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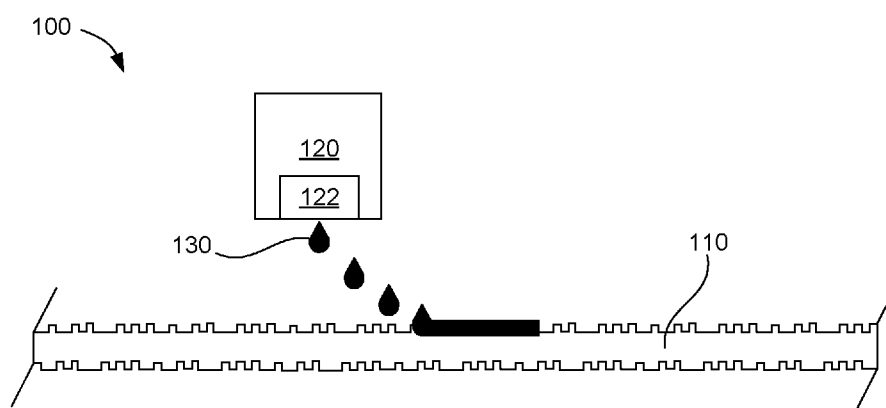


FIG. 1A

(57) Abstract: A textile printing material set includes a fabric substrate and an aqueous ink composition. The aqueous ink composition includes an aqueous ink vehicle, pigment, and from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50°C to 30°C and an acrylic shell copolymer having a glass transition temperature from 50°C to 130°C. The acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles in this example are present at an average weight ratio from 1:1 to 9:1.



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TEXTILE PRINTING

BACKGROUND

[0001] Inkjet printing has become a popular way of recording images on various media. Some of the reasons include low printer noise, variable content recording, capability of high speed recording, and multi-color recording. These advantages can be obtained at a relatively low price to consumers. As the popularity of inkjet printing increases, the types of use also increase providing demand for new ink compositions. In one example, textile printing can have various applications including the creation of signs, banners, artwork, apparel, wall coverings, window coverings, upholstery, pillows, blankets, flags, tote bags, clothing, etc. However, the permanence of printed ink on textiles can be an issue.

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BREIF DESCRIPTION OF DRAWINGS

[0002] FIG. 1A schematically depicts an example textile printing system including an ink composition and a fabric substrate in accordance with the present disclosure;

[0003] FIG. 1B schematically depicts an example textile printing system including an ink composition, a fabric substrate, an inkjet printhead, and a heat curing device in accordance with the present disclosure;

[0004] FIG. 2 provides a flow diagram for an example method of textile printing in accordance with the present disclosure; and

[0005] FIG. 3 is a TOE curve graph showing Turn On Energy comparisons of six (6) different example ink compositions with 6 different example acrylic latex particles in accordance with the present disclosure.

DETAILED DESCRIPTION

[0006] The present disclosure is drawn to textile printing material sets, textile printing systems, and textile printing methods. In one example, a textile printing material set includes a fabric substrate, and an aqueous ink composition. The aqueous ink composition includes an aqueous ink vehicle, pigment, and from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C, wherein the acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles have an average weight ratio from 1:1 to 9:1. In one example, the glass transition temperature of the acrylic core copolymer can be from -25 °C to 15 °C and the glass transition temperature of the acrylic shell copolymer can be from 75 °C to 105 °C. In another example, the acrylic shell copolymer can include from 30 wt% to 80 wt% copolymerized methyl methacrylate, ethyl methacrylate, or a combination thereof. The acrylic shell copolymer can include from 1 wt% to 14 wt% copolymerized acrylic acid, methacrylic acid, or a combination thereof. The acrylic core copolymer and the acrylic shell copolymer can independently both include copolymerized a propyl acrylate, a butyl acrylate, or a combination thereof. In a more specific example, the acrylic core copolymer and the acrylic shell copolymer can both include copolymerized n-butyl acrylate. The fabric substrate can be selected from cotton, polyester, nylon, silk, or a blend thereof, for example.

[0007] In another example, a textile printing system includes a fabric substrate, an inkjet printhead in fluid communication with a reservoir containing an aqueous ink composition, and a heating source positioned to heat the aqueous ink composition after application onto the fabric substrate. The aqueous ink composition includes an aqueous ink vehicle, pigment, and from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to

130 °C. The acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles in this example have an average weight ratio from 1:1 to 9:1. In one example, the acrylic shell copolymer includes from 30 wt% to 80 wt% copolymerized methyl methacrylate, ethyl methacrylate, or a combination thereof, and/or the acrylic
5 shell copolymer also includes from 1 wt% to 14 wt% copolymerized acrylic acid, methacrylic acid, or a combination thereof. In another example, the acrylic core copolymer and the acrylic shell copolymer both include copolymerized n-butyl acrylate. The heating source can be positioned and powerable to generate heat at the fabric substrate at a temperature ranging from above the glass transition temperature of the
10 acrylic shell copolymer to 200 °C. Furthermore, the fabric substrate can be selected from cotton, polyester, nylon, silk, or a blend thereof.

[0008] In another example, a method of textile printing includes jetting an aqueous ink composition onto a fabric substrate. The aqueous ink composition includes an aqueous ink vehicle, pigment, and from 2 wt% to 15 wt% of acrylic core-shell latex
15 particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C. The acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles in this example have an average weight ratio from 1:1 to 9:1. The method can further include heating the fabric substrate with the aqueous ink
20 composition thereon to a temperature ranging from above the glass transition temperature of the acrylic shell copolymer to 200 °C. The fabric substrate can be selected from cotton, polyester, nylon, silk, or a blend thereof.

[0009] It is noted that when discussing the textile printing material sets, textile printing systems, and/or the methods of textile printing herein, these discussions can be
25 considered applicable to one another whether or not they are explicitly discussed in the context of that example. Thus, for example, when discussing an organic co-solvent related to the textile printing systems, such disclosure is also relevant to and directly supported in the context of the textile printing material sets and/or methods of textile printing, and *vice versa*. It is also understood that terms used herein will take on their
30 ordinary meaning in the relevant technical field unless specified otherwise. In some instances, there are terms defined more specifically throughout the specification or

included at the end of the present specification, and thus, these terms have a meaning as described herein.

[0010] Turning now to more specific detail regarding the textile printing systems, in FIG. 1A, an example textile printing system 100 is shown which includes a fabric substrate 110 and an ink composition 130. The ink composition can be printed from an inkjet pen 120 which includes an ejector 122 or printhead, such as a thermal inkjet ejector, for example. The ink composition includes water and organic co-solvent (sometimes referred to collectively as an ink vehicle), and a pigment (dispersed with a dispersant associated with a surface of the pigment). The ink composition also includes acrylic core-shell latex particles. The dispersant can be associated with the pigment by adsorption, ionic attraction, or by covalent attachment thereto. The acrylic core-shell latex particles can have an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C. The acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles have an average weight ratio from 1:1 to 9:1.

[0011] In another example, as shown in FIG. 1B, an example textile printing system 105 is shown that includes a fabric substrate 110, an ink composition 130, an inkjet pen 120 which includes an ejector 122, e.g., inkjet printhead, and a heat curing device 140 which emits heat 150 therefrom. The ink composition includes the acrylic core-shell latex particles described herein. Thus, upon printing the ink composition onto the fabric substrate, the ink composition can be heated to heat cure the ink composition on the fabric substrate, thus providing enhanced image durability on the fabric substrate.

[0012] The acrylic core-shell latex particles can be formed by emulsion polymerization of selected components. The emulsion polymerization can thus be conducted in accordance with conventional polymerization techniques, for example in a batch, feed, or semi-batch process. Particularly, a combination of first phase of monomers and second phase of monomers can be employed in combination with a charge stabilizing agent, an emulsifier, and/or an initiator, for example. The first phase of monomers can be a batch or feed of softer monomers, e.g., monomers having a

lower glass transition temperature (T_g), though higher T_g monomers can be used in smaller amounts, provided the resultant core copolymer results in a core latex polymer that has a T_g from -50 °C to 30 °C. In one example, the acrylic core copolymer can have a T_g from -25 °C to 15 °C.

5 **[0013]** The second phase of monomers can be selected from harder monomers, e.g., monomers having a relatively higher glass transition temperature (T_g), though lower T_g monomers can likewise be used in smaller amounts, provided the resultant shell copolymer results in a shell latex polymer that has a T_g from 50 °C to 130 °C. In another example, the glass transition temperature of the acrylic shell copolymer is from
10 75 °C to 105 °C.

[0014] Reference within the present disclosure to the glass transition temperature (T_g) of an acrylic polymer can refer to the calculated glass transition temperature based on known T_g values for homopolymers prepared from the monomers used to form the copolymer core or the copolymer shell. Thus, “glass transition temperature” or “T_g,” can
15 be calculated by the Fox equation: $\text{copolymer } T_g = 1 / (W_a / (T_g A) + W_b / (T_g B) + \dots)$ where W_a = weight fraction of monomer A in the copolymer and T_{gA} is the homopolymer T_g value of monomer A, W_b = weight fraction of monomer B and T_{gB} is the homopolymer T_g value of monomer B, etc. Example homopolymer T_g values can be found in Table 2 in Example 1 hereinafter.

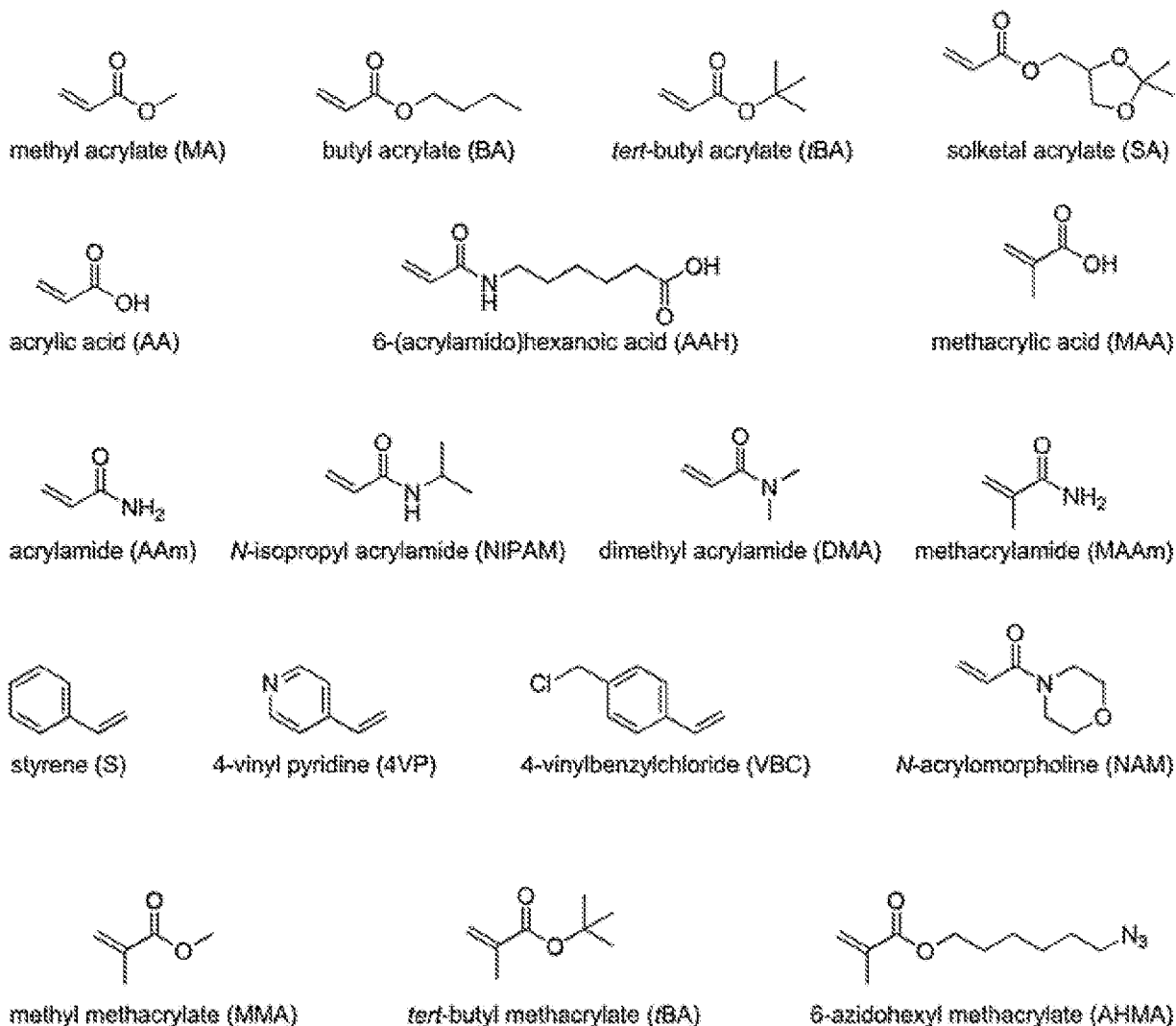
20 **[0015]** Monomers used to prepare the acrylic core/shell latex particles can include, for either the core or the shell (at appropriate concentrations to arrive at the glass transition temperatures described herein), various monomers, but both the core and the shell include a polymerized (meth)acrylic monomer. Thus the term “acrylic core-shell latex” refers to latexes where both the core and the shell include a polymerized
25 (meth)acrylic monomer, which is typically a copolymerized core and a copolymerized shell. The term “(meth)acrylic” refers to monomers, copolymerized monomers, etc., that can either be acrylate or methacrylate (or a combination of both), or acrylic acid or methacrylic acid (or a combination of both), as the acid or salt/ester form can be a function of pH. Furthermore, even if the monomer used to form the polymer was in the
30 form of a (meth)acrylic acid during preparation, pH modifications during preparation or subsequently when added to an ink composition can impact the nature of the moiety as

well (acid form vs. salt or ester form). Thus, a monomer or a moiety of a polymer described as (meth)acrylic should not be read so rigidly as to not consider relative pH levels, ester chemistry, and other general organic chemistry concepts.

