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**(54) Title:** FABRIC PRETREATMENT FOR INKJET PRINTING

**(57) Abstract:** This invention pertains to inkjet printing on fabric and to a pretreatment solution for the fabric that allows high quality printing thereon. The aqueous pretreatment solution/emulsion comprises a nonionic latex polymer and a multivalent cationic salt.

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# TITLE

# FABRIC PRETREATMENT FOR INKJET PRINTING

## BACKGROUND OF THE INVENTION

This invention pertains to inkjet printing on a pretreated fabric with colored inkjet inks, and to a pretreatment solution for the fabric that allows high quality printing thereon.

Digital printing methods such as inkjet printing are becoming increasingly important for the printing of textiles and offer a number of potential benefits over conventional printing methods such as screen printing. Digital printing eliminates the set up expense associated with screen preparation and can potentially enable cost effective short run production. Inkjet printing furthermore allows visual effects such as tonal gradients and infinite pattern repeat sizes that cannot be practically achieved with a screen printing process.

While digital printing provides a breadth of available printing conditions for almost any fabric, there is often a need for achieving a higher color on the fabric. It is an object of this invention to enable higher color, high quality inkjet printing of fabrics, such as cotton and cotton blends, with colored inkjet inks.

## SUMMARY OF THE INVENTION

In one aspect, the present invention relates to a method of digitally printing a textile comprising the steps of:

(a) pretreating the textile with an aqueous pretreatment solution comprising a nonionic latex polymer and a multivalent cationic salt solution,

(b) digitally printing the dried, pretreated textile with a colored ink jet ink,

where the nonionic latex polymer has sufficient nonionic components such that the nonionic latex polymer is stable in the presence of the multivalent cationic salt solution.

The present invention pertains, in another aspect, to a fabric that has been pretreated with an aqueous mixture of nonionic latex polymer and a multivalent cationic salt solution, wherein the multivalent cationic salt is a calcium salt selected from the group consisting of calcium nitrate, calcium nitrate hydrate, calcium chloride, calcium chloride hydrate and mixtures thereof.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description. It is to be appreciated that certain features of the invention which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. In addition, references to in the singular may also include the plural (for example, "a" and "an" may refer to one, or one or more) unless the context specifically states otherwise.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

### Pretreatment Solution

The aqueous pretreatment solution used in the method of the present invention is a nonionic latex polymer and a multivalent cationic salt solution. More preferably, the preteatment solution comprises a solution of a nonionic latex polymer and a multivalent cationic salt in water. By aqueous pretreatment solution it is understood that the nonionic latex polymer may be present as a stable emulsion in the pretreatment solution. Optionally, other ingredients can be added. Ingredient percentages mentioned hereinafter are weight percent based on the total weight of the final solution, unless otherwise indicated.

### Nonionic Latex Polymer

The pretreatments for the particular textile substrates, include a nonionic latex polymer in order to further enhance the adhesion and/or washfastness of ink colorants on the textile fabric substrates. It has been found that pretreated textiles including a nonionic latex polymer provide high color density and saturation relative to untreated textiles, superior print quality relative to untreated textiles, reduction of wicking or bleeding relative to untreated textiles, and enhanced ink absorption relative to untreated textiles. Furthermore, the pretreatment formulations provide a washfast printed image when printing via an ink jet printing process. By way of example only, the nonionic materials may include urethanes, vinylacetate, ethylene-vinylacetate, acrylate, acrylamide, styrene, and styrene-acrylate resins and other nonionic latexes. One or more nonionic latex polymers may be used in the pretreatment solution.

