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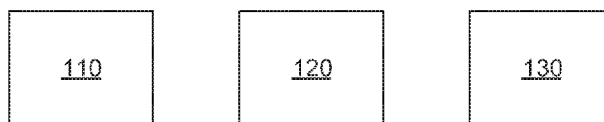


FIG. 1

(57) Abstract: Disclosed herein is a fluid set for printing images on textile substrates. The fluid set comprises a pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle; an inkjet ink including a white pigment, a polyurethane-based binder and an aqueous liquid vehicle; and a fixer composition including a cationic polymer and a fixer vehicle. Also disclosed herein is a textile printing kit and a printing method for generating a print using said fluid set.

FLUID SET FOR TEXTILE PRINTING

BACKGROUND

[0001] Inkjet printing is a non-impact printing method that utilizes electronic signals to control and direct droplets or a stream of ink to be deposited on media. Such technique 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. As the popularity of inkjet printing increases, the types of use also increase providing demand for new ink compositions and substrates to be printed on. Such substrate can be textile. 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.

BRIEF DESCRIPTION OF THE DRAWINGS

[0002] The drawings illustrate various examples of the present fluid set and are part of the specification. Figure 1 schematically illustrates an example fluid set for textile printing in accordance with the present disclosure; Figure 2 schematically illustrates an example printing kit for printing images on textile fabrics in accordance with the present disclosure; Figure 3 is a flow diagram illustrating an example method of printing images on textile fabrics in accordance with the present disclosure.

DETAILED DESCRIPTION

[0003] The textile market is a major industry, and printing on textiles, such as cotton, etc., has been evolving to include digital printing methods. However, the vast majority of textile printing ($\geq 95\%$) is still performed by analog methods, such as screen printing. Multi-color printing with analog screen printing involves the use of a separate screen for each color that is

to be included in the print, and each color is applied separately (with its corresponding screen). In contrast, digital inkjet printing can generate many colors by mixing basic colors in desired locations on the textile, and thus avoids the limitations of analog screen printing. Some digital printing methods enable direct to garment (or other textile) printing. White ink is a heavily used ink in direct to garment printing. Obtaining white images with desirable opacity, however, may be challenging, in part because of fibrillation, e.g., hair-like fibers sticking out of the fabric surface and also due the tendency of white pigments of not being easily suspended.

[0004] In accordance with this, the present disclosure is drawn to fluid sets for textile printing white images, for example. The fluid set is suitable for digital inkjet printing, via thermal inkjet printers, for examples, on a variety of textile fabrics, including cotton and cotton blends. In one example, the present disclosure relates to a fluid set comprising a pre-treatment composition, including a natural water-soluble polysaccharide and an aqueous liquid vehicle ; an inkjet ink including a white pigment, a polyurethane-based binder and an aqueous liquid vehicle; and a fixer composition including a cationic polymer and a fixer vehicle. In another example, the present disclosure is drawn to a textile printing kit comprising a textile fabric; a pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle; an inkjet ink including a white pigment, a polyurethane-based binder and an aqueous liquid vehicle; and a fixer composition including a cationic polymer and a fixer vehicle. The present disclosure also relates to a printing method for generating a print comprising the steps of applying a pre-treatment composition on a textile fabric to form a pre-treatment layer, applying a fixer composition on the pre-treatment layer to form a fixer layer, inkjet printing an ink composition on the fixer layer to form a ink layer, and thermally curing the ink layer on the textile fabric to form an image.

[0005] The fluid set described herein, when used to be printed on textile fabrics, is able to produce white images that have very good opacity performances, even when prints are generated on dark or black textile fabric. The fluid set, described herein, when used to be printed on textile fabrics, has good print performances and also excellent durability.

[0006] With respect to opacity specifically, the opacity may be measured in terms of L^* (or lightness) of the white print generated with the ink composition or fluid set disclosed herein on a colored textile fabric. A greater L^* value indicates a higher opacity of the white ink on the

colored textile fabric. L^* is measured in the CIELAB color space and may be measured using any suitable color measurement instrument (such as those available from HunterLab or X-Rite).

[0007] The durability of a print on a fabric may be assessed by its ability to retain color after being exposed to washing. This is also known as washfastness. Washfastness can be measured in terms of ΔE . The term “ ΔE ,” as used herein, refers to the change in the $L^*a^*b^*$ values of a color (e.g., cyan, magenta, yellow, black, red, green, blue, white) after washing. ΔE can be calculated by different equations, such as the CIEDE1976 (or ΔE_{1976}) color-difference formula, and the CIEDE2000 (or ΔE_{2000}) color-difference formula. ΔE can also be calculated using the color difference method of the Color Measurement Committee (ΔE_{CMC}).

[0008] The present disclosure relates to a fluid set comprising a pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle; an inkjet ink, including a white pigment, a polyurethane-based binder and an aqueous liquid vehicle; and a fixer composition including a cationic polymer and a fixer vehicle. The fluid set may be included in a textile printing kit with any example of the textile fabric described below. It is to be understood that any example of the inkjet ink may be used in the examples of the fluid set. It is also to be understood that any example of the fixer composition may be used in the examples of the fluid set. In an example, the textile printing kit comprises: a textile fabric; a pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle; an inkjet ink composition including a white pigment, a polyurethane-based binder, and an aqueous liquid vehicle; and a fixer composition including a cationic polymer and a aqueous fixer vehicle. Further, it is to be understood that any example of the textile fabric may be used in the examples of the textile printing kit. In one specific example of the textile printing kit, the textile fabric is selected from the group consisting of cotton fabrics, cotton blend fabrics, nylon fabrics, nylon blend fabrics, silk fabrics, silk blend fabrics, wool fabrics, wool blend fabrics, and combinations thereof.

Fluid Sets for Textile Printing

[0009] As shown in Figure 1, a fluid set 100 includes a pre-treatment composition 110 with a natural water-soluble polysaccharide and an aqueous liquid vehicle; a fixer composition 120 is also included, which comprises a cationic polymer and a fixer vehicle. An inkjet ink

composition 130 is also included, which comprises white pigment, a polyurethane-based binder and an aqueous liquid vehicle.

[0010] In one example, the fluid set includes a pre-treatment composition that is formulated for analog application, and a fixer composition and a white ink composition that are formulated for thermal inkjet printing. In any example of the fluid set, the pre-treatment composition, the fixer composition, and the white ink composition may be maintained in separate containers (e.g., respective reservoirs/fluid supplies of respective inkjet cartridges) or separate compartments (e.g., respective reservoirs/fluid supplies) in a single container (e.g., inkjet cartridge).

[0011] In some examples, the pre-treatment composition can be an analog application fluid with a viscosity ranging from about 10 cps to about 500 cps (measured at 25 °C and at 3000 Hz). The fixer composition and the ink composition can both be digital printing fluids individually having viscosities from 1 cps to 30 cps at 25 °C.

Textile Printing Kits

[0012] As shown in Figure 2, the fluid set 100 may also be part of a textile printing kit 200. In an example, the textile printing kit includes a textile fabric 140, as well as the fluid set components shown and described in Figure 1. More specifically, the fluid set can include a pre-treatment composition 110 including a natural water-soluble polysaccharide and an aqueous liquid vehicle. The fluid set includes also a fixer composition 120, which includes a cationic polymer and a fixer vehicle. A white ink composition 130 is also included, which comprises a white pigment, a polyurethane-based binder and an aqueous liquid vehicle. As shown in Figure 2, often with many types of fabrics (e.g., cotton fabrics), there may be hair-like fibers 141 that can extend from the textile fabric substrate material 140, and these fibers can cause problems with printability, particularly with dark fibers used in combination with white inks. In accordance with the present disclosure, in some instances, the use of the pre-treatment composition can flatten the hair-like fibers and also reduce the penetration of fixer and ink into the fabric, thus improving opacity and image quality in some instances.

Pre-treatment composition

[0013] Examples of the pre-treatment composition that is part of the fluid set disclosed herein will now be described. The pre-treatment includes a natural water-soluble polysaccharide and an aqueous liquid vehicle. In some examples, the aqueous liquid vehicle consists of water. On some other examples, the aqueous liquid vehicle consists of water and co-solvent

[0014] By “natural”, it is meant that the polysaccharide polymer is extracted from natural resources. By “water-soluble”, it is meant herein that the polysaccharide polymer is soluble in water. Examples of natural water-soluble polysaccharide includes cellulose, cellulose derivatives, starch, starch derivatives, alginic acid, pectin, carrageenan, gum tamarind, natural gums (gum arabic, guar gum, locust bean gum, gum tragacanth, or xanthan gum), pullulan, dextran; dextran; casein; gelatin; chitin; and chitosan. Other examples of natural water-soluble polysaccharide include also colloids derived from natural sources, such as salts of alginic acid, mannuronic acid, carrageenan (such as the hot water extract of marine algae *Chondrus crispus* or *Rhodophyceae*), guar and xanthan gums, dextran, chitin, and chitosan.

[0015] In some examples, the natural water-soluble polysaccharides are gums. In some other examples, the natural water-soluble polysaccharides are selected from the group consisting of xanthan gum, guar gum, kappa carrageenan and mixtures thereof. In yet some examples, the natural water-soluble polysaccharides are selected from the group consisting of xanthan gum, guar gum and kappa carrageenan.

