) shaking the samples and then allowing them to sit undisturbed for one hour at room temperature; and (3) recording the lowest molar concentration of MgCl_2 when the complete 25 precipitation of pigment dispersion (*i.e.*, clear separation of water and pigment precipitates) was observed. After testing all these examples, their MgCl_2 molar concentrations, at which pigments precipitated completely, were summarized in Table 2. The lower the MgCl_2 concentration required for precipitation, the greater the sensitivity towards magnesium and/or calcium ions, which can indicate capability for calcium and/or magnesium binding.

Table 2

Dispersion	Polymer	Crosslinking	[MgCl ₂], mM
PigDisp-3	Polymer-A	No	2.0
PigDisp-4	Polymer-A	Yes	2.0
PigDisp-5	polyacrylates	Yes	> 5.0

[0121] PigDisp-3 and PigDisp-4, containing Polymer-A, a bisphosphonate--functionalized SMA EF40 polymer, exhibited better 5 calcium and/or magnesium binding capability than PigDisp-5, a polymer-stabilized dispersion, which does not contain any monomer selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof.

PigDisp-6

[0122] Polymer-A (202 g of solution, 19.2 % solids in water) was 10 combined with 223 g of DI water and 90 g of Pigment Blue 15:4 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 1 h to afford a low viscosity, cyan dispersion. To the dispersion were added 4.37 g of TMPTGE (% CO₂ targeted = 30 %), 2.68 g of boric acid, and 257 g of DI water. The 15 resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the solution was first diluted to approximately 13 % solid, followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-6: 20.7 % solid and a mean 20 particle size of 152 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-7

[0123] Polymer-B (220 g of solution, 17.6 % solids in water) was 25 combined with 205 g of DI water and 90 g of Pigment Blue 15:4 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 1 h to afford a low

viscosity, cyan dispersion. To the dispersion were added 4.37 g of TMPTGE (%CO₂ targeted = 30 %), 2.68 g of boric acid, and 257 g of DI water. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the solution was first diluted to approximately 12 % solid, 5 followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-7: 20.4 % solid and a mean particle size of 157 nm (determined by using a Microtrac® Particle Size Analyzer).

10 **PigDisp-8**

[0124] Polymer-E (47 g of solution, 28.7 % solids in water) was combined with 213 g of DI water and 40 g of Pigment Blue 15:4 (as a presscake, the amount of which was determined by its solid content). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for 15 approximately 1 h to afford a low viscosity, cyan dispersion. The resultant solution was centrifuged at 2500 G for 20 minutes, and then decanted to isolate the product. A final solution of Polymer-E-dispersed cyan pigment, PigDisp-8, was obtained: 13.7 % solid and a mean particle size of 163 nm (determined by using a Microtrac® Particle Size Analyzer).

20 **PigDisp-9**

[0125] PigDisp-9 is Pro-Jet™ APD1000 cyan, an aqueous cyan pigment dispersion and commercially available from FUJIFILM Imaging Colorants, Inc. This dispersion is stabilized by using polyacrylates dispersants.

Evaluation of PigDisp 6-9

25 [0126] For these cyan dispersions, their Mg-sensitivity test was conducted by (1) adding one drop (*ca.* 0.05 g) of the dispersion Examples PigDisp-6-9 (as is) into a series of 10-15 mL MgCl₂ solutions with varied levels of molar concentrations: 1.0 mM, 2.0 mM, 3.0 mM, and 5.0 mM; (2) shaking the samples and then allowing them to sit undisturbed for 30 one hour at room temperature; and (3) recording the lowest molar

concentration of MgCl₂ when the complete precipitation of pigment dispersion (*i.e.*, clear separation of water and pigment precipitates) was observed. After testing all these examples, their MgCl₂ molar concentrations, at which pigments precipitated completely, were summarized in Table 3. The lower the MgCl₂ concentration required for precipitation, the greater the sensitivity towards magnesium and/or calcium ions, which can indicate capability for calcium and/or magnesium binding.

Table 3

Dispersion	Polymer	Crosslinking	[MgCl ₂], mM
PigDisp-6	Polymer-A	Yes	2.0
PigDisp-7	Polymer-B	Yes	2.0
PigDisp-8	Polymer-E	No	3.0
PigDisp-9	polyacrylates	Yes	5.0

[0127] PigDisp-6 and PigDisp-7, containing Polymer-A and Polymer-B respectively, a bisphosphonate-functionalized SMA EF40 polymer, exhibited better calcium and/or magnesium binding capability than PigDisp-8, an un-functionalized SMA 2000-dispersed cyan dispersion having no functional groups having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid, and PigDisp-5, a polymer-stabilized dispersion that does not contain any monomer selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof. Higher amounts of bisphosphonate groups are attached to SMA EF40 polymer in Polymer-B than Polymer-A.

PigDisp-10

[0128] Polymer-A (762 g of solution, 19.2 % solids in water) was combined with 1444 g of DI water and 340 g of Pigment Violet 19 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 7 h to afford a low viscosity, magenta dispersion. To the dispersion were added 10.7 g of

TMPTEG, 6.53 g of boric acid, and 273 g of DI water. The resultant mixture was heated at 65 °C for 4 h. After cooling to room temperature, the solution was first diluted to approximately 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and 5 concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-10: 17.1 % solid and a mean particle size of 168 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-11

[0129] Polymer-G (617 g of solution, 20.9 % solids in water) was 10 combined with 1228 g of DI water and 300 g of Pigment Violet 19 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 6 h to afford a low viscosity, magenta dispersion. To the dispersion were added 9.14 g of 15 TMPTEG, 5.61 g of boric acid, and 222 g of DI water. The resultant mixture was heated at 65 °C for 4 h. After cooling to room temperature, the solution was first diluted to approximately 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and 20 concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-11: 18.3 % solid and a mean particle size of 161 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-12

[0130] Polymer-H (59 g of solution, 22.6 % solids in water) was combined 25 with 215 g of DI water and 40 g of Pigment Red 122 (as a presscake, the amount of which was determined by its solid content). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 0.5 h to afford a low viscosity, cyan dispersion. The resultant solution was centrifuged at 2500 G for 20 minutes, and then decanted to isolate the product. A final solution of Polymer-H-dispersed magenta 30 pigment, PigDisp-12, was obtained: 14.0 % solid and a mean particle size of 106 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-13

[0131] PigDisp-13 is Pro-Jet™ APD1000 magenta, an aqueous magenta pigment dispersion and commercially available from FUJIFILM Imaging Colorants, Inc. This dispersion is stabilized by using polyacrylates

5 dispersants.