The preferred use of the nonionic latex polymer is that it is added to the multivalent cationic salt solution. The nonionic latex polymer/multivalent cationic salt solution must be stable as a solution or as a stable emulsion to permit the treatment of the fabric. If the nonionic latex polymer gels, or its emulsion is not stable in the presence of the multivalent cationic salt solution, than it cannot be used as a pretreatment additive. A screening test for whether a nonionic latex polymer is stable in the presence of the multivalent cationic salt solution is to mix a 10 wt % polymer (on a dry basis) and a 15 wt % of calcium nitrate tetrahydrate and observe whether the solution/emulsion is stable. The stability observations at ambient temperature (~ 25 °) and at 10 minutes and 24 hours. The nonionic component must lead to a stable nonionic latex polymer/multivalent cationic solution/emulsion

The nonionic latex polymer can be utilized as a separate pretreatment solution or combined with the multivalent cationic solution described above. A common solution for the nonionic latex polymer and the multivalent cationic salt is preferred.

The nonionic component of the latex polymer can come from the incorporation of a nonionic reactant into the latex polymer. Examples of nonionic components include, ethylene oxide derivatives, acrylamide, hydroxyethyl-substituted monomers, vinylpyrrolidone, ethyleneimines. and the like. The incorporation can occur during the polymerization step, or before after the polymerization step which prepares the latex polymer. In the case of an ethylene oxide nonionic component, the substitution can take the form of incorporating a glycol with sufficient $(\text{-CH}_2\text{-CH}_2\text{O-})_n$ units to impart the nonionic stability. For instance, a polyurethane may have an alkyl polyethylene glycol incorporated into the nonionic polyurethane. The nonionic component can be the main component in nonionic latex polymer, as long as its properties satisfy the stability test described above.

The nonionic latex polymer may also have ionic components incorporated into the polymer. By example, for the polyurethanes ionic components such as acids may be used in the polyurethane reaction and a specific acid example is dimethylolpropionic acid. For the acylamide and hydroxyethyl substituted nonionic latex polymer the ionic source can be from (meth)acrylic acids.There are limits to the amount of ionic components in the nonionic latex polymer, since the nonionic components may complex with the multivalent cationic and form complex that will lead to instability of the nonionic latex polymer/multivalent cationic solution. The balance of nonionic and ionic components must lead to a stable solution as described above.

By example, in the case of a polyurethane nonionic latex polymer the nonionic content must be at least about 15 milliequivalents/gram of ethylene oxide units incorporated into the polyurethane, or in the case of the polyurethane preferably at least about 25 milliequivalents/gram where the milliequivalent/gram calculation is based on the dry polymer weight. In the polyurethane nonionic latex polymer the ionic component can be less than about 10 milliequivalents/gram.

The solution should comprise sufficient nonionic latex polymer content and other ingredients to provide adequate infusion and/or coating of the textile with the nonionic latex polymer. Typically, the pretreatment will comprise at least about 0.5 wt% of the nonionic latex polymer, and amounts can be used up to the solution/emulsion stability of the particularly nonionic latex polymer utilized. Preferably, the pretreatment will comprise from about 1 wt% to about 24 wt% of the nonionic latex polymer.

## Multivalent Cation

The pretreatments of this invention comprise one or more multivalent cations. The effective amounts needed in a particular situation can vary, and some adjustment, as provided for herein, will generally be necessary.

"Multivalent" indicates an oxidation state of two or more and, for an element "Z", are typically described as $Z^{2+}$, $Z^{3+}$, $Z^{4+}$ and so forth. For brevity, multivalent cations may be referred to herein as $Z^x$. The multivalent cations are substantially soluble in the aqueous pretreatment solution and preferably exist (in solution) in a substantially ionized state so that they are in a form where they are free and available to interact with textile when the textile is exposed to the pretreatment solution.

$Z^x$ includes, but is not limited to multivalent cations of the following elements: Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, V, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Cu, Au, Zn, Al, Ga, In, Sb, Bi, Ge, Sn, Pb.. In another embodiment, the multivalent cation comprises at least one of Ca, Ba, Ru, Co, Zn and Ga. In yet another embodiment, the multivalent cation comprises at least one of Ca, Ba, Ru, Co, Zn and Ga. Preferably the multivalent cation is Ca.

$Z^x$ can be incorporated into pretreatment solution by addition in a salt form or by addition in an alkaline form and used as a base in the adjustment of the pretreatment solution pH.