[0016] Examples of monomers that can be used include monoacrylates, diacrylates, or polyfunctional alkoxyated or polyalkoxyated acrylic monomers comprising one or more di- or tri-acrylates. Suitable monoacrylates include, for example, methyl acrylate, methyl methacrylate, solketal acrylate, methacrylic acid, acrylic acid, 6-(acrylamido)hexanoic acid, acrylamide, N-isopropyl acrylamide, dimethyl acrylamide, methacrylamide, styrene, 4-vinyl pyridine, 4-vinyl benzylchloride, N-acrylomorpholine, tert-butyl methacrylate, 6-azidohexyl methacrylate, cyclohexyl acrylate, 2-ethoxy ethyl acrylate, 2-methoxy ethyl acrylate, 2(2-ethoxyethoxy)ethyl acrylate, stearyl acrylate, tetrahydrofurfuryl acrylate, octyl acrylate, lauryl acrylate, behenyl acrylate, 2-phenoxy ethyl acrylate, butyl acrylate (n-butyl acrylate), tertiary butyl acrylate, propyl acrylate, glycidyl acrylate, isodecyl acrylate, benzyl acrylate, hexyl acrylate, isooctyl acrylate, isobornyl acrylate, butanediol monoacrylate, ethoxylated phenol monoacrylate, oxyethylated phenol acrylate, monomethoxy hexanediol acrylate, beta-carboxy ethyl acrylate, dicyclopentyl acrylate, carbonyl acrylate, octyl decyl acrylate, ethoxylated nonylphenol acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, and the like. Suitable polyfunctional alkoxyated or polyalkoxyated acrylates are, for example, alkoxyated, ethoxylated, or propoxylated, variants of the following: neopentyl glycol diacrylates, butanediol diacrylates, butanediol dimethacrylates, e.g., 1,3-butanediol dimethacrylate (BDDMA), trimethylolpropane triacrylates, glyceryl triacrylates, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, 1,6-hexanediol diacrylate, tetraethylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, polybutanediol diacrylate, polyethylene glycol diacrylate, propoxylated neopentyl glycol diacrylate, ethoxylated neopentyl glycol diacrylate, polybutadiene diacrylate, and the like. The monomer can be, for example, propoxylated neopentyl glycol diacrylate, such as, for example, SR-9003 (Sartomer Co., Inc., Exton, Pa.). Suitable reactive monomers are likewise commercially available from, for example, Sartomer Co., Inc., Henkel Corp., Radcure Specialties, and the like.

[0017] The chemical structure and common abbreviations for a few monomers

listed above that can be used are shown as follows:



[0018] The reaction medium used for preparing the acrylic core-shell latex particles can use both a charge stabilizing agent and an emulsifier in order to obtain a target particle size. Particularly, the acrylic core-shell latex particles can have a D50 particle size from about 100 nm to about 350 nm, from about 150 nm to about 350 nm, from about 200 nm to about 300 nm, or from about 240 nm to about 280 nm, for example. "D50" particle size is defined here as the particle size at which about half of the particles are larger than the D50 particle size and about half of the other particles are smaller than the D50 particle size (by weight based on the metal particle content of the particulate build material). As used herein, particle size with respect to the acrylic

core-shell latex particles can be based on volume of the particle size normalized to a spherical shape for a theoretical diameter measurement, for example. Particle size can be collected using a Malvern Zetasizer, for example. Likewise, the “D95” is defined as the particle size at which about 5 wt% of the particles are larger than the D95 particle size and about 95 wt% of the remaining particles are smaller than the D95 particle size. Particle size information can also be determined and/or verified using a scanning electron microscope (SEM).

[0019] The charge stabilizing agent can be a monomer that includes acid groups suitable for stabilizing the particles in the liquid medium of the ink compositions. Various charge stabilizing agents that can be used include methacrylic acid, acrylic acid, and/or a salt thereof. Thus, methacrylic acid and acrylic acid are both also listed as monomers herein, but can have the dual function of copolymerization and charge stabilization. Sodium salts of methacrylic acid and/or acrylic acid can be used in some specific examples. The charge stabilizing agent may be employed in relatively small concentrations, e.g., about 0.1 wt% to about 5 wt% (based on the weight of the emulsion polymerization components).

[0020] The emulsifier, as mentioned, can contribute to achieving a target particle size, but can also contribute to a desired surface tension of the acrylic core-shell latex particles, e.g., from about 35 dynes/cm to about 65 dynes/cm, from about 40 dynes/cm to about 60 dynes/cm, or about 45 dynes/cm to about 55 dynes/cm. The emulsifier can include a fatty acid ether sulfate, such as lauryl ether sulfate. Suitably, the emulsifier may be included at relatively small concentrations, e.g., about 0.1 wt% to about 5 wt% (based on the weight of the emulsion polymerization components). The emulsion polymerization is conducted in accordance with polymerization processes, such as, for example, a semi-batch process.

[0021] The acrylic core-shell latex particles can be synthesized by free radical initiated polymerization using a free radical initiator, for example. The initiator can include a “per” compound such as a diazo compound, persulfate, per-oxygen, or the like. Thermal initiators that can be used include azo compounds: 1,1'-azobis(cyclohexanecarbonitrile) 98%, azobisisobutyronitrile 12 wt. % in acetone, 2,2'-azobis(2-methylpropionitrile) 98%, 2,2'-azobis(2-methylpropionitrile) recrystallized, 99%;

inorganic peroxides: ammonium persulfate reagent grade, 98%; hydroxymethanesulfinic acid monosodium salt dihydrate; potassium persulfate ACS reagent, $\geq 99.0\%$; sodium persulfate reagent grade, $\geq 98\%$; dicumyl peroxide 98%; and organic peroxides: *tert*-butyl hydroperoxide solution packed in FEP bottles, ~ 5.5 M in decane (over molecular sieve $4\text{\AA}$); *tert*-butyl hydroperoxide solution 5.0-6.0 M in nonane; *tert*-butyl peracetate solution 50 wt. % in odorless mineral spirits; cumene hydroperoxide technical grade, 80%; 2,5-di(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne, blend; Luperox[®] 101, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane technical grade, 90%; Luperox[®] 101XL45, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, blend with calcium carbonate and silica;

10 Luperox[®] 224, 2,4-pentanedione peroxide solution ~ 34 wt. % in 4-hydroxy-4-methyl-2-pentanone and *N*-methyl-2-pyrrolidone; Luperox[®] 231, 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane 92%; Luperox[®] 331M80, 1,1-bis(*tert*-butylperoxy)cyclohexane solution ~ 80 wt. % in odorless mineral spirits; Luperox[®] 531M80, 1,1-bis(*tert*-amylperoxy)cyclohexane solution 80 wt. % in odorless mineral spirits; Luperox[®] A70S,

15 benzoyl peroxide 70%, remainder water; Luperox[®] A75, benzoyl peroxide 75%, remainder water; Luperox[®] A75FP, benzoyl peroxide, 75% remainder water contains 25 wt. % water as stabilizer, 75%; Luperox[®] A75FP, benzoyl peroxide, 75% remainder water contains 25 wt. % water as stabilizer, 75%; Luperox[®] A98, benzoyl peroxide reagent grade, $\geq 98\%$; Luperox[®] AFR40, benzoyl peroxide solution 40 wt. % in dibutyl

20 phthalate; Luperox[®] ATC50, benzoyl peroxide ~ 50 wt. % in tricresyl phosphate; Luperox[®] DDM-9, 2-butanone peroxide solution ~ 35 wt. % in 2,2,4-trimethyl-1,3-pentandiol diisobutyrate; Luperox[®] DHD-9, 2-butanone peroxide solution ~ 32 wt. % in phthalate-free plasticizer mixture; Luperox[®] DI, *tert*-butyl peroxide 98%; Luperox[®] P, *tert*-butyl peroxybenzoate 98%; Luperox[®] TBEC, *tert*-butylperoxy 2-

25 ethylhexyl carbonate 95%; Luperox[®] TBH70X, *tert*-butyl hydroperoxide solution 70 wt. % in H₂O.

[0022] The weight ratio of the acrylic latex core polymer to the acrylic latex shell polymer can be from 1:1 to 9:1 (50:50 to 90:10; or 50 wt% core and 50 wt% shell to 90 wt% core to 10 wt% shell). Other weight ratios that can be used include from 60:40 to

30 90:10, from 60:40 to 85:15, from 65:35 to 90:10, or from 65:35 to 85:15, for example.

[0023] The acrylic core-shell latex particles can have any acid number at the surface that is suitable for printing on fabric. However, in some examples, the acid number (or acid value) can be relatively low, e.g., from 0 mg KOH/g to 45 mg KOH/g, from 0 mg KOH/g to 30 mg KOH/g, from 2 mg KOH/g to 20 mg KOH/g, or from 4 mg KOH/g to 15 mg KOH/g, for example. The term "acid value" or "acid number" refers to the mass of potassium hydroxide (KOH) in milligrams that can be used to neutralize one gram of substance (mg KOH/g), such as the latex polymers disclosed herein. This value can be determined, in one example, by dissolving or dispersing a known quantity of a material in organic solvent and then titrating with a solution of potassium hydroxide (KOH) of known concentration for measurement.

[0024] In certain more specific examples, the acrylic core-shell latex particles can have a latex core weight average molecular weight from 30,000 Mw to 1,500,000 Mw, from 50,000 Mw to 1,000,000 Mw, or from 75,000 Mw to 500,000 Mw. Furthermore, the acrylic core-shell latex particles can have a latex shell weight average molecular weight from 10,000 Mw to 1,000,000 Mw, from 20,000 Mw to 500,000 Mw, or from 30,000 Mw to 300,000 Mw.

[0025] In further detail, the acrylic shell copolymer can include from 1 wt% to 14 wt% copolymerized acrylic acid, methacrylic acid, or a combination thereof. In other examples, the copolymerized acrylic acid and/or methacrylic acid can be present at from 2 wt% to 12 wt%, or from 4 wt% to 10 wt%. In one example, there is not acrylic acid, and the charge stabilizing monomer is provided by methacrylic acid, e.g., from 1 wt% to 1 wt%, from 2 wt% to 12 wt%, or from 4 wt% to 10 wt%.

[0026] In further detail, the acrylic shell copolymer can include from 30 wt% to 80 wt% copolymerized methyl methacrylate, ethyl methacrylate, or a combination thereof. In another example, the copolymerized methyl methacrylate and/or ethyl methacrylate can be present at from 35 wt% to 75 wt%, from 40 wt% to 70 wt%, or from 40 wt% to 60 wt%, for example. In another example, the methyl methacrylate can be present at from 30 wt% to 80 wt%, at from 35 wt% to 75 wt%, from 40 wt% to 70 wt%, or from 40 wt% to 60 wt%, and the acrylic shell copolymer can be devoid of ethyl methacrylate.