PigDisp-14-15

[0132] Polymer-A (34 g of solution, 19.2 % solids in water) was combined with 38 g of DI water and 15 g of Pigment Violet 19 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a

10 Misonix® probe sonicator for approximately 0.5 h to afford a low viscosity, magenta dispersion. To the dispersion was added 43 g of DI water to afford PigDisp-14: 16.6 % solid and a mean particle size of 184 nm (determined by using a Microtrac® Particle Size Analyzer).

[0133] To a separate reactor were added 35 g of PigDisp-14, 0.13 g of

15 TMPTGE (% CO₂ targeted = 20 %) and 0.08 g of boric acid. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the final solution of PigDisp-15 was obtained with a mean particle size of 200 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-16-17

20 [0134] Polymer-B (37 g of solution, 17.6 % solids in water) was combined with 35 g of DI water and 15 g of Pigment Violet 19 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a

Misonix® probe sonicator for approximately 0.5 h to afford a low viscosity, magenta dispersion. To the dispersion was added 43 g of DI water to afford 25 PigDisp-16: 16.6 % solid and a mean particle size of 183 nm (determined by using a Microtrac® Particle Size Analyzer).

[0135] To a separate reactor were added 35 g of PigDisp-16, 0.13 g of

TMPTGE (% CO₂ targeted = 20 %) and 0.08 g of boric acid. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the

final solution of PigDisp-17 was obtained with a mean particle size of 205 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-18-19

[0136] Polymer-D (44 g of solution, 14.7 % solids in water) was combined with 27 g of DI water and 15 g of Pigment Violet 19 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 0.5 h to afford a low viscosity, magenta dispersion. To the dispersion was added 43 g of DI water to afford PigDisp-18: 16.6 % solid and a mean particle size of 171 nm (determined by using a Microtrac® Particle Size Analyzer).

[0137] To a separate reactor were added 35 g of PigDisp-18, 0.19 g of TMPTGE (% CO₂ targeted = 17 %) and 0.12 g of boric acid. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the final solution of PigDisp-19 was obtained with a mean particle size of 220 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-20-21

[0138] Polymer-C (51 g of solution, 12.7 % solids in water) was combined with 20 g of DI water and 15 g of Pigment Violet 19 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 0.5 h to afford a low viscosity, magenta dispersion. To the dispersion was added 43 g of DI water to afford PigDisp-20: 16.6 % solid and a mean particle size of 166 nm (determined by using a Microtrac® Particle Size Analyzer).

[0139] To a separate reactor were added 35 g of PigDisp-20, 0.16 g of TMPTGE (% CO₂ targeted = 18 %) and 0.10 g of boric acid. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the final solution of PigDisp-21 was obtained with a mean particle size of 179 nm (determined by using a Microtrac® Particle Size Analyzer).

Evaluation of PigDisp 10-21

[0140] For these magenta dispersions, their Mg-sensitivity test was conducted by (1) first adding one drop (*ca.* 0.05 g) of the dispersion

Examples PigDisp-10-21 (as is) into a series of 10-15 mL MgCl₂ solutions

5 with varied levels of molar concentrations: 1.0 mM, 2.0 mM, 3.0 mM, and 5.0 mM; (2) upon initial shaking, leave the mixture sit undisturbed for one hour at room temperature; (3) record the lowest molar concentration of MgCl₂ when the complete precipitation of pigment dispersion (*i.e.*, clear separation of water and pigment precipitates) was observed. After testing
10 all these examples, their MgCl₂ molar concentrations, at which pigments precipitated completely, were summarized in Table 4. The lower the MgCl₂ concentration required for precipitation, the greater the sensitivity towards magnesium and/or calcium ions, which can indicate capability for calcium and/or magnesium binding.

15

Table 4

Dispersion	Polymer	Crosslinking	[MgCl ₂], mM
PigDisp-10	Polymer-A	Yes	2.0
PigDisp-11	Polymer-G	Yes	5.0
PigDisp-12	Polymer-H	No	> 5.0
PigDisp-13	polyacrylates	Yes	> 5.0
PigDisp-14	Polymer-A	No	2.0
PigDisp-15	Polymer-A	Yes	2.0
PigDisp-16	Polymer-B	No	2.0
PigDisp-17	Polymer-B	Yes	2.0
PigDisp-18	Polymer-D	No	3.0
PigDisp-19	Polymer-D	Yes	3.0
PigDisp-20	Polymer-C	No	3.0
PigDisp-21	Polymer-C	Yes	3.0

[0141] PigDisp-10 and PigDip-14-17, containing Polymer-A and Polymer-B respectively, a bisphosphonate-functionalized SMA EF40 polymer, and PigDisp-18-19, containing Polymer-D, a bisphosphonate-functionalized SMA 2000 polymer, and PigDisp-20-21, 5 containing Polymer-C, a bisphosphonate-functionalized SMA 3000 polymer, exhibited better calcium and/or magnesium binding capability than PigDisp-11, an un-functionalized SMA EF40-stabilized magenta dispersion having no functional groups having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid, and PigDisp-12-13, 10 a polymer-stabilized dispersion that does not contain any monomer selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof. Higher amount of bisphosphonate groups are attached to SMA EF40 polymer in Polymer-B than Polymer-A.

[0142] For the magenta dispersions, a Ca-sensitivity test was also 15 conducted by (1) adding one drop (*ca.* 0.05 g) of the dispersion Examples PigDisp-10 and PigDisp-12-17 (as is) into a series of 10-15 mL CaCl₂ solutions with varied levels of molar concentrations: 1.0 mM, 2.0 mM, 3.0 mM, and 5.0 mM; (2) shaking the samples and allowing them to sit undisturbed for one hour at room temperature; and (3) recording the lowest 20 molar concentration of CaCl₂ when complete precipitation of pigment dispersion (*i.e.*, clear separation of water and pigment precipitates) was observed. Their CaCl₂ molar concentrations of these samples are summarized in Table 5. The lower the CaCl₂ concentration required for precipitation, the greater the sensitivity towards magnesium and/or calcium 25 ions, which can indicate capability for calcium and/or magnesium binding.