The associated anionic material can be chosen from any common anionic material, especially halides, nitrates and sulfates. The anionic form is chosen so that the multivalent cation is soluble in the aqueous pretreatment solution. The multivalent cationic salts can be used in their hydrated form. One or more multivalent cationic salts may be used in the pretreatment solution.

For Ca, the preferred multivalent cation salts are calcium chloride, calcium nitrate, calcium nitrate hydrate and mixtures thereof.

Other optional ingredients in the pretreatment solution may include, but are not limited to, humectants and biocides. Biocides prevent microbial degradation - their selection and use is generally well known in the art. Suitable humectants are the same as those suitable for use in colored inkjet inks, as discussed in further detail below.

The balance of the pretreatment solution is water. A pretreatment solution consisting essentially of a nonionic latex polymer and a multivalent cationic salt in water is particularly suitable.

The solution should comprise sufficient multivalent cation content and other ingredients to provide adequate infusion and/or coating of the textile with the multivalent cation. Typically, the pretreatment will comprise at least about 0.5 wt% of the multivalent cation salt, and amounts can be used up to the solubility limits of the particularly multivalent cation salt or salts utilized. Preferably, the pretreatment will comprise from about 1 wt% to about 30 wt% of the multivalent cation salt. The combined total weight of the nonionic latex polymer and the multivalent cation salt can be up to about 45 wt %.

Fabric

The fabric to be pretreated can be any fabric suitable for printing with colored inkjet inks, and is preferably a fabric comprising cotton and/or cotton blends.

Pretreatment of the Fabric

Application of the pretreatment to the fabric can be any convenient method and such methods are generally well-known in the art. One example is an application method referred to as padding. In padding, a fabric is dipped in the pretreatment solution, then the saturated fabric is passed through nip rollers that squeeze out the excess solution. The amount of solution retained in the fabric can be regulated by the nip pressure applied by the rollers. Other pretreatment techniques include spray application wherein the solution is applied by spraying on the face or face and back of the fabric. Spraying can be limited to the digitally printed area of the printed fabric. An example of where this limited spraying would be particularly applicable is in the digital printing of an image on preformed textile articles such as, for example, a T-shirts, caps, undergarments and like clothing articles.

Preferably, the pretreatment solution is applied to the fabric in a wet pick-up of from about 0.20 to about 7.5 grams of multivalent cationic (calcium) salt per 100 grams of fabric, more preferably from about 0.60 to about 6.0 grams of multivalent cationic (calcium) salt per 100 grams of fabric, and still more preferably from about 0.75 to about 5.0 grams of multivalent cationic (calcium) salt per 100 grams of fabric.

After application of pretreatment, the fabric may be dried in any convenient manner. The fabric is preferably substantially dry at the time of printing, such that the final percent moisture is (approximately) equal to the equilibrium moisture of the pretreated fabric at ambient temperature. The absolute amount of moisture in the fabric, of course, can vary somewhat depending on the relative humidity of the surrounding air.

The nonionic latex polymer remaining in the fabric after drying provide an interactive material that will interact with the inkjet inks during printing and improve the properties such washfastness of the printed textile It will be appreciated that sufficient nonionic latex polymer must be present to effect a brighter/more colorful image. Routine optimization will reveal appropriate nonionic polymer latex levels for a given printer and colored ink or ink set.

The multivalent salts remaining in the fabric after drying provide an interactive material that will interact with the inkjet inks during printing. It will be appreciated that sufficient multivalent salts must be present to effect a brighter/more colorful image. Routine optimization will reveal appropriate multivalent salt levels for a given printer and colored ink or ink set.

## Colored Inkjet Inks

The colorant used for printing the colored image may be a dye or a pigment. Dyes include disperse dyes, reactive dyes, acid dyes and the like. The colored inkjet inks and the white ink are preferably aqueous and do not contain components that are UV curable.