[0016] Carrageenans are water-soluble, cell wall polysaccharides isolated from *Rhodophyceae*. Three usual forms exist: the kappa, iota, and lambda forms. The kappa and iota forms exist as right-handed double helices, while the lambda form has a much less rigid structure. All three polymers interact to form carrageenan. Typical molecular weight ranges of carrageenan are from about 300,000 to 500,000.

[0017] Guar gums isolated from several sources give highly variable structures. They consist mostly of galacto-mannosan residues with small quantities of protein and oil. Estimates of average molecular weight range from about 500,000 to 2,000,000. Many guar gums are polydisperse.

[0018] Xanthan is a high molecular weight polysaccharide produced by fermentation of the bacterium *Xanthomonas campestris*. Xanthan gums have a structure consisting of five repeating

sugar residues: two glucose, one mannose, and one guluronic acid. The polymer consists essentially of a cellulose backbone. A trisaccharide side chain on alternating sugar residues of the backbone distinguishes xanthan gums from cellulose. Examples of commercially available xanthan gum are "Keltrol[®] T", "Keltrol[®] F", "Kelzan[®] AR" and "Kelzan[®]", available from CP Kelco, a Huber Company. In some examples, the xanthan gum utilized herein is that which has been clarified by any of several known clarification processes. Clarified xanthan gum such as "Keltrol[®] T" and "K5B143" (products of CP Kelco, a Huber Company) is commercially available. As defined herein clarified xanthan gum is that which has a 1% (wt./vol.) solution (deionized water) transmittance of not less than 85%, measured on a Bausch & Lomb "Spectronic" photometer, model 21 (600 mm., 25° C., 10 mm. cell).

[0019] In some examples of the pre-treatment composition, the natural water-soluble polysaccharide is present in an amount ranging from about 0.5 wt% active to about 15 wt% active, based on a total weight of the pre-treatment composition. In another example, the natural water-soluble polysaccharide can be present, in the inkjet ink, in an amount ranging from about 1 wt% active to about 10 wt% active based on the total weight of the pre-treatment composition. In still another example, the natural water-soluble polysaccharide can be present, in the pre-treatment composition, in an amount ranging from about 1 wt% active to about 5 wt% active based on the total weight of the pre-treatment composition.

[0020] Examples of the pre-treatment composition 110 disclosed herein may have a viscosity ranging from about 10 centipoises (cps) to about 500 cps at a temperature of about 25°C (measured at a shear rate of 3,000 Hz, e.g., with a Hydramotion Viscolite viscometer). In some other examples, the viscosity of the pre-treatment composition ranges from about 15 cP to about 100 cps. In yet some other examples, the viscosity of the pre-treatment composition ranges from about 20 cps to about 80 cps. It is to be understood that the viscosity of the pre-treatment composition may be adjusted for the type of analog coater that is to be used.

Inkjet Inks

[0021] Examples of the inkjet ink disclosed herein will now be described. As mentioned above, the inkjet ink, when inkjet printed on a black textile fabric, may generate prints that have good printing performances as well as a desirable L* value, which mean thus that good durability and washfastness performance. In some examples, the inkjet ink includes a white

pigment, a polyurethane-based binder and an aqueous liquid vehicle. In some of these examples, the inkjet ink consists of these components with no other components. In these examples, the inkjet ink consists of a white pigment, a polyurethane-based binder, and an aqueous liquid vehicle. In one of these examples, the aqueous liquid vehicle consists of water and a co-solvent. In other examples, the inkjet ink may include additional components.

[0022] Examples of the inkjet ink disclosed herein may be used in a thermal inkjet printer or in a piezoelectric printer to print on a textile fabric. The viscosity of the inkjet ink may be adjusted for the type of printhead by adjusting the co-solvent level, adjusting the polyurethane-based binder level, and/or adding a viscosity modifier. When used in a thermal inkjet printer, the viscosity of the inkjet ink may be modified to range from about 1 cP to about 9 cP (at 20°C to 25°C). When used in a piezoelectric printer, the viscosity of the inkjet ink may be modified to range from about 2 cP to about 20 cP (at 20°C to 25°C), depending on the type of the printhead that is being used (e.g., low viscosity printheads, medium viscosity printheads, or high viscosity printheads).

[0023] White Pigments

[0024] The white pigment may be incorporated into the inkjet ink as a white pigment dispersion. The white pigment dispersion may include a white pigment and a separate pigment dispersant. Examples of suitable white pigments include white metal oxide pigments, such as titanium dioxide (TiO_2), zinc oxide (ZnO), zirconium dioxide (ZrO_2), or the like. In one example, the white pigment is titanium dioxide. In an example, the titanium dioxide is in its rutile form. In some examples, the white pigment may include white metal oxide pigment particles coated with silicon dioxide (SiO_2). In one example, the white metal oxide pigment content to silicon dioxide content can be from 100:3.5 to 5:1 by weight. In other examples, the white pigment may include white metal oxide pigment particles coated with silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3). In one example, the white metal oxide pigment content to total silicon dioxide and aluminum oxide content can be from 50:3 to 4:1 by weight. One example of the white pigment includes Ti-Pure[®] R960 (TiO_2 pigment powder with 5.5 wt% silica and 3.3 wt% alumina (based on pigment content)) available from DuPont. Another example of the white pigment includes Ti-Pure[®] R931 (TiO_2 pigment powder with 10.2 wt% silica and 6.4 wt% alumina (based on pigment content)) available from DuPont.

[0025] The white pigment may have high light scattering capabilities, and the average particle size of the white pigment may be selected to enhance light scattering and lower transmittance, thus increasing opacity. The average particle size of the white pigment may range anywhere from about 100 nm to about 2000 nm. In some examples, the average particle size ranges from about 120 nm to about 2000 nm, from about 150 nm to about 1000 nm, from about 150 nm to about 750 nm, or from about 200 nm to about 500 nm. The term “average particle size”, as used herein, may refer to a volume-weighted mean diameter of a particle distribution.

[0026] In an example, the white pigment is present in an amount ranging from about 3 wt% active to about 20 wt% active, based on a total weight of the inkjet ink. In other examples, the white pigment is present in an amount ranging from about 5 wt% active to about 20 wt% active, or from about 5 wt% active to about 15 wt% active, based on a total weight of the inkjet ink. In still another example, the white pigment is present in an amount of about 10 wt% active or about 9.75 wt% active, based on a total weight of the inkjet ink.

[0027] For the white pigment dispersions, it is to be understood that the white pigment and separate pigment dispersant (prior to being incorporated into the ink formulation), may be dispersed in water alone or in combination with an additional water soluble or water miscible co-solvent, such as 2-pyrrolidone, 1-(2-hydroxyethyl)-2-pyrrolidone, glycerol, 2-methyl-1,3-propanediol, 1,2-butane diol, diethylene glycol, triethylene glycol, tetraethylene glycol, or a combination thereof. It is to be understood however, that the liquid components of the white pigment dispersion become part of the liquid vehicle in the inkjet ink.

[0028] In some examples, the inkjet ink can include, as an optional ingredient, a pigment dispersant. In some examples, the fluid set as described herein will thus comprise a pre-treatment composition; a fixer composition and an inkjet ink including a white pigment, a polyurethane-based binder and an aqueous liquid vehicle. The white pigment of the ink composition may thus be dispersed with a pigment dispersant. In an example, when present, the optional pigment dispersant is selected from the group consisting of a water-soluble acrylic acid polymer, a branched co-polymer of a comb-type structure with polyether pendant chains and acidic anchor groups attached to a backbone, and a combination thereof.

[0029] Some examples of the water-soluble acrylic acid polymer include Carbosperse[®] K7028 (polyacrylic acid having a weight average molecular weight (Mw) of about 2,300), Carbosperse[®] K752 (polyacrylic acid having a weight average molecular weight (Mw) of about 2,000), Carbosperse[®] K7058 (polyacrylic acid having a weight average molecular weight (Mw) of about 7,300), and Carbosperse[®] K732 (polyacrylic acid having a weight average molecular weight (Mw) of about 6,000), all available from Lubrizol Corporation.

[0030] Some examples of the branched co-polymer of the comb-type structure with polyether pendant chains and acidic anchor groups attached to the backbone include Disperbyk[®]-190 (an acid number of about 10 mg KOH/g) and Disperbyk[®]-199, both available from BYK Additives and Instruments, as well as Dispersogen[®] PCE available from Clariant.

[0031] In some examples, when present, the pigment dispersant is present in an amount ranging from about 0.05 wt% active to about 1 wt% active, based on a total weight of the inkjet ink. In one of these examples, the dispersant is present in an amount of about 0.23 wt% active, based on a total weight of the inkjet ink.

[0032] In some examples, the optional pigment dispersant includes both the water-soluble acrylic acid polymer and the branched co-polymer of the comb-type structure with polyether pendant chains and acidic anchor groups attached to the backbone. In some of these examples, the pigment dispersant includes Carbosperse[®] K7028 and Disperbyk[®]-190. In some of these examples, the pigment dispersant includes both the water-soluble acrylic acid polymer and the branched co-polymer of the comb-type structure with polyether pendant chains and acidic anchor groups attached to the backbone, where the water-soluble acrylic acid polymer is present in an amount ranging from about 0.02 wt% active to about 0.4 wt% active, and the branched co-polymer of the comb-type structure with polyether pendant chains and acidic anchor groups attached to the backbone is present in an amount ranging from about 0.03 wt% active to about 0.6 wt% active. In one of these examples, the water-soluble acrylic acid polymer is present in an amount of about 0.09 wt% active, and the branched co-polymer of the comb-type structure with polyether pendant chains and acidic anchor groups attached to the backbone is present in an amount of about 0.14 wt% active.