Table 5

Dispersion	Polymer	Crosslinking	[CaCl ₂], mM
PigDisp-10	Polymer-A	Yes	2.0
PigDisp-12	Polymer-H	No	> 5.0
PigDisp-13	polyacrylates	Yes	> 5.0
PigDisp-14	Polymer-A	No	2.0
PigDisp-15	Polymer-A	Yes	2.0
PigDisp-16	Polymer-B	No	2.0
PigDisp-17	Polymer-B	Yes	2.0

[0143] For the magenta dispersions, the Ca-sensitivity test showed the same results as those based on the Mg-sensitivity test (Table 4). PigDisp-10 and PigDisp-14-17, containing Polymer-A and Polymer-B respectively, a bisphosphonate-functionalized SMA EF40 polymer, exhibited better calcium and/or magnesium binding capability than PigDisp-12-13, a polymer-stabilized dispersion that does not contain any monomer selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof.

PigDisp-22

[0144] Polymer-A (112 g of solution, 19.2 % solids in water) was combined with 124 g of DI water and 50 g of Black Pearls 900 (from Cabot Corporation). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 10 min to afford a low viscosity, black dispersion. To the dispersion were added 0.90 g of TMPTGE (% CO₂ targeted = 10 %), 0.56 g of boric acid, and 144 g of DI water. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the solution was first diluted to approximately 13 % solid, followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-22: 20.6 % solid and a mean

particle size of 102 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-23

[0145] Polymer-G (772 g of solution, 20.9 % solids in water) was 5 combined with 999 g of DI water and 375 g of Black Pearls 900 (from Cabot Corporation). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 1 h to afford a low viscosity, black dispersion. To the dispersion were added 8.1 g of TMPTGE, 4.967 g of boric acid, and 750 g of DI water. The resultant mixture was heated at 65 °C 10 for 4 h. After cooling to room temperature, the solution was first diluted to approximately 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford 15 PigDisp-23: 17.1 % solid and a mean particle size of 101 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-24

[0146] PigDisp-24 is Pro-Jet™ APD1000 black, an aqueous black 20 pigment dispersion and commercially available from FUJIFILM Imaging Colorants, Inc. This dispersion is stabilized by using polyacrylates dispersants.

Evaluation of PigDisp 22-24

[0147] For these black dispersions, their Mg-sensitivity test was 25 conducted by (1) adding one drop (*ca.* 0.05 g) of the dispersion Examples PigDisp-22-24 (as is) into a series of 10-15 mL MgCl₂ solutions with varied levels of molar concentrations: 1.0 mM, 2.0 mM, 3.0 mM, and 5.0 mM; (2) shaking the samples and then allowing them to sit undisturbed for four hour at room temperature; and (3) recording the lowest molar concentration of MgCl₂ when the complete precipitation of pigment dispersion (*i.e.*, clear separation of water and pigment precipitates) was 30 observed. After testing all these examples, their MgCl₂ molar

concentrations, at which pigments precipitated completely, were summarized in Table 6. The lower the MgCl₂ concentration required for precipitation, the greater the sensitivity towards magnesium and calcium ions, which can indicate capability for calcium and/or magnesium binding.

5

Table 6

Dispersion	Polymer	Crosslinking	[MgCl ₂], mM
PigDisp-22	Polymer-A	Yes	2.0
PigDisp-23	Polymer-G	Yes	3.0
PigDisp-24	polyacrylates	Yes	5.0

[0148] PigDisp-22, containing Polymer-A, a bisphosphonate-functionalized SMA EF40 polymer, exhibited better calcium and/or magnesium binding capability than PigDisp-23, an un-functionalized 10 SMA EF40-stabilized magenta dispersion having no functional groups having a calcium index value greater than or equal to a calcium index value of phenylphosphonic acid, and PigDisp-24, a polymer-stabilized dispersion that does not contain any monomer selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof.

15 **PigDisp-25**

[0149] Polymer-K (136 g of solution, 15.8 % solids in water) was combined with 90 g of DI water and 50 g of Pigment Yellow 74 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 3 h to afford a low 20 viscosity, yellow dispersion. To the dispersion (274 g of solution, 25.2 % solids content) were added 1.41 g of TMPTGE (% CO₂ targeted = 14 %), 0.89 g of boric acid, and 140 g of DI water. The resultant mixture was heated at 65 °C for 4 h. After cooling to room temperature, the solution was diluted to 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After that, 25 the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford a yellow PigDisp-25 dispersion:

19.34 % solids and a mean particle size of 158 nm (determined by using a Microtrac® Particle Size Analyzer). For this yellow dispersion, its Mg-sensitivity test was conducted as described in the evaluation of PigDisp 1-5. PigDisp-25, containing Polymer-K, a bisphosphonate-functionalized 5 SMA 3000 polymer, exhibited better calcium and/or magnesium binding capability than PigDisp-5, a yellow polymer-stabilized dispersion, which does not contain any monomer selected from maleic anhydride, maleic acid, and salts, esters, imides, and amides thereof.

PigDisp-26 to PigDisp-34

10 [0150] Dispersions PigDisp-26 to PigDisp-34 were prepared to investigate the effect of stability upon crosslinking. Stability is assessed with a solvent stability test, which were conducted on the dispersions according to the following method:

15 [0151] A 50 µL solvent drop was placed on a microscope glass slide, then a 5 µL dispersion droplet (at approximately 18-20 % solids loading) was placed on top of the solvent drop. A microscope cover was used to flatten the droplet and the appearance of the colorant particles was recorded. When the dispersion has good compatibility, the pigment particles will mix and flow with the liquid and color the liquid area. When the dispersion has bad 20 compatibility, the pigment particles will agglomerate and not spread together with the liquid.

[0152] Table 7 below lists the acid number and percentage of CO₂ targeted (“% CO₂”) for the polymers of each dispersion.