[0027] Turning to further detail regarding other components of the ink compositions that can be used for the systems and methods described herein, the

pigment can be any of a number of pigments of any of a number of primary or secondary colors, or can be black or white, for example. More specifically, colors can include cyan, magenta, yellow, red, blue, violet, red, orange, green, etc. In one example, the ink composition can be a black ink with a carbon black pigment. In another example, the ink composition can be a cyan or green ink with a copper phthalocyanine pigment, e.g., Pigment Blue 15:0, Pigment Blue 15:1; Pigment Blue 15:3, Pigment Blue 15:4, Pigment Green 7, Pigment Green 36, etc. In another example, the ink composition can be a magenta ink with a quinacridone pigment or a co-crystal of quinacridone pigments. Example quinacridone pigments that can be utilized can include PR122, PR192, PR202, PR206, PR207, PR209, PO48, PO49, PV19, PV42, or the like. These pigments tend to be magenta, red, orange, violet, or other similar colors. In one example, the quinacridone pigment can be PR122, PR202, PV19, or a combination thereof. In another example, the ink composition can be a yellow ink with an azo pigment, e.g., PY74 and PY155. Other examples of pigments include the following, which are available from BASF Corp.: PALIOGEN® Orange, HELIOGEN® Blue L 6901F, HELIOGEN® Blue NBD 7010, HELIOGEN® Blue K 7090, HELIOGEN® Blue L 7101F, PALIOGEN® Blue L 6470, HELIOGEN® Green K 8683, HELIOGEN® Green L 9140, CHROMOPHTAL® Yellow 3G, CHROMOPHTAL® Yellow GR, CHROMOPHTAL® Yellow 8G, IGRAZIN® Yellow 5GT, and IGRALITE® Rubine 4BL.

The following pigments are available from Degussa Corp.: Color Black FWI, Color Black FW2, Color Black FW2V, Color Black 18, Color Black, FW200, Color Black 5150, Color Black S160, and Color Black 5170. The following black pigments are available from Cabot Corp.: REGAL® 400R, REGAL® 330R, REGAL® 660R, MOGUL® L, BLACK PEARLS® L, MONARCH® 1400, MONARCH® 1300, MONARCH® 1100, MONARCH® 1000, MONARCH® 900, MONARCH® 880, MONARCH® 800, and MONARCH® 700.

The following pigments are available from Orion Engineered Carbons GMBH: PRINTEX® U, PRINTEX® V, PRINTEX® 140U, PRINTEX® 140V, PRINTEX® 35, Color Black FW 200, Color Black FW 2, Color Black FW 2V, Color Black FW 1, Color Black FW 18, Color Black S 160, Color Black S 170, Special Black 6, Special Black 5, Special Black 4A, and Special Black 4. The following pigment is available from DuPont: TI-PURE® R-101. The following pigments are available from Heubach: MONASTRAL®

Magenta, MONASTRAL® Scarlet, MONASTRAL® Violet R, MONASTRAL® Red B, and MONASTRAL® Violet Maroon B. The following pigments are available from Clariant:

DALAMAR® Yellow YT-858-D, Permanent Yellow GR, Permanent Yellow G, Permanent Yellow DHG, Permanent Yellow NCG-71, Permanent Yellow GG, Hansa Yellow RA, Hansa Brilliant Yellow 5GX-02, Hansa Yellow-X, NOVOPERM® Yellow HR, NOVOPERM® Yellow FGL, Hansa Brilliant Yellow 10GX, Permanent Yellow G3R-01, HOSTAPERM® Yellow H4G, HOSTAPERM® Yellow H3G, HOSTAPERM® Orange GR, HOSTAPERM® Scarlet GO, and Permanent Rubine F6B. The following pigments

are available from Sun Chemical: QUINDO® Magenta, INDOFAST® Brilliant Scarlet,

QUINDO® Red R6700, QUINDO® Red R6713, INDOFAST® Violet, L74-1357 Yellow, L75-1331 Yellow, L75-2577 Yellow, and LHD9303 Black. The following pigments are

available from Birla Carbon: RAVEN® 7000, RAVEN® 5750, RAVEN® 5250, RAVEN® 5000 Ultra® II, RAVEN® 2000, RAVEN® 1500, RAVEN® 1250, RAVEN® 1200,

RAVEN® 1190 Ultra®, RAVEN® 1170, RAVEN® 1255, RAVEN® 1080, and RAVEN®

1060. The following pigments are available from Mitsubishi Chemical Corp.: No. 25, No. 33, No. 40, No. 47, No. 52, No. 900, No. 2300, MCF-88, MA600, MA7, MA8, and MA100. The colorant may be a white pigment, such as titanium dioxide, or other inorganic pigments such as zinc oxide and iron oxide.

[0028] Specific other examples of a cyan color pigment may include C.I. Pigment Blue -1, -2, -3, -15, -15:1, -15:2, -15:3, -15:4, -16, -22, and -60; magenta color pigment may include C.I. Pigment Red -5, -7, -12, -48, -48:1, -57, -112, -122, -123, -146, -168, -177, -184, -202, and C.I. Pigment Violet-19; yellow pigment may include C.I. Pigment Yellow -1, -2, -3, -12, -13, -14, -16, -17, -73, -74, -75, -83, -93, -95, -97, -98, -114, -128, -129, -138, -151, -154, and -180. Black pigment may include carbon black pigment or organic black pigment such as aniline black, e.g., C.I. Pigment Black 1. While several examples have been given herein, it is to be understood that any other pigment can be used that is useful in color modification, or dye may even be used in addition to the pigment.

[0029] Furthermore, pigments and dispersants are described separately herein, but there are pigments that are commercially available which include both the pigment and a dispersant suitable for ink composition formulation. Specific examples of pigment

dispersions that can be used, which include both pigment solids and dispersant are provided by example, as follows: HPC-K048 carbon black dispersion from DIC Corporation (Japan), HSKBPG-11-CF carbon black dispersion from Dom Pedro (USA), HPC-C070 cyan pigment dispersion from DIC, CABOJET® 250C cyan pigment dispersion from Cabot Corporation (USA), 17-SE-126 cyan pigment dispersion from Dom Pedro, HPF-M046 magenta pigment dispersion from DIC, CABOJET® 265M magenta pigment dispersion from Cabot, HPJ-Y001 yellow pigment dispersion from DIC, 16-SE-96 yellow pigment dispersion from Dom Pedro, or Emacol SF Yellow AE12F yellow pigment dispersion from Sanyo (Japan).

[0030] Thus, the pigment(s) can be dispersed by a dispersant that is adsorbed or ionically attracted to a surface of the pigment, or can be covalently attached to a surface of the pigment as a self-dispersed pigment. In one example, the dispersant can be an acrylic dispersant, such as a styrene (meth)acrylate dispersant, or other dispersant suitable for keeping the pigment suspended in the liquid vehicle. In one example, the styrene (meth)acrylate dispersant can be used, as it can promote π -stacking between the aromatic ring of the dispersant and various types of pigments. In one example, the styrene (meth)acrylate dispersant can have a weight average molecular weight from 4,000 Mw to 30,000 Mw. In another example, the styrene-acrylic dispersant can have a weight average molecular weight of 8,000 Mw to 28,000 Mw, from 12,000 Mw to 25,000 Mw, from 15,000 Mw to 25,000 Mw, from 15,000 Mw to 20,000 Mw, or about 17,000 Mw. Regarding the acid number, the styrene (meth)acrylate dispersant can have an acid number from 100 to 350, from 120 to 350, from 150 to 300, from 180 to 250, or about 214, for example. Example commercially available styrene-acrylic dispersants can include Joncryl® 671, Joncryl® 71, Joncryl® 96, Joncryl® 680, Joncryl® 683, Joncryl® 678, Joncryl® 690, Joncryl® 296, Joncryl® 671, Joncryl® 696 or Joncryl® ECO 675 (all available from BASF Corp., Germany).

[0031] The ink compositions of the present disclosure can be formulated to include a liquid vehicle, which can include the water content, e.g., 60 wt% to 90 wt% or from 75 wt% to 85 wt%, as well as organic co-solvent, e.g., from 4 wt% to 30 wt%, from 6 wt% to 20 wt%, or from 8 wt% to 15 wt%. Other liquid vehicle components can also be included, such as surfactant, antibacterial agent, other colorant, etc. However, as part of

the ink composition used in the systems and methods described herein, the pigment, dispersant, and the acrylic core-shell latex particles can be included or carried by the liquid vehicle components. Suitable pH ranges for the ink composition can be from pH 6 to pH 10, from pH 7 to pH 10, from pH 7.5 to pH 10, from pH 8 to pH 10, 6 to pH 9, from
5 pH 7 to pH 9, from pH 7.5 to pH 9, etc.

[0032] In further detail regarding the liquid vehicle, the co-solvent(s) can be present and can include any co-solvent or combination of co-solvents that are compatible with the pigment, dispersant, and acrylic core-shell latex particles. Examples of suitable classes of co-solvents include polar solvents, such as alcohols, amides, esters, ketones, lactones, and ethers. In additional detail, solvents that can be used can
10 include aliphatic alcohols, aromatic alcohols, diols, glycol ethers, polyglycol ethers, caprolactams, formamides, acetamides, and long chain alcohols. Examples of such compounds include primary aliphatic alcohols, secondary aliphatic alcohols, 1,2-alcohols, 1,3-alcohols, 1,5-alcohols, ethylene glycol alkyl ethers, propylene glycol alkyl
15 ethers, higher homologs (C₆-C₁₂) of polyethylene glycol alkyl ethers, N-alkyl caprolactams, unsubstituted caprolactams, both substituted and unsubstituted formamides, both substituted and unsubstituted acetamides, and the like. More specific examples of organic solvents can include 2-pyrrolidone, 2-ethyl-2-(hydroxymethyl)-1, 3-propane diol (EPHD), glycerol, dimethyl sulfoxide, sulfolane, glycol ethers, alkyldiols
20 such as 1,2-hexanediol, and/or ethoxylated glycerols such as LEG-1, etc.

[0033] The liquid vehicle can also include surfactant and/or emulsifier. In general, the surfactant can be water soluble and may include alkyl polyethylene oxides, alkyl phenyl polyethylene oxides, polyethylene oxide (PEO) block copolymers, acetylenic PEO, PEO esters, PEO amines, PEO amides, dimethicone copolyols, ethoxylated
25 surfactants, alcohol ethoxylated surfactants, fluorosurfactants, and mixtures thereof. In some examples, the surfactant can include a nonionic surfactant, such as a Surfynol® surfactant, e.g., Surfynol® 440 (from Evonik, Germany), or a Tergitol™ surfactant, e.g., Tergitol™ TMN-6 (from Dow Chemical, USA). In another example, the surfactant can include an anionic surfactant, such as a phosphate ester of a C10 to C20 alcohol or a
30 polyethylene glycol (3) oleyl mono/di phosphate, e.g., Crodafos® N3A (from Croda International PLC, United Kingdom). The surfactant or combinations of surfactants, if

present, can be included in the ink composition at from about 0.01 wt% to about 5 wt% and, in some examples, can be present at from about 0.05 wt% to about 3 wt% of the ink compositions.

[0034] Consistent with the formulations of the present disclosure, various other additives may be included to provide desired properties of the ink composition for specific applications. Examples of these additives are those added to inhibit the growth of harmful microorganisms. These additives may be biocides, fungicides, and other microbial agents, which are routinely used in ink formulations. Examples of suitable microbial agents include, but are not limited to, Acticide®, e.g., Acticide® B20 (Thor Specialties Inc.), Nuosept™ (Nudex, Inc.), Ucarcide™ (Union carbide Corp.), Vancide® (R.T. Vanderbilt Co.), Proxel™ (ICI America), and combinations thereof. Sequestering agents, such as EDTA (ethylene diamine tetra acetic acid) or trisodium salt of methylglycinediacetic acid, may be included to eliminate the deleterious effects of heavy metal impurities, and buffer solutions may be used to control the pH of the ink. Viscosity modifiers and buffers may also be present, as well as other additives known to those skilled in the art to modify properties of the ink as desired.

[0035] These ink compositions can be suitable for printing on many types of textiles, but can be particularly acceptable on treated or untreated natural fabric textile substrates, e.g., wool, cotton, silk, linen, jute, flax, hemp, rayon fibers, thermoplastic aliphatic polymeric fibers derived from renewable resources (e.g. cornstarch, tapioca products, sugarcane), etc. Treated fabrics can include a coating, for example, such as a coating including a cationic component such as calcium salt, magnesium salt, cationic polymer, etc. These types of substrates can provide acceptable optical density (OD) and/or washfastness properties. The term "washfastness" can be defined as the OD or delta E (ΔE) that is retained after five (5) standard washing machine cycles using warm water and a standard clothing detergent (e.g., Tide® available from Proctor and Gamble, Cincinnati, OH, USA). Essentially, by measuring OD and/or $L^*a^*b^*$ both before and after washing, ΔOD and ΔE value can be determined, which is essentially a quantitative way of expressing the difference between the OD and/or $L^*a^*b^*$ prior to and after undergoing the washing cycles. Thus, the lower the ΔOD and ΔE values, the better. In further detail, ΔE is a single number that represents the "distance" between

two colors, which in accordance with the present disclosure, is the color (or black) prior to washing and the modified color (or modified black) after washing.