Pigmented inks are preferred. Pigmented inkjet inks suitable for use in the present method typically comprise a pigment dispersed in a vehicle. Aqueous vehicles are preferred. Preferably, the pigment ink comprises an anionically stabilized pigment dispersed in an aqueous vehicle.

An "aqueous vehicle" refers to a vehicle comprised of water or a mixture of water and at least one water-soluble organic solvent (co-solvent) or humectant. Selection of a suitable mixture depends on requirements of the specific application, such as desired surface tension and viscosity, the selected colorant, and compatibility with substrate onto which the ink will be printed.

Examples of water-soluble organic solvents and humectants include: alcohols, ketones, keto-alcohols, ethers and others, such as thiodiglycol, sulfolane, 2-pyrrolidone, 1,3- dimethyl-2-imidazolidinone and caprolactam; glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, trimethylene glycol, butylene glycol and hexylene glycol; addition polymers of oxyethylene or oxypropylene such as polyethylene glycol, polypropylene glycol and the like; triols such as glycerol and 1,2,6-hexanetriol; lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl, diethylene glycol monoethyl ether; lower dialkyl ethers of polyhydric alcohols, such as diethylene glycol dimethyl or diethyl ether; urea and substituted ureas.

An aqueous vehicle will typically contain about 30% to about 95% water with the balance (i.e., about 70% to about 5%) being the water-soluble solvent. Ink compositions typically contain about 60% to about 95% water, based on the total weight of the aqueous vehicle.

Pigments suitable for being used with the multivalent pretreatment of the textile are those generally well-known in the art for aqueous inkjet inks. Traditionally, pigments are stabilized by dispersing agents, such as polymeric dispersants or surfactants, to produce a stable dispersion of the pigment in the vehicle. More recently though, so-called "self-dispersible" or "self-dispersing" pigments (hereafter "SDP") have been developed. As the name would imply, SDPs are dispersible in water without dispersants. Dispersed dyes are also considered pigments as they are insoluble in the aqueous inks used herein.

The dispersant or surface treatment applied to the pigment creates an anionic surface charge ("anionic pigment dispersion"). Preferably, that surface charge is imparted predominately by ionizable carboxylic acid (carboxylate) groups.

The pigments which are stabilized by added dispersing agents may be prepared by methods known in the art. It is generally desirable to make the stabilized pigment in a concentrated form. The stabilized pigment is first prepared by premixing the selected pigment(s) and polymeric dispersant(s) in an aqueous carrier medium (such as water and, optionally, a water-miscible solvent), and then dispersing or deflocculating the pigment. The dispersing step may be accomplished in a 2-roll mill, media mill, a horizontal mini mill, a ball mill, an attritor, or by passing the mixture through a plurality of nozzles within a liquid jet interaction chamber at a liquid pressure of at least 5,000 psi to produce a uniform dispersion of the pigment particles in the aqueous carrier medium (microfluidizer). Alternatively, the concentrates may be prepared by dry milling the polymeric dispersant and the pigment under pressure. The media for the media mill is chosen from commonly available media, including zirconia, YTZ and nylon. These various dispersion processes are in a general sense well known in the art, as exemplified by US5022592, US5026427, US5310778, US5891231, US5976232 and US20030089277. The disclosures of each of these publications are incorporated by reference herein for all purposes as if fully set forth. Preferred are 2-roll mill, media mill, and by passing the mixture through a plurality of nozzles within a liquid jet interaction chamber at a liquid pressure of at least 5,000 psi.

After the milling process is complete the pigment concentrate may be "let down" into an aqueous system. "Let down" refers to the dilution of the concentrate with mixing or dispersing, the intensity of the mixing/dispersing normally being determined by trial and error using routine methodology, and often being dependent on the combination of the polymeric dispersant, solvent and pigment.