[0033] Polyurethane-based Binders

[0034] The inkjet ink also includes a polyurethane-based binder. In some examples, the polyurethane-based binders are non-crosslinked polyurethane-based binders. As used herein, “non-crosslinked” refers to a polymer that is not crosslinked with a crosslinker. In some examples, the polyurethane-based binder is selected from the group consisting of a polyester-polyurethane binder, a polyether-polyurethane binder, a polycarbonate-polyurethane binder, and combinations thereof.

[0035] In an example, the inkjet ink includes a polyester-polyurethane binder. In an example, the polyester-polyurethane binder is a sulfonated polyester-polyurethane binder. The sulfonated polyester-polyurethane binder can include diaminesulfonate groups. In an example, the non-crosslinked polyurethane-based binder is the polyester-polyurethane binder, the polyester-polyurethane binder is a sulfonated polyester-polyurethane binder, and is one of: i) an aliphatic compound including multiple saturated C₄ to C₁₀ carbon chains and/or an alicyclic carbon moiety, that is devoid of an aromatic moiety, or ii) an aromatic compound including an aromatic moiety and multiple saturated carbon chain portions ranging from C₄ to C₁₀ in length.

[0036] In one example, the sulfonated polyester-polyurethane binder can be anionic. In further detail, the sulfonated polyester-polyurethane binder can also be aliphatic, including saturated carbon chains as part of the polymer backbone or as a side-chain thereof, e.g., C₂ to C₁₀, C₃ to C₈, or C₃ to C₆ alkyl. These polyester-polyurethane binders can be described as “alkyl” or “aliphatic” because these carbon chains are saturated and because they are devoid of aromatic moieties. An example of an anionic aliphatic polyester-polyurethane binder that can be used is Impranil[®] DLN-SD (CAS# 375390-41-3; Mw 133,000; Acid Number 5.2; Tg -47°C; Melting Point 175-200°C) from Covestro. Example components used to prepare the Impranil[®] DLN-SD or other similar anionic aliphatic polyester-polyurethane binders can include pentyl glycols (e.g., neopentyl glycol); C₄ to C₁₀ alkyldiol (e.g., hexane-1,6-diol); C₄ to C₁₀ alkyl dicarboxylic acids (e.g., adipic acid); C₄-C₁₀ alkyldiamine (e.g., (2, 4, 4)-trimethylhexane-1,6-diamine (TMD), isophorone diamine (IPD)); C₄ to C₁₀ alkyl diisocyanates (e.g., hexamethylene diisocyanate (HDI), (2, 4, 4)-trimethylhexane-1,6-diisocyanate (TMDI)); alicyclic diisocyanates (e.g. isophorone diisocyanate (IPDI), 1,3-bis(isocyanatomethyl)cyclohexane (H6XDI)); diamine sulfonic acids (e.g., 2-[(2-aminoethyl)amino]ethanesulfonic acid); etc.

[0037] Alternatively, the sulfonated polyester-polyurethane binder can be aromatic (or include an aromatic moiety) and can include aliphatic chains. An example of an aromatic polyester-polyurethane binder that can be used is Dispercoll[®] U42 (CAS# 157352-07-3). Example components used to prepare the Dispercoll[®] U42 or other similar aromatic polyester-polyurethane binders can include aromatic dicarboxylic acids, e.g., phthalic acid; C₄ to C₁₀ alkyl dialcohols (e.g., hexane-1,6-diol); C₄ to C₁₀ alkyl diisocyanates (e.g., hexamethylene diisocyanate (HDI)); diamine sulfonic acids (e.g., 2-[(2-aminoethyl)amino]ethanesulfonic acid); etc.

[0038] Other types of polyester-polyurethanes can also be used, including Impranil[®] DL 1380, which can be somewhat more difficult to jet from thermal inkjet printheads compared to Impranil[®] DLN-SD and Dispercoll[®] U42, but still can be acceptably jetted in some examples, and can also provide acceptable washfastness results on a variety of fabric types.

[0039] The polyester-polyurethane binders disclosed herein may have a weight average molecular weight (Mw, g/mol or Daltons) ranging from about 20,000 to about 300,000. In some examples of the inkjet ink, the non-crosslinked polyurethane-based binder is the polyester-polyurethane binder, and the polyester-polyurethane binder has a weight average molecular weight ranging from about 20,000 Mw to about 300,000 Mw. As examples, the weight average molecular weight can range from about 50,000 to about 500,000, from about 100,000 to about 400,000, or from about 150,000 to about 300,000.

[0040] The polyester-polyurethane binders disclosed herein may have an acid number that ranges from about 1 mg KOH/ g to about 50 mg KOH/g. In some examples of the inkjet ink, the non-crosslinked polyurethane-based binder is the polyester-polyurethane binder, and the polyester-polyurethane binder has an acid number that ranges from about 1 mg KOH/ g to about 50 mg KOH/g. As other examples, the acid number of the polyester-polyurethane binder can range from about 1 mg KOH/g to about 200 mg KOH/g, from about 2 mg KOH/g to about 100 mg KOH/g, or from about 3 mg KOH/g to about 50 mg KOH/g. For this binder, the term “acid number” refers to the mass of potassium hydroxide (KOH) in milligrams that is used to neutralize one gram of the polyester-polyurethane binder. As used herein, the term “acid number” refers to the mass of potassium hydroxide (KOH) in milligrams that is used to neutralize one (1) gram of a particular substance. The test for determining the acid number of a particular substance may vary, depending on the substance.

[0041] To determine this acid number, a known amount of a sample of the polyester-polyurethane binder may be dispersed in water and the aqueous dispersion may be titrated with a polyelectrolyte titrant of a known concentration. In this example, a current detector for colloidal charge measurement may be used. An example of a current detector is the Mutek PCD-05 Smart Particle Charge Detector (available from BTG). The current detector measures colloidal substances in an aqueous sample by detecting the streaming potential as the sample is titrated with the polyelectrolyte titrant to the point of zero charge. An example of a suitable polyelectrolyte titrant is poly(diallyldimethylammonium chloride) (i.e., PolyDADMAC).

[0042] The average particle size of the polyester-polyurethane binders disclosed herein may range from about 20 nm to about 500 nm. As examples, the sulfonated polyester-polyurethane binder can have an average particle size ranging from about 20 nm to about 500 nm, from about 50 nm to about 350 nm, or from about 100 nm to about 350 nm. The particle size of any solids herein, including the average particle size of the dispersed polymer binder, can be determined using a NANOTRAC[®] Wave device, from Microtrac, e.g., NANOTRAC[®] Wave II or NANOTRAC[®] 150, etc., which measures particles size using dynamic light scattering. Average particle size can be determined using particle size distribution data (e.g., volume weighted mean diameter) generated by the NANOTRAC[®] Wave device.

[0043] Other examples of the inkjet ink include a polyether-polyurethane binder. Examples of polyether-polyurethanes that may be used include Impranil[®] LP DSB 1069, Impranil[®] DLE, Impranil[®] DAH, or Impranil[®] DL 1116 (Covestro (Germany)); or Hydran[®] WLS-201 or Hydran[®] WLS-201K (DIC Corp. (Japan)); or Takelac[®] W-6061T or Takelac[®] WS-6021 (Mitsui (Japan)).

[0044] Still other examples of the inkjet ink include a polycarbonate-polyurethane binder. Examples of polycarbonate-polyurethanes that may be used as the non-crosslinked polyurethane-based binder include Impranil[®] DLC-F or Impranil[®] DL 2077 (Covestro (Germany)); or Hydran[®] WLS-213 (DIC Corp. (Japan)); or Takelac[®] W-6110 (Mitsui (Japan)).

[0045] In some examples of the inkjet ink, the polyurethane-based binder is present in an amount ranging from about 2 wt% active to about 20 wt% active, based on a total weight of the inkjet ink. In another example, the polyurethane-based binder can be present, in the inkjet ink, in an amount ranging from about 2 wt% active to about 15 wt% active based on the total weight

of the inkjet ink. In still another example, the polyurethane-based binder can be present, in the inkjet ink, in an amount of about 8 wt% active, based on the total weight of the inkjet ink.

[0046] The polyurethane-based binder (prior to being incorporated into the inkjet ink) may be dispersed in water alone or in combination with an additional water soluble or water miscible co-solvent, such as those described for the white pigment dispersion. It is to be understood however, that the liquid components of the binder dispersion become part of the liquid vehicle in the inkjet ink.

[0047] Liquid Vehicles

[0048] In addition to the white pigment, the polyurethane-based binder, and the additive, the inkjet ink includes a liquid vehicle. In some examples, said liquid vehicle is an aqueous liquid vehicle. By aqueous, it is meant herein that water represents more than 50 % of the total weight of the liquid vehicle. As used herein, the term “liquid vehicle” may refer to the liquid with which the white pigment (dispersion), the polyurethane-based binder (dispersion), and the additive (solution) are mixed to form the inkjet ink. A wide variety of vehicles may be used with the inkjet ink of the present disclosure. The liquid vehicle may include water and any of a co-solvent, an anti-decel agent, a surfactant, an antimicrobial agent, a pH adjuster, or combinations thereof. As such, in some examples, the inkjet ink further comprises a second additive selected from the group consisting of a non-ionic or an anionic surfactant, an antimicrobial agent, an anti-decel agent, and combinations thereof. In an example of the inkjet ink, the liquid vehicle includes water and a co-solvent. In another example, the liquid vehicle consists of water and the co-solvent. In still another example, the liquid vehicle consists of water and the co-solvent, the anti-decel agent, the surfactant, the antimicrobial agent, a pH adjuster, or a combination thereof. In still another example, the liquid vehicle consists of the anti-decel agent, the surfactant, the antimicrobial agent, a pH adjuster, and water.