[0036] Colors, for example, can be expressed as CIELAB values. It is noted that color differences may not be symmetrical going in both directions (pre-washing to post washing vs. post-washing to pre-washing). Using the CIE 1976 definition, the color difference can be measured and the ΔE value calculated based on subtracting the pre-washing color values of L^* , a^* , and b^* from the post-washing color values of L^* , a^* , and b^* . Those values can then be squared, and then a square root of the sum can be determined to arrive at the ΔE value. The 1976 standard can be referred to herein as “ ΔE_{CIE} .” The CIE definition was modified in 1994 to address some perceptual non-uniformities, retaining the $L^*a^*b^*$ color space, but modifying to define the $L^*a^*b^*$ color space with differences in lightness (L^*), chroma (C^*), and hue (h^*) calculated from $L^*a^*b^*$ coordinates. Then in 2000, the CIEDE standard was established to further resolve the perceptual non-uniformities by adding five corrections, namely i) hue rotation (R_T) to deal with the problematic blue region at hue angles of about 275°), ii) compensation for neutral colors or the primed values in the L^*C^*h differences, iii) compensation for lightness (S_L), iv) compensation for chroma (S_C), and v) compensation for hue (S_H). The 2000 modification can be referred to herein as “ ΔE_{2000} .” In accordance with examples of the present disclosure, ΔE value can be determined using the CIE definition established in 1976, 1994, and 2000 to demonstrate washfastness. However, in the examples of the present disclosure, ΔE_{CIE} and ΔE_{2000} are used.

[0037] In addition to good durability or washfastness, ink compositions with these acrylic core-shell latex particles can also exhibit good stability over time as well as good thermal inkjet printhead performance such as high drop weight, high drop velocity, good kagation, and acceptable “Turn On Energy” or “TOE” curve values. Turn On Energy (TOE) can be defined as the measurement of energy used to generate a given ink drop weight (DW) upon firing. The goal is to achieve a consistent ink composition firing at a drop weight at a lower energy. At some point, the DW that increases with energy input starts to flatten out. Examples of TOE curves can be found and described in the Examples hereinafter.

[0038] In further detail regarding the fabric substrates, the fabric can include a

substrate, and in some examples can be treated, such as with a coating that includes a calcium salt, a magnesium salt, a cationic polymer, or a combination of a calcium or magnesium salt and cationic polymer. Fabric substrates can include substrates that have fibers that may be natural and/or synthetic, but in some examples, the fabric is particularly useful with natural fabric substrates. The fabric substrate can include, for example, a textile, a cloth, a fabric material, fabric clothing, or other fabric product suitable for applying ink, and the fabric substrate can have any of a number of fabric structures. The term “fabric structure” is intended to include structures that can have warp and weft, and/or can be woven, non-woven, knitted, tufted, crocheted, knotted, and pressured, for example. The terms “warp” and “weft” have their ordinary meaning in the textile arts, as used herein, e.g., warp refers to lengthwise or longitudinal yarns on a loom, while weft refers to crosswise or transverse yarns on a loom.

[0039] It is notable that the term “fabric substrate” does not include materials commonly known as any kind of paper (even though paper can include multiple types of natural and synthetic fibers or mixtures of both types of fibers). Fabric substrates can include textiles in filament form, textiles in the form of fabric material, or textiles in the form of fabric that has been crafted into a finished article (e.g. clothing, blankets, tablecloths, napkins, towels, bedding material, curtains, carpet, handbags, shoes, banners, signs, flags, etc.). In some examples, the fabric substrate can have a woven, knitted, non-woven, or tufted fabric structure. In one example, the fabric substrate can be a woven fabric where warp yarns and weft yarns can be mutually positioned at an angle of about 90°. This woven fabric can include but is not limited to, fabric with a plain weave structure, fabric with a twill weave structure where the twill weave produces diagonal lines on a face of the fabric, or a satin weave. In another example, the fabric substrate can be a knitted fabric with a loop structure. The loop structure can be a warp-knit fabric, a weft-knit fabric, or a combination thereof. A warp-knit fabric refers to every loop in a fabric structure that can be formed from a separate yarn mainly introduced in a longitudinal fabric direction. A weft-knit fabric refers to loops of one row of fabric that can be formed from the same yarn. In a further example, the fabric substrate can be a non-woven fabric. For example, the non-woven fabric can be a flexible fabric that can include a plurality of fibers or filaments that are one or both bonded together and

interlocked together by a chemical treatment process (e.g., a solvent treatment), a mechanical treatment process (e.g., embossing), a thermal treatment process, or a combination of two or more of these processes.

[0040] Regardless of the structure, in one example, the fabric substrate can include natural fibers, synthetic fibers, or a combination thereof. Exemplary natural fibers can include, but are not limited to, wool, cotton, silk, linen, jute, flax, hemp, rayon fibers, thermoplastic aliphatic polymeric fibers derived from renewable resources (e.g. cornstarch, tapioca products, sugarcane), or a combination thereof. In another example, the fabric substrate can include synthetic fibers. Exemplary synthetic fibers can include polymeric fibers such as, polyvinyl chloride (PVC) fibers, PVC-free fibers made of polyester, polyamide, polyimide, polyacrylic, polypropylene, polyethylene, polyurethane, polystyrene, polyaramid (e.g., Kevlar®) polytetrafluoroethylene (Teflon®) (both trademarks of E. I. du Pont de Nemours Company, Delaware), fiberglass, polytrimethylene, polycarbonate, polyethylene terephthalate, polyester terephthalate, polybutylene terephthalate, or a combination thereof. In some examples, the synthetic fiber can be a modified fiber from the above-listed polymers. The term “modified fiber” refers to one or both of the polymeric fiber and the fabric as a whole having undergone a chemical or physical process such as, but not limited to, one or more of a copolymerization with monomers of other polymers, a chemical grafting reaction to contact a chemical functional group with one or both the polymeric fiber and a surface of the fabric, a plasma treatment, a solvent treatment, acid etching, or a biological treatment, an enzyme treatment, or antimicrobial treatment to prevent biological degradation. The term “PVC-free fibers” as used herein means that no polyvinyl chloride (PVC) polymer or vinyl chloride monomer units are in the fibers.

[0041] As previously mentioned, the fabric substrate can be a combination of fiber types, e.g. a combination of any natural fiber with another natural fiber, any natural fiber with a synthetic fiber, a synthetic fiber with another synthetic fiber, or mixtures of multiple types of natural fibers and/or synthetic fibers in any of the above combinations. In some examples, the fabric substrate can include natural fiber and synthetic fiber. The amount of each fiber type can vary. For example, the amount of the natural fiber can vary from about 5 wt% to about 95 wt% and the amount of synthetic fiber can range

from about 5 wt% to 95 wt%. In yet another example, the amount of the natural fiber can vary from about 10 wt% to 80 wt% and the synthetic fiber can be present from about 20 wt% to about 90 wt%. In other examples, the amount of the natural fiber can be about 10 wt% to 90 wt% and the amount of synthetic fiber can also be about 10 wt% to about 90 wt%. Likewise the ratio of natural fiber to synthetic fiber in the fabric substrate can vary. For example, the ratio of natural fiber to synthetic fiber can be 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10, 1:11, 1:12, 1:13, 1:14, 1:15, 1:16, 1:17, 1:18, 1:19, 1:20, or *vice versa*.

[0042] In one example, the fabric substrate can have a basis weight ranging from about 10 gsm to about 500 gsm. In another example, the fabric substrate can have a basis weight ranging from about 50 gsm to about 400 gsm. In other examples, the fabric substrate can have a basis weight ranging from about 100 gsm to about 300 gsm, from about 75 gsm to about 250 gsm, from about 125 gsm to about 300 gsm, or from about 150 gsm to about 350 gsm.

[0043] In addition, the fabric substrate can contain additives including, but not limited to, one or more of colorant (e.g., pigments, dyes, and tints), antistatic agents, brightening agents, nucleating agents, antioxidants, UV stabilizers, fillers and lubricants, for example. Alternatively, the fabric substrate may be pre-treated in a solution containing the substances listed above before applying other treatments or coating layers.

[0044] In another example, and as set forth in FIG. 2, a method 200 of textile printing includes jetting an aqueous ink composition onto a fabric substrate. The aqueous ink composition in this example includes an aqueous ink vehicle, pigment, and from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C. The acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles have an average weight ratio from 1:1 to 9:1 in this example. In further detail, the method can include heating the fabric substrate with the aqueous ink composition thereon to a temperature ranging from above the glass transition temperature of the acrylic shell copolymer to 200 °C. The fabric substrate can include, for example, cotton, polyester,

nylon, silk, or a blend thereof.

[0045] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise.

5 **[0046]** As used herein, the term "about" is used to provide flexibility to a numerical range endpoint by providing that a given value may be "a little above" or "a little below" the endpoint. The degree of flexibility of this term can be dictated by the particular variable and would be within the knowledge of those skilled in the art to determine based on experience and the associated description herein.

10 **[0047]** As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a *de facto* equivalent of any other member of the same
15 list solely based on their presentation in a common group without indications to the contrary.

[0048] Concentrations, dimensions, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only
20 the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a weight ratio range of about 1 wt% to about 20 wt% should be interpreted to include not only the explicitly recited limits of about 1 wt% and about 20 wt%, but also to include individual weights
25 such as 2 wt%, 11 wt%, 14 wt%, and sub-ranges such as 10 wt% to 20 wt%, 5 wt% to 15 wt%, etc.

EXAMPLES

30 **[0049]** The following examples illustrate the technology of the present disclosure. However, it is to be understood that the following are only exemplary or illustrative of the

application of the principles of the presented fabric print media and associated methods. Numerous modifications and alternatives may be devised without departing from the present disclosure. The appended claims are intended to cover such modifications and arrangements. Thus, while the disclosure has been provided with particularity, the following describes further detail in connection with what are presently deemed to be the acceptable examples.

Example 1 – Seed Latex and Acrylic Latexes Prepared Therefrom

[0050] A seed latex (Seed Latex 1) was obtained to use as a common seed latex for the preparation of several acrylic core-shell latexes of several examples hereinafter. The seed latex was selected to control particle size of the core-shell latex prepared in accordance with the examples hereinafter, e.g., Examples 2-19 (Latexes 2-19). The seed latex was an all acrylic latex copolymer with a D50 particle size of approximately 65 nm (diameter) and a solids content of approximately 48 wt%. Tables 1A-1C below summarize the acrylic latexes prepared in Examples 2-19, including the amount of first stage (core) and second stage (shell) monomers used as a percentage of the total monomer of the formulations. Examples 13 and 14 are single-phase acrylic latexes, so they are considered to be 100 wt% core, as notated in the summary tables below. The details on the Seed Latex are not included in the Tables. The examples were either dual-phase preparations to generate acrylic core-shell latex particles (first stage core varied wt% from 65 wt% to 85 wt; second stage shell varied wt% from 15 wt% to 35 wt%); or single-phase (100 wt% first stage monomer). The calculated glass transition temperature (T_g) for the core and the shell (separately) were included, which can be calculated based on the Fox equation using homopolymer T_g values shown in Table 2. Theoretical acid values and measured solid percentages were also provided for the completed acrylic latex polymer particles.