Table 7

Dispersion	AN(SP)	AN (xlink)	% CO ₂ targeted
PigDisp26	285	285	0
PigDisp27	285	285	0
PigDisp28	285	199	30
PigDisp29	285	285	0
PigDisp30	285	285	0
PigDisp31	285	199	30
PigDisp32	156	156	0
PigDisp33	156	156	0
PigDisp34	156	125	20

PigDisp-26

[0153] Polymer-I (298 g of solution, 22.1 % solids in water) was combined with 424 g of DI water and 198 g of carbon black prepared according to the method described in U.S. Pat. No. 9,388,300 and having the following properties: BET surface area = 265 m²/g, STSA = 197 m²/g, OAN = 175 mL/100 g, and COAN = 135 mL/100 g. This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 2 h to afford a low viscosity, black dispersion at 25.8 % solids.

PigDisp-27

[0154] PigDisp-26 (250 g) was diluted to approximately 12 % solids, followed by centrifugation at 2500 G for 20 min. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford the noncrosslinked carbon black PigDisp-27 dispersion: 20.8 % solids and a mean particle size of 146 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-28

[0155] To a 250 g portion of PigDisp-26 were added 2.80 g of TMPTGE, 2.58 g of boric acid, and 115.16 g of DI water. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the solution was 5 diluted to approximately 12 % solids, followed by centrifugation at 2500 G for 20 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford a cross-linked carbon black dispersion: 18.10 % solids and a mean particle size of 148 nm (determined by using a Microtrac®
10 Particle Size Analyzer).

Evaluation of PigDisp-27-28

[0156] The solvent stability test was applied to PigDisp-27 (non-crosslinked carbon black dispersion) and PigDisp-28 (crosslinked carbon black dispersion) with various solvents. The results are listed in 15 Table 8 below.

Table 8

Solvent	PigDisp-27 (non- crosslinked)	PigDisp-28 (crosslinked)
dipropylene glycol	Agglomerated	good spread
2-pyrollidone	Agglomerated	good spread
triethylene glycol monobutyl ether	Agglomerated	good spread
1,2-hexanediol	Agglomerated	good spread with a few agglomerates
2-methyl-1,3-propanediol	Agglomerated	good spread with a few agglomerates
1,4-butanediol	Agglomerated	good spread
tetraethylene glycol	Agglomerated	good spread

[0157] The non-crosslinked dispersion PigDisp-27 immediately destabilized when exposed to the solvents listed in Table 8, as evidenced by 5 large agglomerates of pigment particles crashing out onto the microscope slide. In contrast, crosslinked dispersion PigDisp-28 spread out and dispersed in the solvent, indicative of its stability when exposed to the solvents.

[0158] The contrast in solvent stability is also shown in FIGs. 1A and 1B, 10 which are photographs of PigDisp-27 and PigDisp-28, respectively, upon exposure to dipropylene glycol on the microscopic slide. It can be seen that the non-crosslinked dispersion PigDisp-27 in FIG. 1A is agglomerated whereas the crosslinked dispersion PigDisp-28 in FIG. 1B is evenly spread throughout the slide with no visible agglomeration.

PigDisp-29

[0159] Polymer-I (124 g of solution, 22.1 % solids in water) was combined with 135.6 g of DI water and 118 g of Pigment Green 7 presscake (42.9 % solids). This mixture was then sonicated at approximately 10 °C with a 5 Misonix® probe sonicator for approximately 2h to afford a low viscosity, green dispersion at 25.2 % solids.

PigDisp-30

[0160] PigDisp-29 (75 g) was diluted to approximately 15% solids, followed by centrifugation at 2500 G for 10 min. After centrifugation, the 10 solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford the noncrosslinked green PigDisp-30 dispersion: 19.10 % solids and a mean particle size of 147 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-31

[0161] To a 150 g portion of PigDisp-29 were added 2.04 g of TMPTGE, 3.13 g of boric acid, and 41 g of DI water. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the solution was diluted to approximately 15 % solids, followed by centrifugation at 2500 G for 10 minutes. After centrifugation, the solution was purified and concentrated by 20 diafiltration using a 3000 MW cut-off polysulfone membrane to afford a crosslinked green PigDisp-31 dispersion: 17.87 % solids and a mean particle size of 151 nm (determined by using a Microtrac® Particle Size Analyzer).

Evaluation of PigDisp-30-31

[0162] The solvent stability test was applied to PigDisp-30 25 (non-crosslinked green dispersion) and PigDisp-31 (crosslinked green dispersion) with various solvents. The results are listed in Table 9 below.

Table 9

Solvent	PigDisp-30 (non-crosslinked)	Pig-Disp-31 (crosslinked)
dipropylene glycol	agglomerated	good spread
2-pyrollidone	agglomerated	good spread
triethylene glycol monobutyl ether	agglomerated	good spread
1,2-hexanediol	spread with some agglomerates	good spread
2-methyl-1,3-propanediol	agglomerated	good spread
1,4-butanediol	agglomerated	good spread
tetraethylene glycol	agglomerated	good spread

[0163] The non-crosslinked dispersion PigDisp-30 immediately destabilized when exposed to the solvents listed in Table 9, as evidenced by 5 large agglomerates of pigment particles crashing out onto the microscope slide. In contrast, crosslinked dispersion PigDisp-31 spread out and dispersed in the solvent, indicative of its stability when exposed to the solvents.

PigDisp-32

10 [0164] Polymer-J (90 g of solution, 19.8 % solids in water) was combined with 160 g of DI water and 40 g of Pigment Violet 19 (in powder form). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 2 h to afford a low viscosity, magenta dispersion at 20.1 % solids.

15 **PigDisp-33**

[0165] PigDisp-32 (130 g) was first diluted to approximately 15 % solids, followed by centrifugation at 2500 G for 10 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford a non-crosslinked magenta

PigDisp-33 dispersion: 22.9 % solids and a mean particle size of 162 nm (determined by using a Microtrac® Particle Size Analyzer).