[0049] The liquid vehicle may include co-solvent(s). The co-solvent(s) may be present in an amount ranging from about 4 wt% to about 30 wt% (based on the total weight of the inkjet ink). In an example, the total amount of co-solvent(s) present in the inkjet ink is about 10 wt% (based on the total weight of the inkjet ink).

[0050] In an example, the liquid vehicle includes glycerol. Other examples of co-solvents include aliphatic alcohols, aromatic alcohols, diols, glycol ethers, polyglycol ethers, lactams,

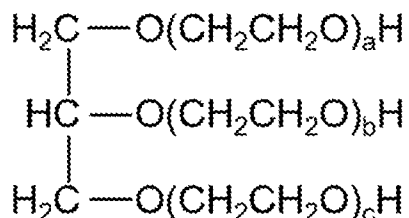
formamides, acetamides, glycols, and long chain alcohols. Examples of these co-solvents include primary aliphatic alcohols, secondary aliphatic alcohols, 1,2-alcohols, 1,3-alcohols, 1,5-alcohols, 1,6-hexanediol or other diols (e.g., 1,5-pentanediol, 2-methyl-1,3-propanediol, etc.), ethylene glycol alkyl ethers, propylene glycol alkyl ethers, higher homologs (C₆-C₁₂) of polyethylene glycol alkyl ethers, triethylene glycol, tetraethylene glycol, tripropylene glycol methyl ether, N-alkyl caprolactams, unsubstituted caprolactams, 2-pyrrolidone, 1-methyl-2-pyrrolidone, N-(2-hydroxyethyl)-2-pyrrolidone, both substituted and unsubstituted formamides, both substituted and unsubstituted acetamides, and the like. Other examples of organic co-solvents include dimethyl sulfoxide (DMSO), isopropyl alcohol, ethanol, pentanol, acetone, or the like.

[0051] The co-solvent may also be a polyhydric alcohol or a polyhydric alcohol derivative. Examples of polyhydric alcohols may include ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,5-pentanediol, 1,2-hexanediol, 1,2,6-hexanetriol, glycerin, trimethylolpropane, and xylitol. Examples of polyhydric alcohol derivatives may include an ethylene oxide adduct of diglycerin.

[0052] The co-solvent may also be a nitrogen-containing solvent. Examples of nitrogen-containing solvents may include 2-pyrrolidone, 1-(2-hydroxyethyl)-2-pyrrolidone, N-methyl-2-pyrrolidone, cyclohexylpyrrolidone, and triethanolamine.

[0053] The liquid vehicle may include anti-decel agent(s). The anti-decel agent may function as a humectant. Decel refers to a decrease in drop velocity over time with continuous firing. In the examples disclosed herein, the anti-decel agent (s) is/are included to assist in preventing decel. In some examples, the anti-decel agent may improve the jettability of the inkjet ink. The anti-decel agent(s) may be present in an amount ranging from about 0.2 wt% active to about 5 wt% active (based on the total weight of the inkjet ink). In an example, the anti-decel agent is present in the inkjet ink in an amount of about 1 wt% active, based on the total weight of the inkjet ink.

[0054] An example of a suitable anti-decel agent is ethoxylated glycerin having the following formula:



in which the total of $a+b+c$ ranges from about 5 to about 60, or in other examples, from about 20 to about 30. An example of the ethoxylated glycerin is Liponic[®] EG-1 (LEG-1, glycereth-26, $a+b+c=26$, available from Lipo Chemicals).

[0055] The liquid vehicle of the inkjet ink may also include surfactant(s). In any of the examples disclosed herein, the surfactant may be present in an amount ranging from about 0.01 wt% active to about 5 wt% active (based on the total weight of the inkjet ink). In an example, the surfactant is present in the inkjet ink in an amount ranging from about 0.05 wt% active to about 3 wt% active, based on the total weight of the inkjet ink. In another example, the surfactant is present in the inkjet ink in an amount of about 0.3 wt% active, based on the total weight of the inkjet ink.

[0056] The surfactant may include anionic and/or non-ionic surfactants. Examples of the anionic surfactant may include alkylbenzene sulfonate, alkylphenyl sulfonate, alkyl naphthalene sulfonate, higher fatty acid salt, sulfate ester salt of higher fatty acid ester, sulfonate of higher fatty acid ester, sulfate ester salt and sulfonate of higher alcohol ether, higher alkyl sulfosuccinate, polyoxyethylene alkylether carboxylate, polyoxyethylene alkylether sulfate, alkyl phosphate, and polyoxyethylene alkyl ether phosphate. Specific examples of the anionic surfactant may include dodecylbenzenesulfonate, isopropyl-naphthalene-sulfonate, monobutylphenylphenol monosulfonate, monobutylbiphenyl sulfonate, monobutylbiphenylsulfonate, and dibutylphenylphenol disulfonate. Examples of the non-ionic surfactant may include polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, glycerin fatty acid ester, polyoxyethylene glycerin fatty acid ester, polyglycerin fatty acid ester, polyoxyethylene alkylamine, polyoxyethylene fatty acid amide, alkylalkanolamide, polyethylene glycol polypropylene glycol block copolymer, acetylene glycol, and a polyoxyethylene adduct of acetylene glycol. Specific examples of the non-ionic

surfactant may include polyoxyethylenenonyl phenylether, polyoxyethyleneoctyl phenylether, and polyoxyethylenedodecyl. Further examples of the non-ionic surfactant may include silicon surfactants such as a polysiloxane oxyethylene adduct; fluorine surfactants such as perfluoroalkylcarboxylate, perfluoroalkyl sulfonate, and oxyethyleneperfluoro alkylether; and biosurfactants such as spiculisporic acid, rhamnolipid, and lysolecithin.

[0057] In some examples, the liquid vehicle may include a silicone-free alkoxylated alcohol surfactant such as, for example, Tego[®] Wet 510 (Evonik Degussa) and/or a self-emulsifiable wetting agent based on acetylenic diol chemistry, such as, for example, Surfynol[®] SE-F (Evonik Degussa). Other suitable commercially available surfactants include Surfynol[®] 465 (ethoxylatedacetylenic diol), Surfynol[®] 440 (an ethoxylated low-foam wetting agent) Surfynol[®] CT-211 (now Carbowet[®] GA-211, non-ionic, alkylphenylethoxylate and solvent free), and Surfynol[®] 104 (non-ionic wetting agent based on acetylenic diol chemistry), (all of which are from Evonik Degussa); Zonyl[®] FSO (a.k.a. Capstone[®], which is a water-soluble, ethoxylated non-ionic fluorosurfactant from DuPont); Tergitol[®] N-3 and Tergitol[®] N-6 (both of which are branched secondary alcohol ethoxylate, non-ionic surfactants), and Tergitol[®] 15-S-3, Tergitol[®] 15-S-5, and Tergitol[®] 15-S-7 (each of which is a secondary alcohol ethoxylate, non-ionic surfactant) (all of the Tergitol[®] surfactants are available from The Dow Chemical Company); and BYK[®] 345, BYK[®] 346, BYK[®] 347, BYK[®] 348, BYK[®] 349 (each of which is a silicone surfactant) (all of which are available from BYK Chemie).

[0058] The liquid vehicle may also include antimicrobial agent(s). Antimicrobial agents are also known as biocides and/or fungicides. In an example, the total amount of antimicrobial agent(s) in the inkjet ink ranges from about 0.01 wt% active to about 0.05 wt% active (based on the total weight of the inkjet ink). In another example, the total amount of antimicrobial agent(s) in the inkjet ink is about 0.04 wt% active (based on the total weight of the inkjet ink). In some instances, the antimicrobial agent may be present in the pigment dispersion that is mixed with the liquid vehicle.

[0059] Examples of suitable antimicrobial agents include the NUOSEPT[®] (Ashland Inc.), UCARCIDE[™] or KORDEK[™] or ROCIMA[™] (The Dow Chemical Company), PROXEL[®] (Arch Chemicals) series, ACTICIDE[®] B20 and ACTICIDE[®] M20 and ACTICIDE[®] MBL (blends of 2-methyl-4-isothiazolin-3-one (MIT), 1,2-benzisothiazolin-3-one (BIT) and Bronopol) (Thor Chemicals), AXIDE[™] (Planet Chemical), NIPACIDE[™] (Clariant), blends of

5-chloro-2-methyl-4-isothiazolin-3-one (CIT or CMIT) and MIT under the tradename KATHON™ (The Dow Chemical Company), and combinations thereof.

[0060] The liquid vehicle may also include a pH adjuster. A pH adjuster may be included in the inkjet ink to achieve a desired pH (e.g., 8.5) and/or to counteract any slight pH drop that may occur over time. In an example, the total amount of pH adjuster(s) in the inkjet ink ranges from greater than 0 wt% to about 0.1 wt% (based on the total weight of the inkjet ink). In another example, the total amount of pH adjuster(s) in the inkjet ink is about 0.03 wt% (based on the total weight of the inkjet ink).