Table 1A – Summary of Examples 2-8 Acrylic Latex Polymer Particles (Latexes 2-8)

	Latex 2	Latex 3	Latex 4	Latex 5	Latex 6	Latex 7	Latex 8
CORE							
Monomers	BA Styrene	BA Styrene	BA Styrene	BA Styrene BBDA	BA Styrene DAAM	BA Styrene WAMII	BA Styrene
Wt% Core	75	65	85	75	75	75	75
Tg (°C)	5	5	5	5	10	7	-14
SHELL							
Monomers	BA MMA Styrene MAA	BA MMA Styrene MAA	BA MMA Styrene MAA	BA MMA Styrene MAA	BA MMA Styrene MAA DAAM	BA MMA Styrene MAA WAMII	BA MMA Styrene MAA
Wt% Shell	25	35	15	25	25	25	25
Tg (°C)	106	106	106	106	105	105	103
LATEX PARTICLES							
Acid Value (mgKOH/g)	9.8	13.7	5.9	9.8	9.8	6.5	6.5
D50 Particle Size (nm)	220	222	236	236	216	259	226
pH	7.4	8	7.2	9.1	7.5	7.5	8.2
Wt% Solids	38.5	38.5	38.7	39.3	39.2	36.9	38.85
Morphology	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell

Table 1B – Summary of Examples 9-14 Acrylic Latex Polymer Particles (Latexes 9-14)

	Latex 9	Latex 10	Latex 11	Latex 12	Latex 13 (Comp)	Latex 14 (Comp)
CORE						
Monomers	BA Styrene	BA Styrene	BA Styrene WAMII	BA Styrene WAMII	BA Styrene MAA	BA Styrene MAA
Wt% Core	65	85	75	85	100	100
Tg (°C)	5	-14	-12	7	5	-14
SHELL						
Monomers	BA Styrene	BA Styrene	BA Styrene	BA Styrene	-	-

	MMA	MMA	MMA WAMII	MMA		
Wt% Shell	35	15	25	15	-	-
Tg (°C)	103	103	105	105	-	-
LATEX PARTICLES						
Acid Value (mgKOH/g)	9.1	3.9	6.5	3.9	6.5	6.5
D50 Particle Size (nm)	221	224	229	237	239	226
pH	8.2	7.4	7.7	8.1	7.8	9.2
Wt% Solids	38.3	38.96	37.68	37.27	41.8	38.83
Morphology	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell	Single- phase	Single- phase

Table 1C -Summary of Examples 15-19 Acrylic Latex Polymer Particles (Latexes 15-19)

	Latex 15	Latex 16	Latex 17	Latex 18	Latex 19
CORE					
Monomers	Styrene BA AA	Styrene EHA AA BA MMA	BDDMA MAAM BA MAA	MAAM BA MMA	MAAM BDDMA BA MMA
Wt% Core	75	75	75	75	75
Tg (°C)	-16.8	28.3	116.2	19.6	27.1
SHELL					
Monomers	Styrene EHA MAA BA MMA	Styrene EHA MAA BA MMA	Styrene EHA MAA BA MMA	Styrene EHA MAA BA MMA	Styrene EHA MAA BA MMA
Wt% Shell	25	25	25	25	25
Tg (°C)	105.7	105.7	105.7	105.7	105.7
LATEX PARTICLES					
Acid Value (mgKOH/g)	23.9	30.8	12.3	12.3	12.3
D50 Particle Size (nm)	178.9	175.2	185.2	178.2	197.5
pH	12	12	11	11	11
Wt% Solids	29.43	29.19	23.58	26.77	27.2

Morphology	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell	Core/ Shell
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Table 2 – Monomer IDs and Homopolymer Glass Transition Temperatures (T_g)

Monomer	Abbreviation	Homopolymer T _g (°C)
methyl methacrylate	MMA	119
n-butyl acrylate	BA	-45
styrene	Styrene	104
methacrylic acid	MAA	182
diacetone acrylamide	DAAM	77
Sipomer® WAMII	WAMII	87
2-ethylhexyl acrylate	EHA	-50
acrylic acid	AA	103

5

Example 2 – Preparation of Acrylic Core-Shell Latex 2

[0051] 13.7 grams of Seed Latex 1 of Example 1 and 335.9 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 45.6 grams water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [149.8 grams n-butyl acrylate (BA), 123.2 grams styrene, 13.7 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 58.2 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [66.8 grams methyl methacrylate (MMA), 13.7 grams styrene, 4.6 grams n-butyl acrylate (BA), 5.5 grams methacrylic acid (MAA), 0.5 gram iso-octyl thioglycolate (i-OTG), 4.71 grams Hitenol AR-1025 and 18.4 grams water]. Ten minutes after the end of the second monomer feed, 75 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes.

Next, a mixture of 0.73 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.73 grams of iso-ascorbic acid in 9.7 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 220 nm (diameter), the pH was 7.4, and the solids content was 38.5 wt%.

Example 3 – Preparation of Acrylic Core-Shell Latex 3

[0052] 13.7 grams of Seed Latex 1 of Example 1 and 336 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.6 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.38 grams in 48.1 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [136.8 n-butyl acrylate (BA), 112.6 grams styrene, 12.5 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 53.2 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [98.6 grams methyl methacrylate (MMA), 20.2 grams styrene, 6.7 grams n-butyl acrylate (BA), 8.1 grams methacrylic acid (MAA), 0.7 grams iso-octyl thioglycolate (i-OTG), 6.9 grams Hitenol AR-1025 and 27.1 grams water]. Ten minutes after the end of the second monomer feed, 75.3 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex

filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 222 nm (diameter), the pH was 8, and the solids content was 38.5 wt%.

Example 4 – Preparation of Acrylic Core-Shell Latex 4

5 **[0053]** 14 grams of Seed Latex 1 of Example 1 and 343 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.3 grams of deionized water was added to the reactor and held for 5
10 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 46.6 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [173.3 n-butyl acrylate (BA), 142.6 grams styrene, 15.8 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and
15 67.3 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [40.9 grams methyl methacrylate (MMA), 8.4 grams styrene, 2.8 grams n-butyl acrylate (BA), 3.4 grams methacrylic acid (MAA), 0.3 grams iso-octyl thioglycolate (i-OTG), 2.9 grams Hitenol AR-1025 and 11.3 grams water]. Ten minutes after the end of the second
20 monomer feed, 41 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex
25 filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 236 nm (diameter), the pH was 7.2, and the solids content was 38.7 wt%.

Example 5 – Preparation of Acrylic Core-Shell Latex 5

30 **[0054]** 14 grams of Seed Latex 1 of Example 1 and 335 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The

reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.3 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.36 grams in 45.5 water) was started and fed continuously over 270 minutes.

5 Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [149.3 n-butyl acrylate (BA), 122.9 grams styrene, 2.7 grams of butanediol diacrylate (BDDA), 13.6 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 58 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the
10 second monomer feed was fed over 90 minutes [66.1 grams methyl methacrylate (MMA), 13.7 grams styrene, 4.6 grams n-butyl acrylate (BA), 5.5 grams methacrylic acid (MAA), 0.5 gram iso-octyl thioglycolate (i-OTG), 4.7 grams Hitenol AR-1025 and 18.3 grams water]. Ten minutes after the end of the second monomer feed, 60.8 grams of a
15 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 236 nm (diameter), the pH
20 was 9.1, and the solids content was 39.3 wt%.

Example 6 – Preparation of Acrylic Core-Shell Latex 6

[0055] 13.6 grams of Seed Latex 1 of Example 1 and 296.8 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed
25 throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 68.8 grams water) was started and fed continuously over 270 minutes.
30 Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [137.6 grams n-butyl acrylate (BA), 122.2 grams styrene, 10.9 grams diacetone

acrylamide (DAAM), 13.6 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 57.7 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [64.4 grams methyl methacrylate (MMA), 13.6 grams styrene, 4.5 grams n-butyl acrylate (BA), 5.4 grams methacrylic acid (MAA), 0.5 gram iso-octyl thioglycolate (i-OTG), 1.8 grams DAAM, 4.6 grams Hitenol AR-1025 and 18.2 grams water]. Ten minutes after the end of the second monomer feed, 60.8 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and then 4.6 grams of adipic dihydrazide was added and allowed to dissolve. Finally, the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 216 nm (diameter), the pH was 7.5, and the solids content was 39.2 wt%.

Example 7 – Preparation of Acrylic Core-Shell Latex 7

[0056] 13.7 grams of Seed Latex 1 of Example 1 and 336.4 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 45.6 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [144.3 grams n-butyl acrylate (BA), 123.2 grams styrene, 5.5 grams of Sipomer® WAMII (allyl ether of a substituted urea co-monomer from Solvay, Belgium), 13.6 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 58.8 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [65 grams methyl methacrylate (MMA), 13.7 grams

styrene, 4.6 grams n-butyl acrylate (BA), 3.7 grams methacrylic acid (MAA), 0.5 gram iso-octyl thioglycolate (i-OTG), 3.7 grams Sipomer® WAMII, 4.7 grams Hitenol AR-1025 and 18.4 grams water]. Ten minutes after the end of the second monomer feed, 62.9 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 259 nm (diameter), the pH was 7.5, and the solids content was 36.9 wt%.

Example 8 – Preparation of Acrylic Core-Shell Latex 8

[0057] 13.7 grams of Seed Latex 1 of Example 1 and 336 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 45.6 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [190.9 n-butyl acrylate (BA), 82.2 grams styrene, 13.7 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 58.2 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [68.6 grams methyl methacrylate (MMA), 13.7 grams styrene, 4.6 grams n-butyl acrylate (BA), 3.7 grams methacrylic acid (MAA), 0.5 gram iso-octyl thioglycolate (i-OTG), 4.7 grams Hitenol AR-1025 and 18.4 grams water]. Ten minutes after the end of the second monomer feed, 60.8 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3

grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 226 nm (diameter), the pH was 8.2, and the solids content was 38.9 wt%.

5 Example 9 – Preparation of Acrylic Core-Shell Latex 9

10 **[0058]** 13.7 grams of Seed Latex 1 of Example 1 and 336 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 45.6 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [164.9 n-butyl acrylate (BA), 71 grams styrene, 11.8 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 50.3 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [95.8 grams methyl methacrylate (MMA), 19.1 grams styrene, 6.4 grams n-butyl acrylate (BA), 5.1 grams methacrylic acid (MAA), 0.6 grams iso-octyl thioglycolate (i-OTG), 6.6 grams Hitenol AR-1025 and 25.6 grams water]. Ten minutes after the end of the second monomer feed, 64.5 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 221 nm (diameter), the pH was 8.2, and the solids content was 38.3 wt%.

30 Example 10 – Preparation of Acrylic Core-Shell Latex 10

[0059] 13.7 grams of Seed Latex 1 of Example 1 and 335.8 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed

throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution
5 (0.37 gram in 45.6 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [216.2 n-butyl acrylate (BA), 93.1 grams styrene, 15.5 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 65.9 grams water]. When the first monomer feed finished, the reactor was held at 77 °C
10 for 30 minutes, and then the second monomer feed was fed over 90 minutes [41.2 grams methyl methacrylate (MMA), 8.2 grams styrene, 2.7 grams n-butyl acrylate (BA), 2.2 grams methacrylic acid (MAA), 0.3 grams iso-octyl thioglycolate (i-OTG), 2.8 grams Hitenol AR-1025 and 11 grams water]. Ten minutes after the end of the second monomer feed, 60.2 grams of a 5 wt% solution of KOH in water was fed to the reactor
15 over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer
20 was 224 nm (diameter), the pH was 7.4, and the solids content was 39 wt%.

Example 11 – Preparation of Acrylic Core-Shell Latex 11

[0060] 13.8 grams of Seed Latex 1 of Example 1 and 335.8 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed
25 throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 45.8 water) was started and fed continuously over 270 minutes.
30 Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [185.4 grams n-butyl acrylate (BA), 82.2 grams styrene, 5.5 grams of Sipomer®

WAMII (allyl ether of a substituted urea co-monomer from Solvay, Belgium), 13.7 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 58.2 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [65 grams methyl methacrylate (MMA), 13.7 grams styrene, 4.6 grams n-butyl acrylate (BA), 3.7 grams methacrylic acid (MAA), 0.5 gram iso-octyl thioglycolate (i-OTG), 3.7 grams Sipomer® WAMII, 4.7 grams Hitenol AR-1025 and 18.4 grams water]. Ten minutes after the end of the second monomer feed, 51.5 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 229 nm (diameter), the pH was 7.7, and the solids content was 37.7 wt%.

Example 12 – Preparation of Acrylic Core-Shell Latex 12

[0061] 13.8 grams of Seed Latex 1 of Example 1 and 335.8 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.37 gram of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feeds. After 5 minutes, a feed of KPS solution (0.37 gram in 45.8 water) was started and fed continuously over 270 minutes. Concurrently with the start of the KPS feed, the first monomer feed was fed over 150 minutes [163.5 grams n-butyl acrylate (BA), 139.6 grams styrene, 6.2 grams of Sipomer® WAMII (allyl ether of a substituted urea co-monomer from Solvay, Belgium), 15.5 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 65.9 grams water]. When the first monomer feed finished, the reactor was held at 77 °C for 30 minutes, and then the second monomer feed was fed over 90 minutes [39 grams methyl methacrylate (MMA), 8.2 grams

styrene, 2.7 grams n-butyl acrylate (BA), 2.2 grams methacrylic acid (MAA), 0.3 grams iso-octyl thioglycolate (i-OTG), 2.2 grams Sipomer® WAMII, 2.8 grams Hitenol AR-1025 and 11 grams water]. Ten minutes after the end of the second monomer feed, 50.8 grams of a 5 wt% solution of KOH in water was fed to the reactor over 10 minutes and then the reactor was held at 77 °C for another 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes. The reactor was then cooled and the latex filtered using a 200 mesh sieve. The D50 particle size measured by Malvern Zetasizer was 237nm (diameter), the pH was 8.1, and the solids content was 37.3 wt%.