PigDisp-34

[0166] To a 130 g portion of PigDisp-32 were added 0.86 g of TMPTGE and 1.24 g of boric acid. The resultant mixture was heated at 65 °C for 5 h. After cooling to room temperature, the solution was first diluted to approximately 15 % solid, followed by centrifugation at 2500 G for 10 minutes. After centrifugation, the solution was purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford a cross-linked PigDisp-34 magenta dispersion: 18.56 % solids and a mean particle size of 166 nm (determined by using a Microtrac® Particle Size Analyzer).

Evaluation of PigDisp-33-34

[0167] The solvent stability test was applied to PigDisp-33 (non-crosslinked magenta dispersion) and PigDisp-34 (crosslinked magenta dispersion) with various solvents. The results are listed in Table 10 below.

Table 10

Solvent	PigDisp-33 (non-crosslinked)	PigDisp-34 (crosslinked)
dipropylene glycol	agglomerated	good spread
2-pyrollidone	agglomerated	good spread
triethylene glycol	agglomerated	good spread
monobutyl ether		
1,2-hexanediol	agglomerated	good spread
2-methyl-1,3-propanediol	agglomerated	good spread
1,4-butanediol	agglomerated	good spread
tetraethylene glycol	agglomerated	good spread

[0168] The non-crosslinked dispersion PigDisp-33 immediately destabilized when exposed to the solvents listed in Table 10, as evidenced by

large agglomerates of pigment particles crashing out onto the microscope slide. In contrast, crosslinked dispersion PigDisp-34 spread out and dispersed in the solvent, indicative of its stability when exposed to the solvents.

5 **PigDisp-35**

[0169] Polymer-L (152 g of solution, 14.1 % solids in water) was combined with 72.5 g of DI water and 50 g of Pigment Yellow 74 (in the form of dry powder). This mixture was then sonicated at approximately 10 °C with a Misonix® probe sonicator for approximately 3 h to afford a low 10 viscosity, yellow dispersion. To the dispersion (288 g of solution, 26 % solid content) were added 1.13 g of TMPTGE, 0.70 g of boric acid, and 140 g of DI water. The resultant mixture was heated at 65 °C for 4 h. After cooling to room temperature, the solution was diluted to 10 % solid, followed by centrifugation at 2500 G for 20 minutes. After that, the solution was 15 purified and concentrated by diafiltration using a 3000 MW cut-off polysulfone membrane to afford PigDisp-35: 20.16 % solid and a mean particle size of 165 nm (determined by using a Microtrac® Particle Size Analyzer).

[0170] The use of the terms “a” and “an” and “the” are to be construed to 20 cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (*i.e.*, meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand 25 method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The 30 use of any and all examples, or exemplary language (*e.g.*, “such as”) provided

herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

Conclusies

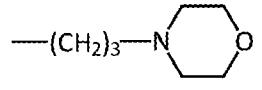
1. Een samenstelling omvattend:
 - ten minste één pigment;
 - een vloeibaar dragermateriaal; en
 - ten minste één polymeer die het ten minste één pigment inkapselt
- 5 waarbij het ten minste één polymeer eerste monomeren omvat geselecteerd uit ethyleenachtig onverzadigde hydrofobe monomeren, en tweede monomeren geselecteerd uit maleïnezuuranhydride, maleïnezuur, en zouten, esters, imiden, en amiden daarvan, waarbij de ethyleenachtig onverzadigd hydrofobe monomeren de formule $\text{CH}_2=\text{CR}^1\text{R}^2$ omvat, waarbij R^1 en R^2 onafhankelijk geselecteerd zijn uit H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, en C₆-C₂₀ alkaryl, en de koolstofatomen van R^1 en R^2 optioneel gesubstitueerd kunnen zijn met ten minste één heteroatoom geselecteerd uit O, N, en S, en waarbij het ten minste één polymeer vernet is met carboxylaatgroepen van de tweede monomeren,
- 10 waarbij de eerste monomeren aanwezig zijn in het ten minste één polymeer in een hoeveelheid variërend van 40 tot en met 90 mol% relatief ten opzichte van het ten minste één polymeer en de tweede monomeren aanwezig zijn in het ten minste één polymeer in een hoeveelheid variërend van 10 tot en met 60 mol% relatief ten opzicht van het ten minste één polymeer, en
- 15 waarbij het ten minste één polymeer een zuurnummer heeft variërend van 90 tot en met 325 volgens de volgende vergelijking:
- 20
$$AN(xlink) = AN(SP) - (\%CO_2\ gericht) \times AN(SP),$$
 waarbij "AN(xlink)" het zuurnummer van het ten minste één polymeer, dat is vernet, is, "AN(SP)" het zuurnummer van het startpolymeer en

“%CO₂ gericht” het percentage carboxylaatgroepen van de tweede monomeren gericht op vernetting.

2. De samenstelling van conclusie 1, waarbij de tweede monomeren geselecteerd zijn uit maleïnezuuranhydride, maleïnezuur, en zouten daarvan.
3. De samenstelling van één van conclusie 1 of 2, waarbij het ten minste één polymeer vernet is met ten minste 10 % van carboxylaatgroepen van het tweede monomeer.
4. De samenstelling van één van de conclusies 1-3, waarbij het ten minste één polymeer vernet is *via* ten minste één koppeling geselecteerd uit amide-, imide-, en esterkoppelingen.
5. De samenstelling van één van de conclusies 1-4, waarbij de ethyleenachtig onverzadigd hydrofobe monomeren de formule CH₂=CR¹R² omvatten, waarbij R¹ en R² onafhankelijk geselecteerd zijn uit H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, C₆-C₂₀ aralkyl, en C₆-C₂₀ alkaryl.
6. De samenstelling van één van de conclusies 1-4, waarbij de ethyleenachtig onverzadigd hydrofobe monomeren de formule CH₂=CR¹R² omvatten, waarbij R¹ en R² onafhankelijk geselecteerd zijn uit H, C₁-C₁₂ alkyl, C₅-C₂₀ aryl, en C₆-C₂₀ alkaryl.
7. De samenstelling van één van de conclusies 1-4, waarbij de ethyleenachtig onverzadigd hydrofobe monomeren de formule CH₂=CR¹R² omvatten, waarbij R¹ en R² onafhankelijk geselecteerd zijn uit H, C₅-C₂₀ aryl, en C₆-C₂₀ alkaryl.
8. De samenstelling van één van de conclusies 1-4, waarbij de ethyleenachtig onverzadigd hydrofobe monomeren geselecteerd zijn uit styreen, α -methylstyreen, ethyleen, propyleen, 1-butyleen, isobutyleen, butadieen, en methylvinylether.