[0061] Examples of suitable pH adjusters include metal hydroxide bases, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), etc. In an example, the metal hydroxide base may be added to the inkjet ink in an aqueous solution. In another example, the metal hydroxide base may be added to the inkjet ink in an aqueous solution including 5 wt% of the metal hydroxide base (e.g., a 5 wt% potassium hydroxide aqueous solution). Suitable pH ranges for examples of the inkjet ink can be from pH 7 to pH 11, from pH 7 to pH 10, from pH 7.2 to pH 10, from pH 7.5 to pH 10, from pH 8 to pH 10, 7 to pH 9, from pH 7.2 to pH 9, from pH 7.5 to pH 9, from pH 8 to pH 9, from 7 to pH 8.5, from pH 7.2 to pH 8.5, from pH 7.5 to pH 8.5, from pH 8 to pH 8.5, from 7 to pH 8, from pH 7.2 to pH 8, or from pH 7.5 to pH 8.

[0062] The balance of the inkjet ink is water. In an example, purified water or deionized water may be used. The water included in the inkjet ink may be: i) part of the white pigment dispersion, the binder dispersion, and/or the additive solution, ii) part of the liquid vehicle, iii) added to a mixture of the white pigment dispersion, the binder dispersion, and/or the additive solution and the liquid vehicle, or iv) a combination thereof. In some examples the inkjet ink is a thermal inkjet ink, and the liquid vehicle includes at least 70% by weight of water. In examples where the inkjet ink is a piezoelectric inkjet ink, the liquid vehicle is a solvent based vehicle including at least 50% by weight of the co-solvent.

Fixer composition

[0063] The fluid set 100 of the present disclosure comprises a pre-treatment composition 110; an inkjet ink 130 and a fixer composition 120. The fixer composition includes a cationic polymer and a fixer vehicle. In some examples, the fixer composition consists of the cationic polymer and the fixer vehicle. In other examples, the fixer composition may include additional

components. The cationic polymer included in the fixer composition can have a weight average molecular weight ranging from 3,000 Mw to 3,000,000 Mw. Any weight average molecular weight (Mw) throughout this disclosure may be expressed as Mw, and is in Daltons. In some examples, e.g., when the fixer composition is to be thermally printed, the cationic polymer included in the fixer composition can have a weight average molecular weight from 3,000 Mw to 200,000, or from 3,000 Mw to 100,000 Mw, or from 3,000 Mw to 50,000 Mw, for example. This molecular weight may provide for the cationic polymer to be printed by thermal inkjet printheads with good print reliability in many instances. When using other technology to eject the fixer composition, higher molecular weights may be useable, such as from 200,000 Mw to 3,000,000 Mw, e.g., applied by piezoelectric printheads and/or analog methods.

[0064] Examples of the cationic polymer include poly(diallyldimethylammonium chloride); or poly(methylene-co-guanidine) anion with the anion is selected from the hydrochloride, bromide, nitrate, sulfate, or sulfonate; a polyamine; poly(dimethylamine-co-epichlorohydrin); a polyethylenimine; a polyamide epichlorohydrin resin; a polyamine epichlorohydrin resin; or a combination thereof. Some examples of commercially available polyamine epichlorohydrin resins may include Crepetrol[®]73, Kymene[®]736, Kymene[®]736NA, Polycup[®]7360, and Polycup[®] 7360A, each of which is available from Solenis LLC.

[0065] In an example, the cationic polymer of the fixer composition 120 can be present in an amount ranging from 0.5 wt% to 15 wt% based on a total weight of the pre-treatment composition. In other examples, the cationic polymer is present in an amount ranging from 1 wt% to 15 wt%, from 1 wt% to 10 wt%, from 4 wt% to 8 wt%, from 2 wt% to 7 wt%, or from 6 wt% to 10 wt%, based on a total weight of the pre-treatment composition

[0066] The fixer composition can further include a fixer vehicle to carry the cationic polymer, for example. As used herein, the term “fixer vehicle” may refer to the liquid in which the cationic polymer is mixed to form the fixer composition. The fixer vehicle can be an aqueous vehicle including water, and may include other liquid components, such as organic co-solvent, surfactant, chelating agent, a pH adjuster, etc.

[0067] If a surfactant is included, the surfactant in the fixer composition 120 may be an anionic, non-ionic, or cationic surfactant in any amount set forth herein based on a total weight of the fixer composition. The surfactant may be present in an amount ranging from 0.01 wt% to 5 wt% (based on the total weight of the fixer composition). In an example, the surfactant is

present in the fixer composition in an amount ranging from 0.05 wt% to 3 wt%, based on the total weight of the fixer composition. In another example, the surfactant is present in the white ink composition in an amount of 0.3 wt%, based on the total weight of the fixer composition.

[0068] The co-solvent in the fixer composition 120 may be any example of the co-solvents set forth herein for the pre-treatment composition 110 previously, in any amount set forth herein for the pre-treatment composition (except that the amount(s) are based on the total weight of the fixer composition instead of the pre-treatment composition).

[0069] Examples of the anionic surfactant may include alkylbenzene sulfonate, alkylphenyl sulfonate, alkylnaphthalene sulfonate, higher fatty acid salt, sulfate ester salt of higher fatty acid ester, sulfonate of higher fatty acid ester, sulfate ester salt and sulfonate of higher alcohol ether, higher alkyl sulfosuccinate, polyoxyethylene alkylether carboxylate, polyoxyethylene alkylether sulfate, alkyl phosphate, and polyoxyethylene alkyl ether phosphate. Specific examples of the anionic surfactant may include dodecylbenzenesulfonate, isopropylphenylsulfonate, monobutylphenylphenol monosulfonate, monobutylbiphenyl sulfonate, monobutylbiphenylsulfonate, and dibutylphenylphenol disulfonate. Examples of the cationic surfactant include quaternary ammonium salts, such as benzalkonium chloride, benzethonium chloride, methylbenzethonium chloride, cetalkonium chloride, cetylpyridinium chloride, cetrimonium, cetrimide, dofanium chloride, tetraethylammonium bromide, didecyltrimethylammonium chloride, domiphen bromide, alkylbenzyltrimethylammonium chlorides, distearyltrimethylammonium chloride, diethyl ester trimethyl ammonium chloride, dipalmitoylethyl hydroxyethylmonium methosulfate, and ACCOSOFT[®] 808 (methyl (1) tallow amidoethyl (2) tallow imidazolinium methyl sulfate available from Stepan Company). Other examples of the cationic surfactant include amine oxides, such as lauryldimethylamine oxide, myristamine oxide, cocamine oxide, stearamine oxide, and cetamine oxide. Examples of the non-ionic surfactant may include polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, glycerin fatty acid ester, polyoxyethylene glycerin fatty acid ester, polyglycerin fatty acid ester, polyoxyethylene alkylamine, polyoxyethylene fatty acid amide, alkylalkanolamide, polyethylene glycol polypropylene glycol block copolymer, acetylene glycol, and a polyoxyethylene adduct of acetylene glycol. Specific examples of the non-ionic surfactant may include polyoxyethylenenonyl phenylether,

polyoxyethyleneoctyl phenylether, and polyoxyethylenedodecyl. Further examples of the non-ionic surfactant may include silicon surfactants such as a polysiloxane oxyethylene adduct; fluorine surfactants such as perfluoro-alkylcarboxylate, perfluoroalkyl sulfonate, and oxyethyleneperfluoro alkylether; and biosurfactants such as spiculisporic acid, rhamnolipid, and lysolecithin.

[0070] A chelating agent may be present in the fixer composition in an amount from 0.01 wt% to 0.5 wt% based on the total weight of the fixer composition. In an example, the chelating agent is present in an amount ranging from 0.05 wt% to 0.2 wt% based on the total weight of the fixer composition. The chelating agent may be selected from methylglycinediacetic acid, trisodium salt; 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate, ethylenediaminetetraacetic acid (EDTA), hexamethylenediamine tetra(methylene phosphonic acid), potassium salt, or a combination thereof. Methylglycinediacetic acid, trisodium salt (Na₃MGDA) is commercially available as Trilon[®] M from BASF Corp. 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate is commercially available as TIRON[™] monohydrate. Hexamethylenediamine tetra(methylene phosphonic acid), potassium salt is commercially available as Dequest[®] 2054 from Italmatch Chemicals.

[0071] An anti-kogation agent may also be included in a fixer composition that is to be thermal inkjet printed. Kogation refers to the deposit of dried printing liquid on a heating element of a thermal inkjet printhead. Anti-kogation agent(s) is/are included to assist in preventing the buildup of kogation. In some examples, the anti-kogation agent may improve the jettability of the fixer composition. The anti-kogation agent(s) may be present in the pre-treatment composition in a total amount ranging from about 0.1 wt% active to about 1.5 wt% active, based on the total weight of the fixer composition. In an example, the anti-kogation agent(s) is/are present in an amount of about 0.5 wt% active, based on the total weight of the fixer composition.

[0072] Examples of suitable anti-kogation agents include oleth-3-phosphate (commercially available as Crodafos[®] O3A or Crodafos[®] N-3A) or dextran 500k. Other suitable examples of the anti-kogation agents include Crodafos[®] HCE (phosphate-ester from Croda Int.), Crodafos[®] N10 (oleth-10-phosphate from Croda Int.), or Dispersogen[®] LFH (polymeric dispersing agent with aromatic anchoring groups, acid form, anionic, from Clariant), etc. It is to be understood that any combination of the anti-kogation agents listed may be used.