Example 13 – Preparation of Acrylic Single-phase Latex 13 (Comparative)

[0062] 13.7 grams of Seed Latex 1 of Example 1 and 335.6 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77°C and then a mixture of 0.36 grams of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5 minutes before starting the monomer feed. After 5 minutes, a feed of KPS solution (0.37 gram in 45.6 water) was started and fed continuously over 180 minutes. Concurrently with the start of the KPS feed, the monomer feed was fed over 150 minutes [195.9 grams n-butyl acrylate (BA), 164.2 grams styrene, 3.65 grams methacrylic acid (MAA), 18.2 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium sulfate anionic surfactant) and 77.5 grams water] and afterwards the reactor was held at 77 °C for 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes, followed by cooling the reactor to room temperature. At room temperature, the pH was adjusted by adding 12.8 grams of a 5 wt% solution of KOH in water and was fed to the reactor over approximately 10 minutes. The latex was then filtered using a 200 mesh sieve. The D50

particle size measured by a Malvern Zetasizer was 239 nm (diameter), the pH was 7.8, and the solids content was 41.8 wt%.

Example 14 – Preparation of Acrylic Single-phase Latex 14 (Comparative)

5 **[0063]** 13.7 grams of Seed Latex 1 of Example 1 and 335.6 grams of water were added to a 1 liter round bottom flask. Thermostatic temperature control was employed throughout the process and the reactor was continuously flushed with nitrogen gas. The reactor was heated to 77 °C and then a mixture of 0.36 grams of potassium persulfate (KPS) and 9.1 grams of deionized water was added to the reactor and held for 5
10 minutes before starting the monomer feed. After 5 minutes, a feed of KPS solution (0.37 gram in 45.6 water) was started and fed continuously over 180 minutes. Concurrently with the start of the KPS feed, the monomer feed was fed over 150 minutes [250.6 grams n-butyl acrylate (BA), 109.4 grams styrene, 3.7 grams methacrylic acid (MAA), 18.2 grams Hitenol AR-1025 (polyoxyethylene styrenated phenyl ether ammonium
15 sulfate anionic surfactant) and 77.5 grams water] and afterwards the reactor was held at 77 °C for 30 minutes. Next, a mixture of 0.72 grams of 70 wt% tert-butyl hydroperoxide in water plus 9.7 grams water was added to the reactor, and then a solution of 0.72 grams of iso-ascorbic acid in 8.3 grams water was fed over 60 minutes, followed by cooling the reactor to room temperature. At room temperature, the pH was adjusted by
20 adding 60.2 of a 5 wt% solution of KOH in water and was fed to the reactor over approximately 10 minutes. The latex was then filtered using a 200 mesh sieve. The D50 particle size measured by a Malvern Zetasizer was 226 nm (diameter), the pH was 9.2, and the solids content was 38.8 wt%.

25 Example 15 – Preparation of Acrylic Core-Shell Latex 15

[0064] 3.1 grams of Seed Latex 1 of Example 1 was added into a 4-neck round bottom flask (500 mL) equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet tube under nitrogen atmosphere. The flask was then heated to 80 °C. A mixture of 17.263 grams of styrene, 0.375 grams of sodium persulfate, 1.5 grams of
30 sodium dodecyl sulfate, 53.112 grams of n-butyl acrylate (BA) and 1.493 grams of acrylic acid (AA) in 111 grams of DI water were mixed thoroughly and then pumped into

the flask for a duration of 1.5 hours. The reaction mixture was kept at 80 °C for an additional 1 hour to allow it for continuing polymerization. After that, 15.174 grams of styrene, 0.317 grams of sodium persulfate, 0.5 gram of sodium dodecyl sulfate, 0.168 of 2-ethylhexyl acrylate (EHA), 1.575 grams of methacrylic acid (MAA), 0.468 grams of n-butyl acrylate (BA), and 7.299 grams of methyl methacrylate (MMA) in 38 grams DI water were mixed and added to the reactor within 1 hr. The reaction mixture was continuously stirred at 80 °C for 3 hours. Then 3.576 grams of NaOH (50 wt% in water) and 63.106 grams of DI water were added to the flask. All polymerization was carried out under a nitrogen atmosphere. The latex was filtered through 400 mesh stainless sieve. The D50 particle size measured by Malvern Zetasizer was 178.9 nm (diameter), the pH was 12, and the solid contents was 29.43 wt%.

Example 16 – Preparation of Acrylic Core-Shell Latex 16

[0065] 3.1 grams of Seed Latex 1 of Example 1 was added into a 4-neck round bottom flask (500 mL) equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet tube under nitrogen atmosphere. The flask was then heated to 80 °C. A mixture of 14.919 grams of styrene, 0.375 grams of sodium persulfate, 1.5 grams of sodium dodecyl sulfate, 15.839 grams of 2-ethylhexyl acrylate (EHA), 2.374 grams of acrylic acid (AA), 14.688 grams of n-butyl acrylate (BA) and 24.401 grams of methyl methacrylate (MMA) in 111 grams of DI water were mixed thoroughly and then pumped into the flask for a duration of 1.5 hours. The reaction mixture was kept at 80 °C for an additional 1 hour to allow it for continuing polymerization. After that, 15.174 grams of styrene, 0.317 grams of sodium persulfate, 0.5 gram of sodium dodecyl sulfate, 0.168 of 2-ethylhexyl acrylate (EHA), 1.575 grams of methacrylic acid (MAA), 0.468 grams of n-butyl acrylate (BA), 7.299 grams of methyl methacrylate (MMA) and 38 grams DI water were mixed and added to the reactor within 1 hr. The reaction mixture was continuously stirred at 80 °C for 3 hours. Then 4.604 grams of NaOH (50 wt% in water) and 63.490 grams of DI water were added to the flask. All polymerization was carried out under a nitrogen atmosphere. The latex was filtered through 400 mesh stainless sieve. The D50

particle size measured by Malvern Zetasizer was 175.2 nm (diameter), the pH was 12, and the solids content was 29.19 wt%.

Example 17 – Preparation of Acrylic Core-Shell Latex 17

5 **[0066]** 3.1 grams of Seed Latex 1 of Example 1 was added into a 4-neck round bottom flask (500 mL) equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet tube under nitrogen atmosphere. The flask was then heated to 80 °C. A mixture of 1.756 grams of 1,3-butanediol dimethacrylate (1,3-BDDMA), 0.569 grams of sodium persulfate, 1.5 grams of sodium dodecyl sulfate, 1.156 grams of
10 methacrylamide (MAAM), 12.435 grams of n-butyl acrylate (BA) and 50.553 grams of methyl methacrylate (MMA) in 99 grams of DI water were mixed thoroughly and then pumped into the flask for a duration of 1.5 hours. The reaction mixture was kept at 80 °C for an additional 1 hour to allow it for continuing polymerization. After that, 15.174 grams of styrene, 0.317 grams of sodium persulfate, 0.5 gram of sodium dodecyl sulfate, 0.168
15 of 2-ethylhexyl acrylate (EHA), 1.575 grams of methacrylic acid (MAA), 0.468 grams of n-butyl acrylate (BA), 7.299 grams of methyl methacrylate (MMA) and 38 grams DI water were mixed and added to the reactor within 1 hr. The reaction mixture was continuously stirred at 80 °C for 3 hours. Then 1.836 grams of NaOH (50 wt% in water) and 83.197 grams of DI water were added to the flask. All polymerization was carried
20 out under a nitrogen atmosphere. The latex was filtered through 400 mesh stainless sieve. The D50 particle size measured by Malvern Zetasizer was 185.2 nm (diameter), the pH was 11, and the solids content was 23.58 wt%.

Example 18 – Preparation of Acrylic Core-Shell Latex 18

25 **[0067]** 3.1 grams of Seed Latex 1 of Example 1 was added into a 4-neck round bottom flask (500 mL) equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet tube under nitrogen atmosphere. The flask was then heated to 80 °C. A mixture of 0.569 grams of sodium persulfate, 1.5 grams of sodium dodecyl sulfate, 1.043 grams of methacrylamide (MAAM), 34.730 grams of n-butyl acrylate (BA) and
30 36.201 grams of methyl methacrylate (MMA) in 111 grams of DI water were mixed thoroughly and then pumped into the flask for a duration of 1.5 hours. The reaction

mixture was kept at 80 °C for an additional 1 hour to allow it for continuing polymerization. After that, 15.174 grams of styrene, 0.317 grams of sodium persulfate, 0.5 gram of sodium dodecyl sulfate, 0.168 of 2-ethylhexyl acrylate (EHA), 1.575 grams of methacrylic acid (MAA), 0.468 grams of n-butyl acrylate (BA), 7.299 grams of methyl methacrylate (MMA) and 38 grams DI water were mixed and added to the reactor within 1 hr. The reaction mixture was continuously stirred at 80 °C for 3 hours. Then 1.836 grams of NaOH (50 wt% in water) and 63.621 grams of DI water were added to the flask. All polymerization was carried out under a nitrogen atmosphere. The latex was filtered through 400 mesh stainless sieve. The D50 particle size measured by Malvern Zetasizer was 178.2 nm (diameter), the pH was 11, and the solids content was 26.77 wt%.

Example 19 – Preparation of Acrylic Core-Shell Latex 19

[0068] 3.1 grams of Seed Latex 1 of Example 1 was added into a 4-neck round bottom flask (500 mL) equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet tube under nitrogen atmosphere. The flask was then heated to 80 °C. A mixture of 0.569 grams of sodium persulfate, 1.5 grams of sodium dodecyl sulfate, 1.017 grams of methacrylamide (MAAM), 1.879 grams of 1,3-Butanediol dimethacrylate (1,3-BDDMA), 33.860 grams of n-butyl acrylate (BA) and 35.295 grams of methyl methacrylate (MMA) in 108 grams of DI water were mixed thoroughly and then pumped into the flask for a duration of 1.5 hours. The reaction mixture was kept at 80 °C for an additional 1 hour to allow it for continuing polymerization. After that, 15.174 grams of styrene, 0.317 grams of sodium persulfate, 0.5 gram of sodium dodecyl sulfate, 0.168 of 2-ethylhexyl acrylate (EHA), 1.575 grams of methacrylic acid (MAA), 0.468 grams of n-butyl acrylate (BA), 7.299 grams of methyl methacrylate (MMA) and 38 grams DI water were mixed and added to the reactor within 1 hr. The reaction mixture was continuously stirred at 80 °C for 3 hours. Then 1.836 grams of NaOH (50 wt% in water) and 68.128 grams of DI water were added to the flask. All polymerization was carried out under a nitrogen atmosphere. The latex was filtered through 400 mesh stainless sieve. The D50

particle size measured by Malvern Zetasizer was 197.5 nm (diameter), the pH was 11.0, and the solids content was 27.20 wt%.

Example 20 – Preparation of Ink Compositions

5 **[0069]** Magenta (M) ink compositions were prepared in accordance with the general formulations shown in Tables 3, with the Latex Polymer (2-19) being the only component modified. The Ink ID numbering hereinafter refers to the Ink formulation of Table 3 combined with the specific Latex Polymer ID number used to prepare the ink composition. For example, Latex 2 corresponds to Ink 2, Latex 5 corresponds to Ink 5,
10 and so forth.

Table 3 – Ink Compositions

Ingredient	Type	Magenta (M) Ink (Wt%)
HPF-M046 Pigment Dispersion	Pigment Solids	3
Latex Polymer (2-19)	Core/Shell or Single-phase Acrylic Latex	6
Glycerol	Organic Co-solvent	6
LEG-1	Organic Co-solvent	1
Crodafos™ N3 Acid	Surfactant	0.5
Surfynol® 440	Surfactant	0.3
Acticide® B20	Biocide	0.22
Deionized water	Solvent	Balance

HPF-M046 is a Magenta Pigment dispersed with styrene-acrylic polymer dispersant from DIC Corporation (Japan).

15 Crodafos™ N3A is available from Croda International Plc. (Great Britain).

Surfynol® 440 is available from Evonik, (Germany).

Acticide® B20 is available from Thor Specialties, Inc. (USA).

Example 21 – Ink Composition Stability

20 **[0070]** Ten of the Ink Compositions (listed in Table 4 below) prepared in accordance with Example 20 were evaluated for particle stability. The stability data was collected and evaluated based on accelerated shelf-life (ASL) testing, where the ink compositions were evaluated at the time of formulation, and then subjected to 1 week of

elevated temperature (60 °C), and then the same data was collected to see what had changed.

Table 4 – ASL Stability of Latex Particles in Ink Compositions

Ink ID/Latex ID	%Δ Viscosity	Δ pH	%Δ Mv	%Δ D95
2	-5.3	-0.15	-2.1	1.0
3	0	0.08	-5.3	-5.9
4	0	-0.10	2.5	20.6
8	-5.3	0.06	4.9	0
9	0	0.01	-0.7	2.3
10	0	-0.07	-6.3	-1.6
11	0	-0.08	5.8	8.4
12	0	0.05	-4.3	3.5
13*	-5.3	0.01	-3.7	6.8
14*	-5.3	-0.12	-3.5	-3.1

5 *Single-phase latex

Example 22 – Ink Composition *Printability Performance*

10 [0071] Several of the Ink Compositions prepared in accordance with Example 20 were evaluated for print performance. Additionally, for comparison, a Control Ink Composition was prepared using a commercially available acrylic latex binder (Jantex® 924 - styrene butyl acrylic polymer binder; 320,000 Mw; Acid Number 17.4; Tg -15 °C; available from Jantex Inks, USA). Print performance evaluations were based on jetting from a thermal inkjet pen (A3410, available from HP, Inc.), and the data collected based on several parameters, including:

15 Decap is determined using the indicated time (1 second or 7 seconds) where nozzles remain open (uncapped), and then the number of lines missing during a print event are recorded. Thus, the lower the number the better for decap performance

20 Percent Missing Nozzles (%MNZ), which is calculated based on the number of nozzles incapable of firing at the beginning of a jetting sequence as a percentage of the total number of nozzles on an inkjet printhead

attempting to fire. Thus, the lower the percentage number, the better the Percent Missing Nozzles value.