9. De samenstelling van één van de conclusies 1-4, waarbij de ethyleenachtig onverzadigd hydrofobe monomeren geselecteerd zijn uit styreen.
10. De samenstelling van één van de conclusies 1-9, waarbij de tweede monomeren maleïnezuuranhydride omvatten.
11. De samenstelling van één van de conclusies 1-9, waarbij de tweede monomeren maleïnezuur omvatten, en zouten, esters, imiden, en amiden daarvan.
12. De samenstelling van één van de conclusies 1-9, waarbij de tweede monomeren een mengsel van maleïnezuuranhydride en maleïnezuur omvatten, en zouten, esters, imiden, en amiden daarvan.
13. De samenstelling van één van de conclusies 1-9, waarbij de tweede monomeren geselecteerd zijn uit maleïnezuuranhydride, maleïnezuur, en zouten en esters daarvan.
14. De samenstelling van één van de conclusies 1-13, waarbij het ten minste één polymeer een zuurgetal heeft van 90 tot en met 250.
15. De samenstelling van één van de conclusies 1-13, waarbij het ten minste één polymeer een zuurgetal heeft van 90 tot en met 200.
16. De samenstelling van één van de conclusies 1-15, waarbij een gedeelte van de tweede monomeren gefunctionaliseerd is met ten minste één organische groep omvattende de formule -A-N(R³)(R⁴), waarbij R³ en R⁴ onafhankelijk geselecteerd zijn uit H, C₁-C₁₀ alkyl, C₄-C₁₈ aryl, C₄-C₁₈ heteroaryl, en C₃-C₂₀ heterocycloalkyl, en A geselecteerd is uit C₁-C₁₀ alkyleen, C₃-C₂₀ cycloalkyleen, C₃-C₂₀ heterocycloalkyleen, aryleen, heteroaryleen, en C₂-C₂₀ ether.
17. De samenstelling van één van de conclusies 1-15, waarbij een gedeelte van de tweede monomeren gefunctionaliseerd is met ten minste één

organische groep omvattende de formule geselecteerd uit -CH₂CH₂-N(CH₃)₂, -CH₂CH₂CH₂-N(CH₃)₂, -CH(CH₃)CH₂-N(CH₃)₂, -CH₂CH₂CH₂CH₂-N(CH₃)₂, -CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂CH₂CH₂-N(CH₂CH₃)₂, -CH₂CH₂NHCH₂

5 CH₂OH, -CH₂CH₂-N(CH₂CH₂OH)₂, en .

18. De samenstelling van één van de conclusies 1-15, waarbij een gedeelte van de tweede monomeren gefunctionaliseerd is met ten minste één organische groep omvattende de formule -A-N⁺(R³)(R⁴)(R⁵), waarbij R³, R⁴ en R⁵ onafhankelijk geselecteerd zijn uit H, C₁-C₁₀ alkyl, C₄-C₁₈ aryl, C₄-C₁₈ heteroaryl, en C₃-C₂₀ heterocycloalkyl, en A geselecteerd is uit C₁-C₁₀ alkyleen, C₃-C₂₀ cycloalkyleen, C₃-C₂₀ heterocycloalkyleen, arylen, heteroarylen en C₂-C₂₀ ether.

19. De samenstelling van één van de conclusies 16-18, waarbij de ten minste één organische groep gebonden is met het tweede monomeer via ten minste één koppeling geselecteerd uit amide-, imide-, en esterbindingen.

20. De samenstelling van één van de conclusies 1-19, waarbij de ten minste één pigment ongemodificeerd is.

21. De samenstelling van één van de conclusies 1-19, waarbij de ten minste één pigment zelf-gedisperseerd is.

20 22. De samenstelling van één van de conclusies 1-21, waarbij het vloeibare dragermateriaal waterig is.

23. De samenstelling van één van de conclusies 1-22, verder omvattend ten minste één oppervlakte-actieve stof.

24. De samenstelling van één van de conclusies 1-23, waarbij de samenstelling een waterige dispersie is.

25. De samenstelling van één van de conclusies 1-24, waarbij de samenstelling een inktjet inktsamenstelling is.

26. De samenstelling van één van de conclusies 1-25, verder omvattend ten minste één viscositeitsregelaar.
27. De samenstelling van één van de conclusies 1-26, verder omvattend ten minste één polymeerachtig bindmiddel.
- 5 28. De samenstelling van één van de conclusies 1-27, verder omvattend ten minste één duurzaamheidsbevorderend polymeer.