[0073] A pH adjuster may also be included in the fixer composition 120, such as to achieve a target pH level, e.g., from 1 to 7, from 2 to 6 or from 3 to 4, and/or to counteract any slight pH increase that may occur over time or during formulation. In an example, the total amount of pH adjuster(s) in the fixer composition, if used, can be from 0.01 wt% to 0.5 wt%, based on the total weight of the fixer composition. In another example, the total amount of pH adjuster(s) in the fixer composition can be from 0.02 wt% to 0.1 wt%, based on the total weight of the fixer composition. An example of a pH adjuster that may be used in the fixer composition includes methane sulfonic acid.

[0074] The viscosity of the fixer composition 120 may vary depending upon the application method that is to be used to apply the fixer composition. As an example, when the fixer composition is to be applied with an analog applicator, the viscosity of the fixer composition may range from 1 centipoise (cp) to 300 cps (at 25°C and a shear rate of 3,000 Hz), from 10 cps to 300 cps, or from 20 cP to 300 cps. As other examples, when the fixer composition is to be applied with an thermal inkjet applicator/printhead, the viscosity of the fixer composition may range from 1 cps to 15 cps (at 25°C and a shear rate of 3,000 Hz), and when the fixer composition is to be applied with an piezoelectric inkjet applicator/printhead, the viscosity of the fixer composition may range from 1 cp to 30 cps (at 25°C and a shear rate of 3,000 Hz).

Textile Fabrics

[0075] As shown in Figure 2, the fluid set 100 may also be part of a textile printing kit 200. In an example, the textile printing kit includes a textile fabric 140, as well as the fluid set components shown and described in Figure 1. More specifically, the textile printing kit 200 includes a textile fabric 140 and the fluid set 100 with a pre-treatment composition 110; a fixer composition 120, and an ink composition 130. Said textile printing kit 200 can be used in an example of printing method (as shown in Figure 3).

[0076] The textile fabric can be selected from the group consisting of cotton fabrics, cotton blend fabrics, nylon fabrics, nylon blend fabrics, polyester fabrics, polyester blend fabrics, silk fabrics, silk blend fabrics, wool fabrics, wool blend fabrics, and combinations thereof. In a further example, textile fabric is selected from the group consisting of cotton fabrics and cotton blend fabrics.

[0077] It is to be understood that organic textile fabrics and/or inorganic textile fabrics may be used for the textile fabric. Some types of fabrics that can be used include various fabrics of natural and/or synthetic fibers. In another example, the textile fabric may be selected from nylons (polyamides) or other synthetic fabrics.

[0078] Example natural fiber fabrics that can be used include 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. Example synthetic fibers used in the textile fabric/substrate can include polymeric fibers such as nylon fibers, polyester fibers, polyvinyl chloride (PVC) fibers, polyamide, polyimide, polyacrylic, polypropylene, polyethylene, polyurethane, polystyrene, polyaramid (e.g., Kevlar[®]) polytetrafluoroethylene (Teflon[®]) (both trademarks of E.I. du Pont de Nemours and Company, Delaware), fiberglass, polytrimethylene, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, or a combination thereof. In some examples, the 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, 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.

[0079] It is to be understood that the terms “textile fabric” or “fabric substrate” do 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 finished articles (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 fabric with a plain weave structure, fabric with 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 multiple processes.

Textile Printing Methods

[0080] The fluid set 100 described herein and the textile printing kit 200 are used in a printing method. Example textile printing methods are illustrated at 300 in Figure 3. In Figure 3 more specifically, a flow diagram of a method of textile printing 300 includes applying 310 a pre-treatment composition on a textile fabric to form a pre-treatment layer, the pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle. The method further includes applying 320 a fixer composition (which includes including a cationic polymer and a fixer vehicle) on the pre-treatment layer to form a fixer layer. Application of the fixer can be by digitally printing, for example, or by some other application method, digital or analog. The method further includes 330 an inkjet ink composition on the fixer layer to form an ink layer, wherein the ink composition includes a pigment, a polyurethane-based binder and an aqueous liquid vehicle. In some examples, the ink composition is digitally printed on the fixer layer. The fixer and ink can be applied multiple times to reach a good opacity of the white image. Furthermore, the method includes thermally curing 340 the white ink layer on the textile fabric.

[0081] The method can utilize the fluid sets and/or textile printing kits shown and described in Figures 1 and 2, and the components thereof described in greater detail by way of example hereinafter. In some examples of the method 100, the inkjet ink is printed to achieve greater than 250 grams per square meter (gsm) of the ink. In other examples, the inkjet ink is printed to achieve about 300 gsm of the ink.

[0082] The inkjet ink and the fixer composition may be inkjet printed using any suitable inkjet applicator, such as a thermal inkjet printhead, a piezoelectric printhead, a continuous inkjet printhead, etc. In some examples, the inkjet ink and the fixer composition are applied with thermal inkjet printheads. The inkjet ink may be inkjet printed in a single pass or in multiple passes. As an example of single pass printing, the cartridge(s) of an inkjet printer deposit(s) the desired amount of the inkjet ink during the same pass of the cartridge(s) across the textile fabric. As an example of multiple pass printing, the cartridge(s) of an inkjet printer deposit the desired amount of the inkjet ink over several passes of the cartridge(s) across the textile fabric. In an example, the inkjet ink may be inkjet printed in 6 printing passes.

[0083] The pre-treatment composition can be applied by any analogue coating method. Screen printing is a method used to apply the pre-treatment composition to the textile substrate.

[0084] In some examples, the pre-treatment composition is applied through a screen (e.g., Mesh size 200) and a frame (a transparent film). The coating composition is then applied directly with a squeegee. The screen-printing method allows a better control of the treated area than drawing down without a screen. The screen used can be, for example, a White Screen-Printing Mesh Silk (Etpuviumbe[®] 200 Mesh) having 50-inch (1.27m) Width and 3 Yard (2.7m) Length. In the screen-printing method, the screen is placed on the fabric, the pre-treatment composition is then placed on the screen and pushed through the screen onto the fabric by a squeegee.

[0085] The pre-treatment composition can be applied to any textile fabric using any method appropriate for the coating application properties, e.g., grams per square meter (gsm), viscosity, etc. Application of the coating composition to the fabric substrate can be at from 0.5 gsm to 400 gsm, from 1 gsm to 300 gsm, or from 10 gsm to 200 gsm, without being limiting. In one example, the pre-treatment composition can be applied to the textile fabric at from 15 gsm to 250 gsm. In one other example, the pre-treatment composition can be applied to the textile fabric at from 40 gsm to 200 gsm

[0086] The viscosity of the pre-treatment composition can be from about 10 to about 500 cps at a temperature of about 25°C (measured at a shear rate of 3,000 Hz). In some other examples, the viscosity of the pre-treatment composition ranges from about 15 cps to about 100

cps. In yet some other examples, the viscosity of the pre-treatment composition ranges from about 20 cP to about 80 cps.

[001] Other non-limiting examples of coating methods include paddler size press, slot die, blade coating, and Meyer rod coating, dip coating, etc. In one example, any of a variety of spray coating methods may be used with the present embodiment. In one example, the fabric substrate can be passed under an adjustable spray nozzle. The adjustable spray nozzle may be configured to alter the rate at which the pre-treatment composition is sprayed onto the fabric substrate

[0087] Throughout this disclosure, a weight percentage that is referred to as “wt % active” refers to the loading of an active component of a dispersion or other formulation that is present in the inkjet ink or the fixer composition. For example, the white pigment may be present in a water-based formulation (e.g., a stock solution or dispersion) before being incorporated into the inkjet ink. In this example, the wt% actives of the white pigment accounts for the loading (as a weight percent) of the white pigment that is present in the inkjet ink, and does not account for the weight of the other components (e.g., water, etc.) that are present in the formulation with the white pigment. The term “wt%,” without the term actives, refers to either i) the loading (in the inkjet ink or the fixer composition) of a 100% active component that does not include other non-active components therein, or the loading (in the inkjet ink or the pre-treatment composition) of a material or component that is used “as is” and thus the wt% accounts for both active and non-active components.

[0088] It is to be understood that the ranges provided herein include the stated range and any value or sub-range within the stated range, as if the value(s) or sub-range(s) within the stated range were explicitly recited. For example, a range from about 0.1 wt% active to about 0.6 wt% active, should be interpreted to include not only the explicitly recited limits of from about 0.1 wt% active to about 0.6 wt% active, but also to include individual values, such as about 0.15 wt% active, about 0.25 wt% active, about 0.40 wt% active, about 0.577 wt% active, etc., and sub-ranges, such as from about 0.133 wt% active to about 0.365 wt% active, from about 0.23 wt% active to about 0.47 wt% active, from about 0.35 wt% active to about 0.595

wt% active, etc. Furthermore, when “about” is utilized to describe a value, this is meant to encompass minor variations (up to +/- 10%) from the stated value.

[0089] Reference throughout the specification to “one example”, “another example”, “an example”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the example is included in at least one example described herein, and may or may not be present in other examples. In addition, it is to be understood that the described elements for any example may be combined in any suitable manner in the various examples unless the context clearly dictates otherwise.

[0090] In describing and claiming the examples disclosed herein, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

[0091] While several examples have been described in detail, it is to be understood that the disclosed examples may be modified. Therefore, the foregoing description is to be considered non-limiting.