Drop Weight (DW), which is an average drop weight in nanograms (ng) across the number of nozzles fired measured using a burst mode or firing at 30 kHz.

Drop Weight 2,000 (DW 2K), which is measured using a 2-drop mode of firing, firing 2,000 drops and then measuring/calculating the average ink composition drop weight in nanograms (ng) at 30 kHz.

Drop Velocity (DV), which measures an average velocity of the drop as initially fired from the thermal inkjet nozzles measured in meters per second (m/s).

Decel, which measures the loss in drop velocity (m/s) after 5 seconds of ink composition firing. 0 indicates no drop velocity loss. A positive number indicates how much drop velocity was lost. "Miss" indicates missing, where data was not collectable.

Turn On Energy (TOE) Curve, which measures the energy used to generate consistent ink composition firing at a drop weight (DW) threshold. Lower energy to achieve higher drop weights tend to be desirable, with DW increasing with increased energy and then flattening out as still more energy is applied. The TOE Curve Scale can be graded as Good, Soft, or Bad. On a scale of 0-3, with 3 being the best, Good=3, Soft=2, Bad=1. Furthermore, low drop volume is also notated for informational purposes, as low drop volumes can be acceptable in some circumstances.

The data collected is provided in Table 4, as follows:

Table 4 – Printability Performance

Ink ID/ Latex ID	Decap (1s)	Decap (7s)	%MNZ	DW (ng)	DW 2K (ng)	DV (m/s)	Decel (-Δm/s)	TOE Curve
Control Ink	21	43	0.5	11.7	12.8	10.2	0.2	Soft
2	24	25	1	12.5	12.9	12	0	Good
3	15	32	0	12.6	12.8	12.1	0	Good
4	22	32	0	12.4	12.6	12	0	Good
5	15	31	11	12.4	13.6	9	0.2	Good
6	31	39	8.5	12	13	7.4	0	Good

7	18	45	6	13	13.5	10.9	0	Good
8	24	39	45.8	11.2	12.1	7.7	0	Good, Low DV
9	32	46	2.1	11.4	12	7.9	0	Good, Low DV
10	14	24	0	12.7	12.5	12.5	0	Good
11	25	50	1	11.7	10.9	7.5	0	Good, Low DV
12	19	42	0	12.4	11.6	11.9	0	Good
13*	14	25	0	12.1	13.4	11.7	0	Good
14*	18	28	0	12.3	11.8	11.7	0	Good
15	50	50	41	2.7	5.6	0	Miss	Bad
16	29	50	7.5	11	11.8	10.6	0	Soft
17	35	50	29	11.4	13.3	2.8	0.5	Bad
18	28	50	23	10.8	13.5	4.5	0.2	Bad
19	29	50	10	11.5	12.6	7.2	0.2	Soft

*Single-phase latex

[0072] As can be seen in Table 4 above, many of the ink compositions with the various corresponding acrylic latex core-shell particles showed reasonable or good print performance from a thermal inkjet printhead using varied testing protocols, with Latexes 2-4 and 12-14 providing particularly good results when combining both Decap and TOE Curve performance. Some of the ink compositions had acceptable or reasonable TOE Curve data, but the drop weight (DW) was slightly lower. TOE Curve data is considered Acceptable or Good when lower levels of energy are used to achieve higher drop weights (DW) as measured in nanograms (ng). For example, achieving a drop weight (DW) of 10 ng or above at an energy level 0.75 Joule may be considered "Good" TOE (with DW getting larger with more energy input until the curve flattens out) for this particular ink composition. Achieving a drop weight (DW) of 8 ng or above at an energy level 0.75 Joule may be considered "Acceptable" TOE (with DW getting larger with more energy input until the curve flattens out). In further detail, however, lower drop weights (DW) below 8 ng or even below 7 ng at 0.75 Joules may provide for a "Good" TOE as long as the drop weights continue to get larger as the energy increases and then flatten out at an acceptable drop weight. Achieving a drop weight below 7 ng at an energy level of 0.75 Joule may be considered "Good" TOE (with DW getting larger with more energy

input until the curve flattens out, as long as the drop weight is acceptable for inkjet printing applications).

Example 23 – Washfastness Durability

5 **[0073]** Several of the Ink Compositions (Inks 2-19) prepared in accordance with Example 20 were evaluated for washfastness durability when printed on fabric. Additionally, for comparison, a Control Ink Composition (Control Ink) was prepared using a commercially available acrylic latex binder (Jantex® 924 - styrene butyl acrylic polymer binder; 320,000 Mw; Acid Number 17.4; Tg 15 °C; available from Jantex Inks, 10 USA). The Ink Compositions were jetted (3 dots per pixel or “dpp”) onto gray cotton fabric print media at 20 grams per meter (gsm) using a thermal inkjet pen (A3410, available from HP, Inc.). Individual samples were cured at either 80 °C or at 150 °C for 3 minutes. Printed samples were washed 5 times with a conventional washer at 40 °C with detergent and air drying between each wash. Each sample was measured for OD 15 and Lab before and after the 5 washes at 40 °C using Tide® laundry detergent available from Proctor and Gamble, Cincinnati, OH, USA. After the five cycles, optical density (OD) and L*a*b* values were measured for comparison, and delta E (ΔE) values were calculated using the 1976 standard denoted as ΔE_{CIE} . Results are depicted in Tables 5A-5B, as follows:

20

Table 5A – Gray Cotton Print Media; Cured at 80 °C for 3 Minutes

Ink ID/ Latex ID	OD (Pre-wash)	OD (5 washes)	% Δ OD	ΔE_{CIE}
Control Ink	1.014	0.862	-15	7.6
2	1.022	0.762	-25.5	14.5
3	1.025	0.758	-26.1	14
4	1.028	0.778	-24.3	13.5
5	1.029	0.574	-44.2	25.8
6	1.033	0.791	-23.5	12.6
7	1.013	0.828	-18.3	9.6
8	1.012	0.814	-19.6	11.8
9	1.025	0.785	-23.5	12.6
10	1.034	0.823	-20.4	10.6
11	1.033	0.865	-16.2	9
12	1.021	0.817	-20	11.6

13*	1.037	0.800	-22.8	12.1
14*	1.038	0.869	-16.3	9.2
15	0.994	0.810	-18.5	10.1
16	1.006	0.748	-25.6	12.3
17	1.005	0.501	-50.1	29
18	1.012	0.680	-32.9	17.4
19	1.003	0.599	-40.2	22.8

*Single-phase latex

Table 5B – Gray Cotton Print Media; Cured at 150 °C for 3 Minutes

Ink ID/ Latex ID	OD (Pre-wash)	OD (5 washes)	% Δ OD	ΔE_{CIE}
Control Ink	1.013	0.996	-1.7	1.8
2	1.034	0.853	-17.5	8.8
3	1.038	0.866	-16.6	7.6
4	1.028	0.845	-17.8	9.0
5	1.040	0.827	-20.4	9.1
6	1.034	0.889	-14.0	7.6
7	1.034	0.933	-9.8	4.6
8	1.016	0.874	-14.0	7.3
9	1.032	0.885	-14.2	6.3
10	1.033	0.895	-13.3	7.2
11	1.035	0.925	-10.6	6.2
12	1.022	0.888	-13.1	7.3
13*	1.039	0.910	-12.4	6.3
14*	1.030	0.917	-10.9	5.7
15	0.985	0.904	-8.2	4.4
16	1.015	-0.906	-10.7	5.9
17	1.005	0.942	-6.3	3.8
18	1.013	0.918	-9.4	4.6
19	1.003	0.922	-8.1	3.7

*Single-phase latex

5

[0074] As can be seen in the data presented in Tables 5A-5B, acceptable washfastness for individual ink compositions with a ΔE around 5, e.g., ranging from 3.7 to 9, was verified by comparing pre-wash optical density (OD) with post-wash OD and ΔE_{CIE} or ΔE_{2000} calculated from pre- and post-wash $L^*a^*b^*$ values. Thus, most core-shell latex polymers have reasonable washfastness with a ΔE around 5, without external cross-linkers. Some of them have better washfastness such as Latexes 17-19.

10

[0075] As can be seen from the data collected above, most of the latex-based ink compositions printed on gray cotton fabric substrate showed good durability even without external crosslinkers, with a few showing excellent durability which is similar to commercially available Jantex™ polymers, available from JANTEX INKS, (USA), which includes melamine crosslinkers that can be toxic.

Example 24 - Acrylic Core/Shell Latex Particles vs. Acrylic Single-phase Latex Particles
Compared using TOE Curve Analysis

[0076] Printability with respect to Turn On Energy (TOE) can be evaluated using a TOE curve, where the amount of energy (Joules) was evaluated to determine where a more consistent ink composition firing at a drop weight (DW) can be achieved. With this evaluation, higher drop weights achieved at lower energy levels is considered good. At some point the drop weight levels off so that more energy does not generate a greater drop weight. At the location on the TOE curve where an acceptable drop weight is achieved, and where it is starting to flatten out, can indicate an ink composition that has a desirable TOE curve. Stated another way, higher TOE curve is better, meaning higher drop weight at a given firing energy input level. With this analysis, it was found that adding even a thin acrylic latex polymer shell to a latex polymer core tended to increase drop weight and reduce energy input.

[0077] The data collected for six (6) different ink compositions is shown in FIG. 3. Two of the ink compositions (Ink 13 and Ink 14) included acrylic single-phase latex particles, and the remaining four ink compositions (Ink 2, Ink 3, Ink 4, and Ink 10) included acrylic core/shell latex particles. As can be seen in the data, in all four cases, the higher curves were with the ink compositions with the core/shell latex particles.

[0078] To compare one set of curves, the TOE curve of Ink 10 can be compared to the TOE curve of Ink 14. These two ink compositions include a latex with the same acrylic latex core (Latex 14 is 100 wt% "core"; Latex 10 includes the same core with a 15 wt% shell thereon), and the TOE curve for Ink 10 is better at every point along the curve where the curve starts to flatten out (shown in FIG. 3 at (B) with an expanded Y-axis to more fully show the separation between the respective TOE curves).

[0079] Another comparison to consider is to compare Ink 13 with 100 wt% acrylic single-phase latex particles to Inks 2-4, which include different weight percentages of acrylic shell, but are otherwise similar (except that the methacrylic acid is included in the “core” of Ink 13 to provide dispensability). More specifically, Ink 2 included 25 wt% shell
5 polymer, Ink 3 included 35 wt% shell polymer, and Ink 4 included 15 wt% shell polymer. The Ink that performed the best in the TOE curve analysis was Ink 3, which had the thickest acrylic shell, but even at 15 wt% shell as in Ink 4, the TOE curve was better than with Ink 13.

[0080] These comparisons tend to show that jettability can be improved with
10 core-shell latexes as opposed to similar single-phase latexes. In further detail, the core-shell latexes had a higher surface Tg than the single-phase latexes, which may have also contributed to the improved jettability as illustrated by the TOE curve data.

[0081] While the present technology has been described with reference to certain examples, various modifications, changes, omissions, and substitutions can be made
15 without departing from the spirit of the disclosure. It is intended, therefore, that the disclosure be limited only by the scope of the following claims.

CLAIMS

What is Claimed Is:

- 5 1. A textile printing material set, comprising:
a fabric substrate; and
an aqueous ink composition including:
 an aqueous ink vehicle,
 pigment, and
10 from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic
 core copolymer with a glass transition temperature from -50 °C to
 30 °C and an acrylic shell copolymer having a glass transition
 temperature from 50 °C to 130 °C, wherein the acrylic core
 copolymer and the acrylic shell copolymer of the acrylic core-shell
15 latex particles have an average weight ratio from 1:1 to 9:1.
2. The textile printing material set of claim 1, wherein the glass transition
temperature of the acrylic core copolymer is from -25 °C to 15 °C and the glass
transition temperature of the acrylic shell copolymer is from 75 °C to 105 °C.
20
3. The textile printing material set of claim 1, wherein the acrylic shell copolymer
includes from 30 wt% to 80 wt% copolymerized methyl methacrylate, ethyl
methacrylate, or a combination thereof.
- 25 4. The textile printing material set of claim 1, wherein the acrylic shell copolymer
includes from 1 wt% to 14 wt% copolymerized acrylic acid, methacrylic acid, or a
combination thereof.
5. The textile printing material set of claim 1, wherein the acrylic core copolymer
30 and the acrylic shell copolymer independently both include copolymerized propyl
 acrylate, butyl acrylate, or a combination thereof.