The dispersant used to stabilize the pigment is preferably a polymeric dispersant. Either structured or random polymers may be used, although structured polymers are preferred for use as dispersants for reasons well known in the art. The term "structured polymer" means polymers having a block, branched or graft structure. Examples of structured polymers include AB or BAB block copolymers such as disclosed in US5085698; ABC block copolymers such as disclosed in EP-A-0556649; and graft polymers such as disclosed in US5231131. Other polymeric dispersants that can be used are described, for example, in US6117921, US6262152, US6306994 and US6433117. The disclosure of each of these publications is incorporated herein by reference for all purposes as if fully set forth.

Polymer dispersants suitable for use in the present invention comprise both hydrophobic and hydrophilic monomers. Some examples of hydrophobic monomers used in random polymers are methyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, 2-phenylethyl methacrylate and the corresponding acrylates. Examples of hydrophilic monomers are methacrylic acid, acrylic acid, dimethylaminoethyl(meth)acrylate and salts thereof. Also quaternary salts of dimethylaminoethyl(meth)acrylate may be employed.

A wide variety of organic and inorganic pigments, alone or in combination, may be selected to make the ink. The term "pigment" as used herein means an insoluble colorant. The pigment particles are sufficiently small to permit free flow of the ink through the inkjet printing device, especially at the ejecting nozzles that usually have a diameter ranging from about 10 micron to about 50 micron. The particle size also has an influence on the pigment dispersion stability, which is critical throughout the life of the ink. Brownian motion of minute particles will help prevent the particles from flocculation. It is also desirable to use small particles for maximum color strength and gloss. The range of useful particle size is typically about 0.005 micron to about 15 micron. Preferably, the pigment particle size should range from about 0.005 to about 5 micron and, most preferably, from about 0.005 to about 1 micron. The average particle size as measured by dynamic light scattering is less than about 500 nm, preferably less than about 300 nm.

The selected pigment(s) may be used in dry or wet form. For example, pigments are usually manufactured in aqueous media and the resulting pigment is obtained as water-wet presscake. In presscake form, the pigment is not agglomerated to the extent that it is in dry form. Thus, pigments in water-wet presscake form do not require as much deflocculation in the process of preparing the inks as pigments in dry form. Representative commercial dry pigments are listed in previously incorporated US5085698.

In the case of organic pigments, the ink may contain up to approximately 30%, preferably about 0.1 to about 25%, and more preferably about 0.25 to about 10%, pigment by weight based on the total ink weight. If an inorganic pigment is selected, the ink will tend to contain higher weight percentages of pigment than with comparable inks employing organic pigment, and may be as high as about 75% in some cases, since inorganic pigments generally have higher specific gravities than organic pigments.

Self-dispersed pigments can be used and are often advantageous over traditional dispersant stabilized pigments from the standpoint of greater stability and lower viscosity at the same pigment loading. This can provide greater formulation latitude in final ink.

SDPs, and particularly self-dispersing carbon black pigments, are disclosed in, for example, US2439442, US3023118, US3279935 and US3347632. Additional disclosures of SDPs, methods of making SDPs and/or aqueous inkjet inks formulated with SDP's can be found in, for example,

US5554739, US5571311, US5609671, US5672198, US5698016, US5707432, US5718746, US5747562, US5749950, US5803959, US5837045, US5846307, US5851280, US5861447, US5885335, US5895522, US5922118, US5928419, US5976233, US6057384, US6099632, US6123759, US6153001, US6221141, US6221142, US6221143, US6281267, US6329446, US2001/0035110, EP-A-1114851, EP-A-1158030, WO01/10963, WO01/25340 and WO01/94476.

Titanium dioxide is also an example of a pigment that can be used, and is potentially advantageous because it is white in color. Titanium dioxide can be difficult to disperse in an ink vehicle that is compatible with an ink jet printer system. Those dispersions and/or ink vehicles that provide inkjet stable titanium dioxide can be used with the nonionic latex polymer and multivalent cation pretreated textile.