Figure 1A

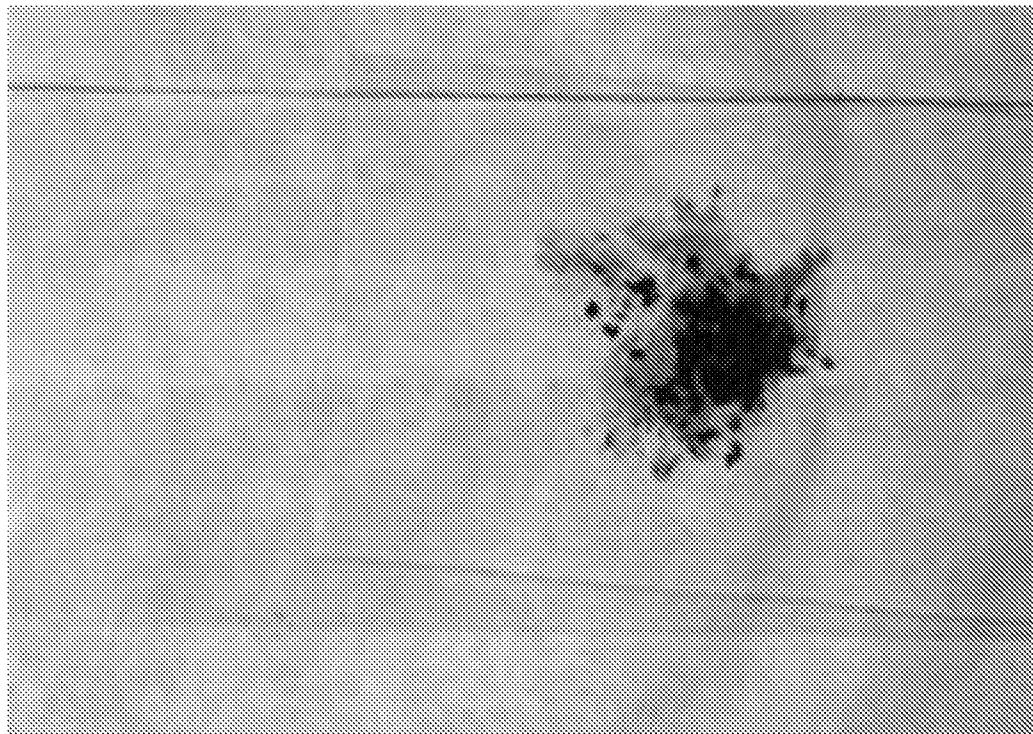
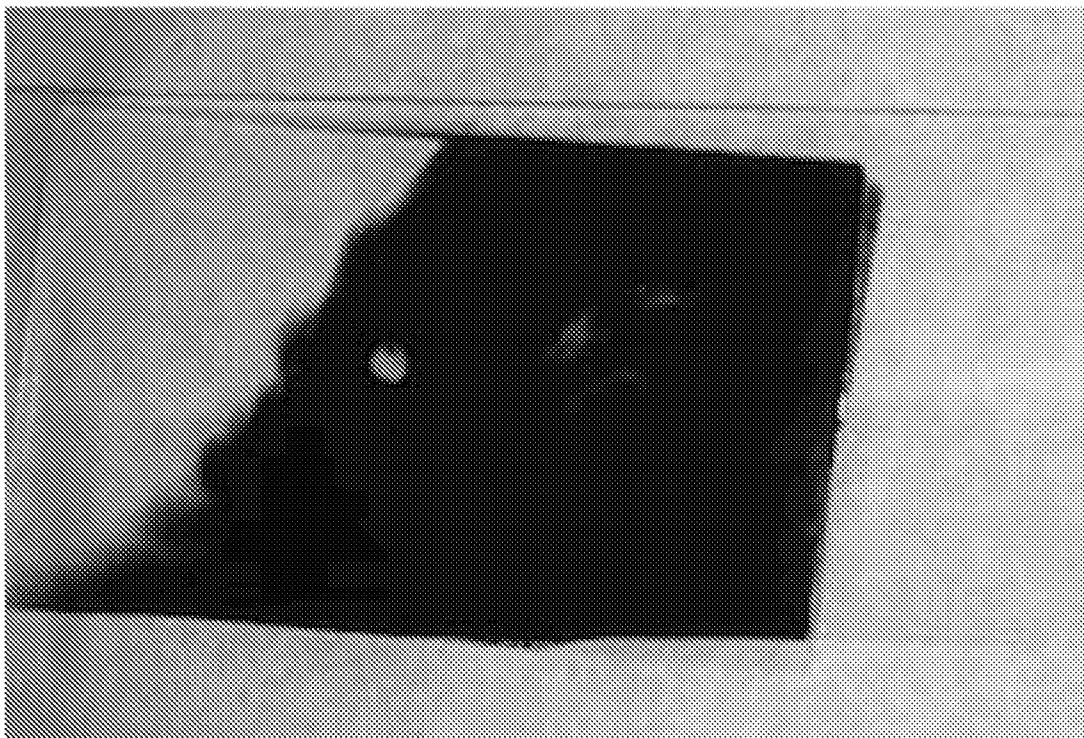
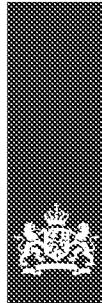


Figure 1B





Rijksdienst voor Ondernemend
Nederland

RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK

Octrooiaanvrage 2032660

Classificatie van het onderwerp ¹ : C09D11/326; C08F212/08; C08L35/06; C08F222/06; C08F222/08; C09D125/14; C09D135/02; C09D11/107	Onderzochte gebieden van de techniek ¹ : C09D; C08F; C08L
Computerbestanden: KIME	Omvang van het onderzoek: Volledig
Datum van de onderzochte conclusies: 2 augustus 2022	Niet onderzochte conclusies: -

Van belang zijnde literatuur

Categorie ²	Vermelding van literatuur met aanduiding, voor zover nodig, van speciaal van belang zijnde tekstgedeelten of figuren	Van belang voor conclusie(s)
X	EP 1086975 A (MIKUNI COLOR WORKS) 28 maart 2001 * paragrafen [0015], [0053]-[0057]; voorbeeld 3 * -----	1-20, 25-36
Datum waarop het onderzoek werd voltooid: 2 december 2022	De bevoegde ambtenaar: dr. R. Boers	Octrooicentrum Nederland onderdeel van Rijksdienst voor Ondernemend Nederland

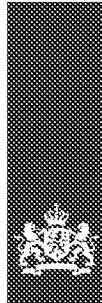
Toelichting:**1 Classificatie gebieden van de techniek:**

gedefinieerd volgens International Patent Classification (IPC).

2 Categorie van de vermelde literatuur:

- X: op zichzelf van bijzonder belang zijnde stand van de techniek
- Y: in samenhang met andere geciteerde literatuur van bijzonder belang zijnde stand van de techniek
- A: niet tot de categorie X of Y behorende van belang zijnde stand van de techniek
- O: verwijzend naar niet op schrift gestelde stand van de techniek
- P: literatuur gepubliceerd tussen voorrangs- en indieningsdatum

- T: niet tijdig gepubliceerde literatuur over theorie of principe ten grondslag liggend aan de uitvinding
- E: octrooiliteratuur gepubliceerd op of na de indieningsdatum van de onderhavige aanvraag en waarvan de indieningsdatum of de voorrangsdatum ligt voor de indieningsdatum van de onderhavige aanvraag
- D: in de aanvraag genoemd
- L: om andere redenen vermelde literatuur
- &: lid van dezelfde octrooifamilie; corresponderende literatuur



Rijksdienst voor Ondernemend
Nederland

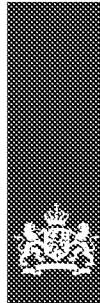
AANHANGSEL

Behorende bij het Rapport betreffende het Onderzoek naar de Stand van de Techniek

Octrooiaanvraag 2032660

Het aanhangsel bevat een opgave van elders gepubliceerde octrooiaanvragen of octrooien (zogenaamde leden van dezelfde octrooifamilie), die overeenkomen met octrooigeschriften genoemd in het rapport. De opgave is samengesteld aan de hand van gegevens uit het computerbestand van het Europees Octrooibureau per 2 december 2022. De juistheid en volledigheid van deze opgave wordt noch door het Europees Octrooibureau, noch door Octrooicentrum Nederland gegarandeerd; de gegevens worden verstrekt voor informatiedoeleinden.