6. The textile printing material set of claim 5, wherein the acrylic core copolymer and the acrylic shell copolymer both include copolymerized n-butyl acrylate.

5 7. The textile printing material set of claim 1, wherein the fabric substrate is selected from cotton, polyester, nylon, silk, or a blend thereof.

8. A textile printing system, comprising:
a fabric substrate;

10 an inkjet printhead in fluid communication with a reservoir containing an aqueous ink composition, comprising:

an aqueous ink vehicle,
pigment, and

15 from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C, wherein the acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles have an average weight ratio from 1:1 to 9:1; and

20 a heating source positioned to heat the aqueous ink composition after application onto the fabric substrate.

9. The textile printing system of claim 8, wherein the acrylic shell copolymer includes from 30 wt% to 80 wt% copolymerized methyl methacrylate, ethyl
25 methacrylate, or a combination thereof, and wherein the acrylic shell copolymer also includes from 1 wt% to 14 wt% copolymerized acrylic acid, methacrylic acid, or a combination thereof.

10. The textile printing system of claim 8, wherein the acrylic core copolymer and
30 the acrylic shell copolymer both include copolymerized n-butyl acrylate.

11. The textile printing system of claim 8, wherein the heating source is positioned and powerable to generate heat at the fabric substrate at a temperature ranging from above the glass transition temperature of the acrylic shell copolymer to 200 °C.

5

12. The textile printing system of claim 8, wherein the fabric substrate is selected from cotton, polyester, nylon, silk, or a blend thereof.

13. A method of textile printing, comprising:

10 jetting an aqueous ink composition onto fabric substrate, wherein the aqueous ink composition comprises:

an aqueous ink vehicle,
pigment, and

15 from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C, wherein the acrylic core copolymer and the acrylic shell copolymer of the acrylic core-shell latex particles have an average weight ratio from 1:1 to 9:1.

20 14. The method of textile printing of claim 13, further comprising heating the fabric substrate with the aqueous ink composition thereon to a temperature a temperature ranging from above the glass transition temperature of the acrylic shell copolymer to 200 °C.

25 15. The method of textile printing of claim 13, wherein the fabric substrate is selected from cotton, polyester, nylon, silk, or a blend thereof.

30

1/2

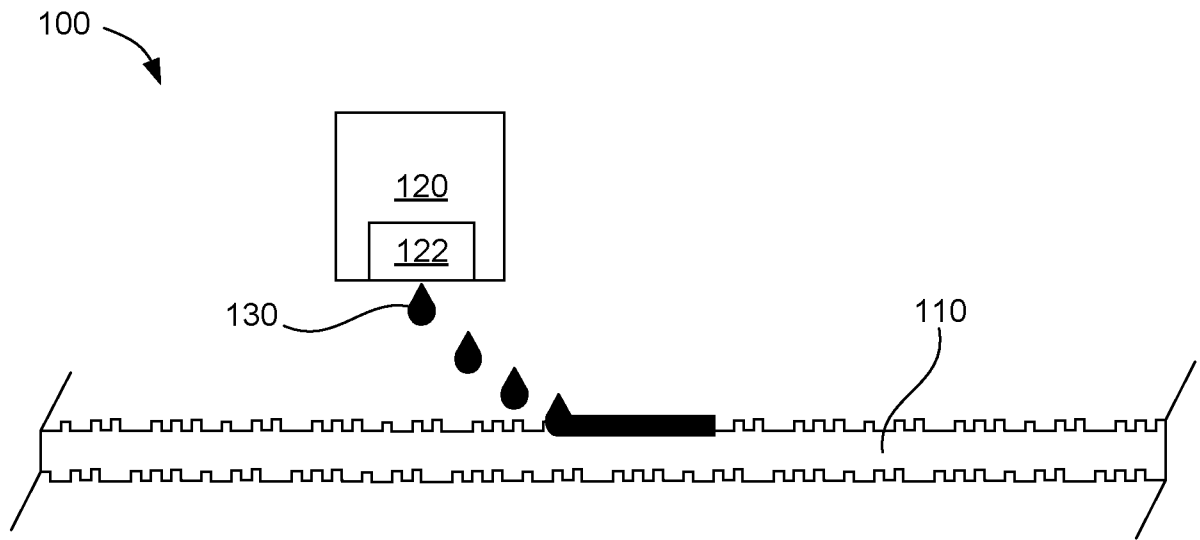


FIG. 1A

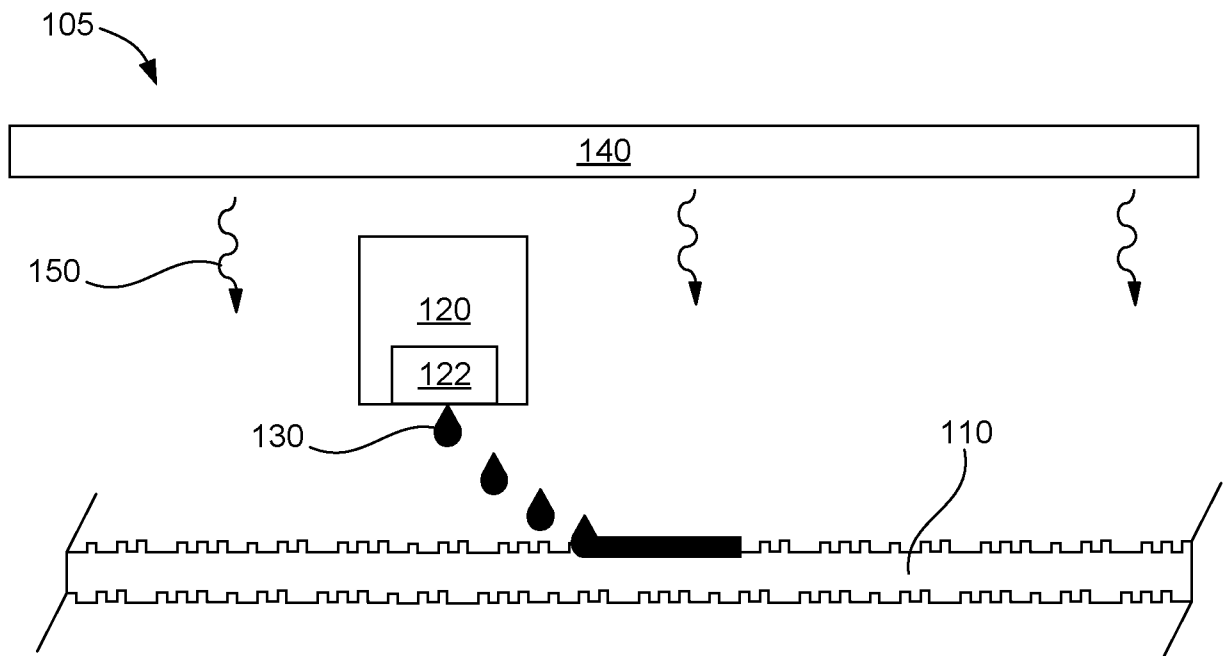


FIG. 1B

2/2

200

jetting an aqueous ink composition onto fabric substrate, wherein the aqueous ink composition comprises: an aqueous ink vehicle, pigment, and from 2 wt% to 15 wt% of acrylic core-shell latex particles having an acrylic core copolymer with a glass transition temperature from -50 °C to 30 °C and an acrylic shell copolymer having a glass transition temperature from 50 °C to 130 °C, wherein the acrylic core copolymer and the acrylic shell copolymer of the core-shell latex particles have an average weight ratio from 1:1 to 9:1

210

FIG. 2

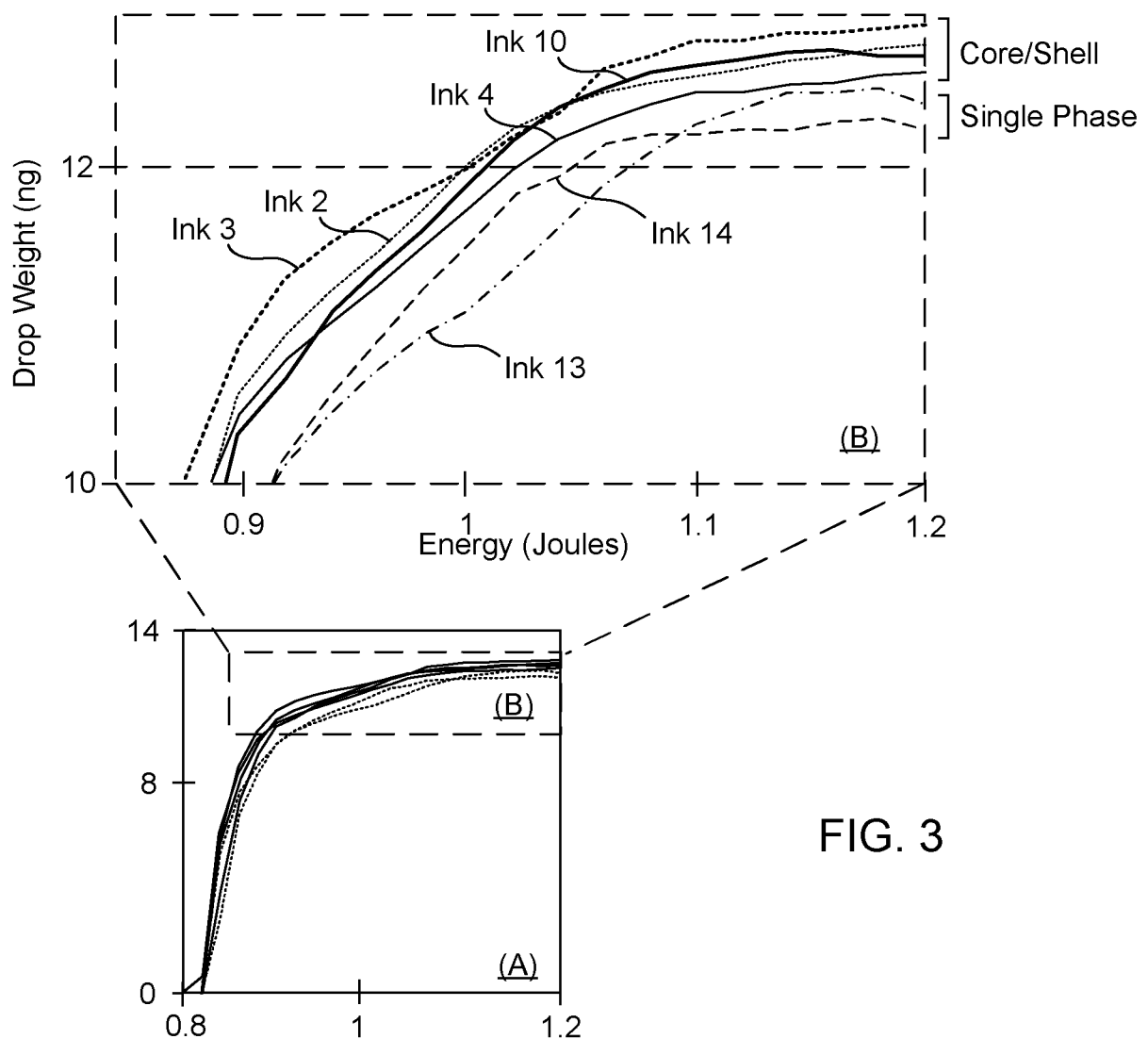


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2019/016487

A. CLASSIFICATION OF SUBJECT MATTER		
D06P 1/46 (2006.01) D06P 5/30 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
D06P 1/46, 5/00, 5/30, B41M 7/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
PatSearch (RUPTO Internal), USPTO, PAJ, Espacenet, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/0293209 A1 (INKTEC CO., LTD) 03.12.2009	1-15
A	US 2018/0305863 A1 (FIJIFILM IMAGING CORPORANTS, INC. et al) 25.10.2018	1-15
A	GB 1467292 A (UGINE KUHLMANN) 16.03.1977	1-15
A	GB 1157345 A (ROHM & HAAS) 09.07.1969	1-15
A	US 2007/0040879 A1 (KWANG-CHOON CHUNG et al) 22.02.2007	1-15
A	US 6698879 B1 (COLOR WINGS B.V.) 02.03.2004	1-15
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
13 September 2019 (13.09.2019)		26 September 2019 (26.09.2019)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer I. Doroshenko Telephone No. (495) 531 64 81