EXAMPLES

Example 1 –Preparation of Pre-treatment, inkjet ink and fixer compositions

[0092] Three examples of the pre-treatment composition disclosed herein are prepared with either a Guar Gum, a Kappa Carrageenan or a Xanthan Gum (PT1-PT3). To prepare the pre-treatment compositions, 3 different commercially available gum are diluted with deionized water to obtain respective pre-treatment compositions having 1.5 wt% or 2 wt% gum content. The viscosity is measured for all three samples. The viscosity is measured at room temperature (25°C) using a Viscolite viscometer. Pre-treatment composition properties were measured and are shown in Table 1.

Table 1. Pre-treatment Compositions

Sample ID	Viscosity (cP)	Wt % active
PT1	26.5	1.5% Guar Gum
PT2	48.2	1.5% Kappa Carrageenan
PT3	56.8	2% Xanthan Gum

[0093] One examples of the inkjet ink disclosed herein (ex. ink 1) is prepared. The example white pigment dispersion included in each of the inks comprises an example white pigment and example pigment dispersants. The general formulation of the example white pigment dispersion included in each of the inks is shown in Table 1, with the wt% active of each component that is used.

Table 2. White pigment dispersion

Ingredient	Specific Component	wt% active
White pigment	Ti-pure [®] R960	55
Pigment dispersant	Disperbyk [®] -190	1.1
Water	Deionized water	Balance

[0094] The general formulation of the inks, except for type and amount of the additive, is shown in Table 3, with the wt% active of each component that was used (e.g., wt% active white pigment). A 5 wt % potassium hydroxide aqueous solution is added to each of the inks until a pH of about 8.5 was achieved.

Table 3. Inkjet ink composition

Ingredient	Specific Component	INK 1 – W1- (wt %)
Pigment dispersion	White pigment dispersion	10
Co-solvent	1,3-Propanediol	15
Co-solvent	Dowanol [®] TPM	1
Surfactant	Surfynol [®] 440	0.3
Binder	Polyester polyurethane	10
Anti-decel agent	Liponic [®] EG-1	2
Antimicrobial agent	Acticide [®] B20	0.2
Water	Deionized water	Balance

[0095] An example fixer composition as disclosed herein is prepared. The general formulation of the example fixer composition is shown in Table 4, with the wt% of each component that was used. Polycup[®] 7360A includes a polyamine epichlorohydrin and is available from Solenis LLC (USA). Surfynol[®] 440 is a nonionic surfactant and is available from Evonik (Germany).

Table 4. Fixer composition

Ingredient	Specific Component	FIXER 1 (Wt %)
2,2-Dimethyl-1,3-Propanediol	Organic Co-solvent	4
Crodafos [®] N10A	Anti-Kogation agent	0.5
Surfynol [®] 440	Surfactant	0.3
Polycup [®] 7360A	Cationic Polymer	4
Deionized water	Water	Balance

[0096] Example 2 –Image Quality and Durability on Dark Textile Fabric

[0097] Gildan black mid-weight 780 cotton T-shirts (having a basis weight of 180 gsm) are used as the textile fabric substrates in this example. More specifically, several black textile fabric samples (F1-F10) are individually pre-treated with pre-treatment compositions PT1-PT3 or with nothing (control).

[0098] If a pre-treatment composition is applied, it was applied at different grams per square meter (gsm) based on the weight of the liquid formulation by screen printing. Some variability of the weight basis was noted, with weight basis application ranging from 40 gsm to 208 gsm (see Table 5 for details).

[0099] After the 10 fabric substrate samples (F1-F10) are pre-treated with pre-treatment composition or with nothing), example prints were generated using the fixer composition (Fixer 1) of Table 4 applied at a total loading of 55 gsm and the white ink composition (White 1) of Example 3 at a total loading of 300 gsm in 6 passes. The prints are generated using a thermal inkjet printhead via wet on wet printing, e.g., White 1 on Fixer 1 while the fixer was still wet. The black textile fabrics imaged with the white ink were then cured with a heat press at 150 °C for 3 minutes at 44 psi of pressure.

[0100] All 10 printed textile fabric samples were then tested for washfastness and image quality. For washfastness, an initial L*a*b* value of the white images on the black textile

fabric was measured, and then a second $L^*a^*b^*$ value for the white images was collected after the 5 washes. L^* is lightness, a^* is the color channel for color opponents green-red, and b^* is the color channel for color opponents blue-yellow. The 5 washes were carried out using a Whirlpool Washer (Model WTW5000DW) with warm water (at 40°C) and standard washing machine detergent. Each of the printed textile fabric samples were allowed to air dry between washes.

[0101] The color change ΔE was calculated by:

$$\Delta E_{1976} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$

[0102] Additionally, optical images were taken at locations where the white printed image was located on the various printed textile fabric samples. The quality of the images was visually assessed, and was designated “Poor” (fibers sticking up through the image with very non-uniform white coloration), “Marginal” (more uniform than “poor”, but fibers still sticking up through the image), “Good” (uniform print surface, very few fibers sticking up), and “Very Good (uniform print surface, no fibers sticking up).

[0103] The washfastness (Durability) and optical microscope (Image Quality) data are presented in Tables 5 and 6, as follows:

Table 5. Image quality summary

Sample ID	PT fluid	PT amount (in gsm)	Image Quality
F1	no	0	Poor
F2	PT1	40	Marginal
F3	PT1	83	Good
F4	PT1	126	Very good
F5	PT1	208	Very good
F6	PT2	92	Good
F7	PT2	106	Very good
F8	PT2	128	Very good
F9	PT3	74	Very good
F10	PT3	127	Very good

Table 6. Washfastness summary

Sample ID	Washfastness							
	Before wash			After 5 washes			Washfastness (5 washes)	
	L*	a*	b*	L*	a*	b*	ΔL^*	ΔE_{1976}
F1	84.6	-2.3	-4.6	84.5	-2.2	-4.8	-0.1	0.23
F2	91.6	-1.8	-2.1	91.6	-1.5	-2.5	-0.1	0.49
F3	94.3	-1.3	-1.2	94.4	-1.2	-1.4	0.1	0.29
F4	94.2	-1.3	-1.3	94.4	-1.2	-1.5	0.2	0.32
F5	95.3	-1.2	-0.6	95.8	-1.0	-0.6	0.5	0.51
F6	94.4	-1.3	-1.4	94.1	-1.3	-1.7	-0.3	0.47
F7	95.1	-1.2	-0.8	94.9	-1.2	-1.3	-0.2	0.56
F8	95.0	-1.2	-1.0	95.1	-1.1	-1.4	0.0	0.42
F9	95.5	-1.2	-0.8	95.3	-1.1	-1.2	-0.2	0.48
F10	95.0	-1.2	-1.0	95.2	-1.1	-1.3	0.2	0.39

[0104] As can be seen in Tables 5 and 6, the white prints on black cotton fabrics printed with the pre-treatment composition of the present disclosure, exhibit an initial L* value above 90, which is very good for white ink. The ink composition when used in combination with the fixer and the pre-treatment according to the present disclosure gives good image quality, good opacity and washfastness on black T-shirts.

CLAIMS

1. A fluid set comprising:
 - a. a pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle ;
 - b. an inkjet ink including a white pigment, a polyurethane-based binder and an aqueous liquid vehicle; and
 - c. a fixer composition including a cationic polymer and a fixer vehicle.
2. The fluid set as defined in claim 1 wherein, in the pre-treatment composition, the natural water-soluble polysaccharide is natural gum.
3. The fluid set as defined in claim 1 wherein, in the pre-treatment composition, the natural water-soluble polysaccharide is selected from the group consisting of xanthan gum, guar gum, kappa carrageenan and mixtures thereof.
4. The fluid set as defined in claim 1 wherein, in the inkjet ink, the polyurethane-based binder is selected from the group consisting of a polyester-polyurethane binder, a polyether-polyurethane binder, a polycarbonate-polyurethane binder, and combinations thereof.
5. The fluid set as defined in claim 1 wherein, in the inkjet ink, the polyurethane-based binder is present in an amount ranging from about 2 wt % active to about 20 wt % active, based on a total weight of the inkjet ink.
6. The fluid set as defined in claim 1 wherein, in the inkjet ink, the white pigment is present in an amount ranging from about 3 wt % active to about 20 wt % active, based on a total weight of the inkjet ink.
7. The fluid set as defined in claim 1 wherein, in the inkjet ink, the white pigment include white metal oxide pigments, such as titanium dioxide (TiO₂), zinc oxide (ZnO), zirconium dioxide (ZrO₂), or the like.