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomende octrooigeschriften	Datum van publicatie
EP 1086975	A1 28-03-2001	DE 69932052 JP 4527281 US 7008994 WO 9952966	T2 09-11-2006 B2 18-08-2010 B1 07-03-2006 A1 21-10-1999



Rijksdienst voor Ondernemend
Nederland

SCHRIJFELIJKE OPINIE

Octrooiaanvraag 2032660

Indieningsdatum ('moederaanvraag' 2019837): 31 oktober 2017	Voorrangsdatum: 31 oktober 2016
Classificatie van het onderwerp ¹ : C09D11/326; C08F212/08; C08L35/06; C08F222/06; C08F222/08; C09D125/14; C09D135/02; C09D11/107	Aanvrager: Cabot Corporation

Deze schriftelijke opinie bevat een toelichting op de volgende onderdelen:

- Onderdeel I Basis van de schriftelijke opinie
- Onderdeel II Voorrang
- Onderdeel III Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk
- Onderdeel IV De aanvraag heeft betrekking op meer dan één uitvinding
- Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid
- Onderdeel VI Andere geciteerde documenten
- Onderdeel VII Overige gebreken
- Onderdeel VIII Overige opmerkingen

	De bevoegde ambtenaar: dr. R. Boers Octrooicentrum Nederland onderdeel van Rijksdienst voor Ondernemend Nederland
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¹ Gedefinieerd volgens International Patent Classification (IPC).

Schriftelijke Opinie

Octrooiaanvrage 2032660

Onderdeel I Basis van de schriftelijke opinie

Deze schriftelijke opinie is opgesteld op basis van de op 2 augustus 2022 ingediende conclusies.

Onderdeel II Voorrang

Het controleren van de voorrang maakt geen deel uit van het reguliere onderzoek naar de stand van de techniek. Deze schriftelijke opinie is daarom opgesteld zonder dat onderzocht is of de ingeroepen voorrang geldig is, tenzij hieronder anders is aangegeven.

Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid

1. Verklaring

Nieuwheid	Ja: conclusie(s)	7, 13, 15, 21-24, 33-36
	Nee: conclusie(s)	1-6, 8-12, 14, 16-20, 25-32
Inventiviteit	Ja: conclusie(s)	21-24
	Nee: conclusie(s)	7, 13, 15, 33-36
Industriële toepasbaarheid	Ja: conclusie(s)	1-36
	Nee: conclusie(s)	-

2. Literatuur en toelichting

In het rapport betreffende het onderzoek naar de stand van de techniek wordt de volgende publicatie genoemd:

D1: EP 1086975 A (MIKUNI COLOR WORKS) 28 maart 2001

D1 openbaart een samenstelling omvattende een pigment, een waterig vloeibaar dragermateriaal en een styreen-maleïnezuur copolymer (60/40; acid value:190), waarbij na het vormen van de pigment/styreen-maleïnezuur-dispersie het polymeer wordt vernet met een oxazoline-groep bevattend polymeer (tot een "gel percent: 50%"), wat met de zuurgroepen van het maleïnezuur zal reageren, zodat een ingekapseld pigment wordt verkregen ("was strongly adsorbed on the pigment"; zie paragraaf [0015]; voorbeeld 3). D1 openbaart ook een werkwijze om dit polymeer te maken. D1 openbaart daarmee alle materie van conclusies 1-6, 8-12, 14, 16-20, 25-32, welke conclusies daarmee niet nieuw zijn.

D1 benoemt ook andere vernettingsmiddelen (zie paragrafen [0053]-[0057]) en daarnaast is de deskundige bekend met diverse andere vernettingsmiddelen die vergelijkbare resultaten zullen geven. De materie van conclusie 7 wordt daardoor niet inventief bevonden.

De deskundige is ook bekend met maleïnezuuranhydride als alternatief monomeer voor maleïnezuur als tweede polymeer. Maleïnezuuranhydride zal overigens na verloop van tijd in een waterige omgeving (deels) hydrolyseren tot maleïnezuur. De materie van conclusies 13 en 15 wordt daardoor

Schriftelijke Opinie

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niet inventief bevonden.

Ook wordt het toevoegen van een duurzaamheidsbevorderend polymeer niet inventief gevonden, waardoor conclusie 33 niet inventief is.

Werkwijzeconclusie 34 verschilt met het aangehaalde voorbeeld in D1 in dat het vernettingsmiddel geselecteerd wordt uit epoxy-houdende verbindingen. Zoals hiervoor aangegeven benoemt D1 diverse vernettingsmiddelen, waaronder epoxy-houdende middelen. Het wordt dan ook niet inventief bevonden om in het aangehaalde voorbeeld als alternatief een epoxy-houdend vernettingsmiddel te gebruiken, die overigens algemeen bekend zijn bij de deskundige. De materie van conclusie 34 wordt daardoor niet inventief bevonden.

De materie van conclusies 35 en 36 omvat maatregelen die algemeen bekend zijn en binnen het bereik van de deskundige liggen. Deze conclusies worden daardoor evenmin inventief bevonden.

Conclusies 21-24 verschillen met D1 in een modificatie van het tweede monomeer. D1 geeft ook geen aanwijzingen om die modificaties aan te brengen. De materie van conclusies 21-24 wordt daardoor nieuw en inventief bevonden ten opzichte van D1.