8. The fluid set as defined in claim 1 wherein the inkjet ink further comprises a pigment dispersant selected from the group consisting of a water-soluble acrylic acid polymer, a branched co-polymer of a comb-type structure with polyether pendant chains and acidic anchor groups attached to a backbone, and a combination thereof.
9. The fluid set as defined in claim 8 wherein in the inkjet ink, the pigment dispersant is present in an amount ranging from about 0.05 wt% active to about 1 wt% active, based on a total weight of the inkjet ink.
10. The fluid set as defined in claim 1 wherein the cationic polymer of the fixer composition is selected from the group consisting of poly(diallyldimethylammonium chloride); poly(methylene-co-guanidine) anion, wherein the anion is selected from the group consisting of hydrochloride, bromide, nitrate, sulfate, and sulfonates; a polyamine; poly(dimethylamine-co-epichlorohydrin); a polyethylenimine; a polyamide epichlorohydrin resin; a polyamine epichlorohydrin resin; and a combination thereof.
11. A textile printing kit comprising:
 - a. a textile fabric;
 - b. a pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle;
 - c. an inkjet ink including a white pigment, a pigment dispersant, a polyurethane-based binder and an aqueous liquid vehicle; and,
 - d. a fixer composition including a cationic polymer and a fixer vehicle.
12. The textile printing kit as defined in claim 11 wherein the textile fabric is selected from the group consisting of polyester fabric, polyester blend fabric, cotton fabric, cotton blend fabric, nylon fabric, nylon blend fabric, polyester fabrics, polyester blend fabrics, silk fabric, silk blend fabric, wool fabric, wool blend fabric, and a combination thereof

13. A textile printing method comprising:
 - a. applying a pre-treatment composition on a textile fabric to form a pre-treatment layer, the pre-treatment composition including a natural water-soluble polysaccharide and an aqueous liquid vehicle ;
 - b. applying a fixer composition on the pre-treatment layer to form a fixer layer, the fixer composition including a cationic polymer and a fixer vehicle;
 - c. applying an inkjet ink composition on the fixer layer to form an ink layer, the ink including a white pigment, a pigment dispersant, a polyurethane-based binder and an aqueous liquid vehicle; and
 - d. thermally curing the ink layer on the textile fabric to form an image.
14. The printing method as defined in claim 13, wherein the pre-treatment composition is applied via an analogue method on the textile fabric at a coat weight ranging from 15 gsm to 250 gsm.
15. The printing method as defined in claim 13 wherein the curing is performed at a temperature ranging from about 80 °C to about 200 °C.

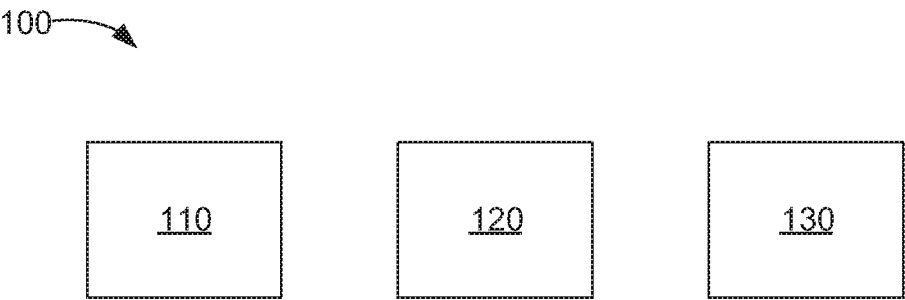


FIG. 1

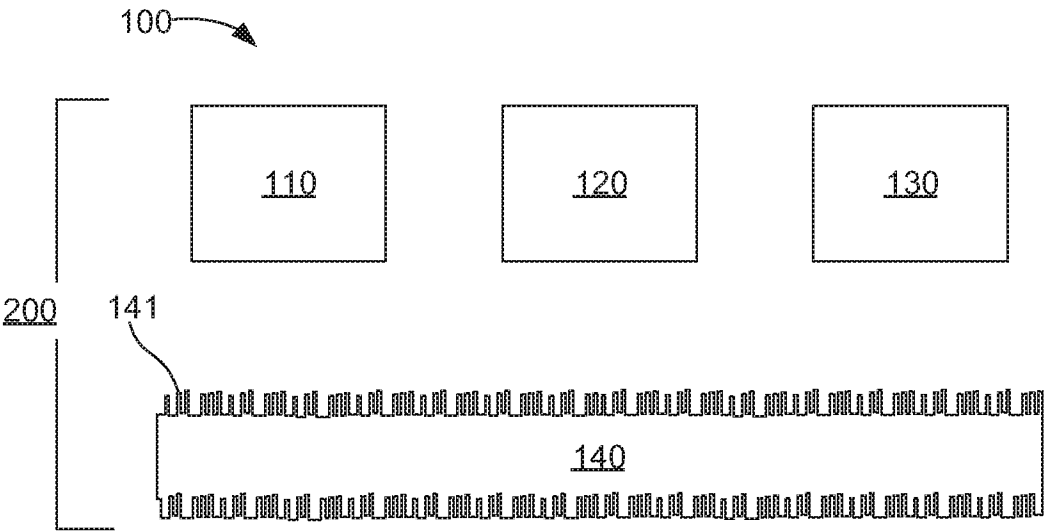


FIG. 2

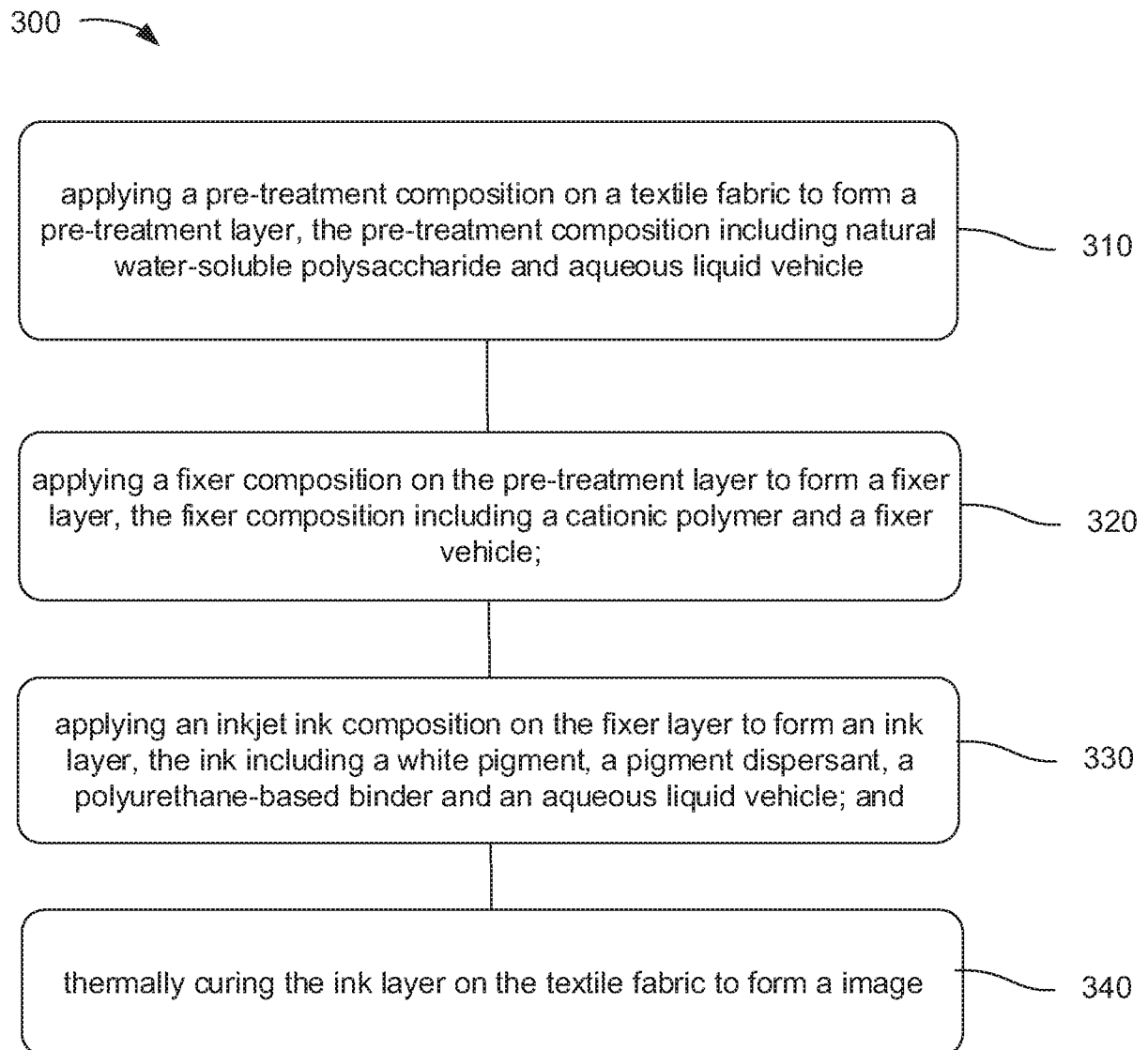


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2020/040669

A. CLASSIFICATION OF SUBJECT MATTER		
C09D 11/322 (2014.01) C09D 11/34 (2014.01) 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)		
C09D 11/30, C09D 11/322, C09D 11/34, C09D 101/00, C09D 175/00, D06P 5/00-5/30		
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)		
EAPATIS, ESPACENET, J-PlatPat, PatSearch, RUABRU, RUABU1, RUPAT, RUPAT OLD, RUPTO, USPTO DB, google.com		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 3339502 B1 (AGFA NV) 12.02.2020	1-15
A	WO 2020/046341 A1 (HEWLETT PACKARD DEVELOPMENT CO) 05.03.2020	1-15
A	JP 2015163678 A (DAINIPPON INK & CHEMICALS) 10.09.2015	1-15
A	EP 2641943 A1 (SEIKO EPSON CORP) 25.09.2013	1-15
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “D” document cited by the applicant in the international application “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
04 March 2021 (04.03.2021)		18 March 2021 (18.03.2021)
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 N. Plekhanova Telephone No. (499) 240-25-91