In a preferred embodiment, a combination of a graft and block copolymers are used as co-dispersants for the titanium dioxide pigment, such as described in US Application Serial No. 10/872,856 (filed June 21, 2004), the disclosure of which is incorporated by reference herein for all purposes as if fully set forth. This combination of dispersants is effective in stabilizing titanium dioxide pigment slurries and, furthermore, provides enhanced stability in the ink formulations. Other preferred titanium dioxide ink jet inks are described in commonly owned US Provisional Appln. Serial No. 60/717,438 (filed September 15, 2005), the disclosure of which is incorporated by reference herein for all purposes as if fully set forth.

The white ink can be used in an ink set as a process color. Alternatively, it can be used as an underlayer to the colored image. When used in the underlayer scheme, the colored inks are printed within 60 minutes of printing the white ink to optimize the colored image on the textile. The use of white ink followed by colored inks is particularly useful with colored textiles.

## Additives

Other ingredients (additives) may be formulated into the inkjet ink, to the extent that such other ingredients do not interfere with the stability and jetability of the finished ink, which may be readily determined by routine experimentation. Such other ingredients are in a general sense well known in the art.

Commonly, surfactants are added to the ink to adjust surface tension and wetting properties. Suitable surfactants include ethoxylated acetylene diols (e.g. Surfynols® series from Air Products), ethoxylated primary (e.g. Neodol® series from Shell and Tomadol® series from Tomah Products) and secondary (e.g. Tergitol® series from Union Carbide) alcohols, sulfosuccinates (e.g. Aerosol® series from Cytec), organosilicones (e.g. Silwet® series from GE Silicons) and fluoro surfactants (e.g. Zonyl® series from DuPont). Surfactants are typically used in the amount of about 0.01 to about 5% and preferably about 0.2 to about 2%, based on the total weight of the ink.

Polymers may be added to the ink to improve durability. The polymers can be soluble in the vehicle or dispersed (e.g. "emulsion polymer" or "latex"), and can be ionic or nonionic. Useful classes of polymers include acrylics, styrene-acrylics and polyurethanes. A particularly useful preferred binder additive is a crosslinked polyurethane as described in US20050182154, the disclosure of which is incorporated by reference herein for all purposes as if fully set forth.

Biocides may be used to inhibit growth of microorganisms. Buffers may be used to maintain pH. Buffers include, for example, tris(hydroxymethyl)-aminomethane ("Trizma" or "Tris").

Inclusion of sequestering (or chelating) agents such as ethylenediaminetetraacetic acid (EDTA), iminodiacetic acid (IDA), ethylenediamine-di(o-hydroxyphenylacetic acid) (EDDHA), nitrilotriacetic acid (NTA), dihydroxyethylglycine (DHEG), trans-1,2- cyclohexanediaminetetraacetic acid (CyDTA), dethylenetriamine-N,N,N',N", N"-pentaacetic acid (DTPA), and glycoletherdiamine-N,N,N',N'-tetraacetic acid (GEDTA), and salts thereof, may be advantageous, for example, to eliminate deleterious effects of heavy metal impurities.

The components described above can be combined to make an ink in various proportions and combinations in order to achieve desired ink properties, as generally described above, and as generally recognized by those of ordinary skill in the art. Some experimentation may be necessary to optimize inks for a particular end use, but such optimization is generally within the ordinary skill in the art.

The amount of vehicle in an ink is typically in the range of about 70% to about 99.8%, and more typically about 80% to about 99%. Colorant is generally present in amounts up to about 10%. If a white ink is used, the white pigment can be up 25 % in concentration. Percentages are weight percent of the total weight of ink.

Other ingredients (additives), when present, generally comprise less than about 15% by weight, based on the total weight of the ink. Surfactants, when added, are generally in the range of about 0.2 to about 3% by weight based on the total weight of the ink. Polymers can be added as needed, but will generally be less than about 15% by weight based on the total weight of the ink.

Drop velocity, separation length of the droplets, drop size and stream stability are greatly affected by the surface tension and the viscosity of the ink. Ink jet inks typically have a surface tension in the range of about 20 dyne/cm to about 70 dyne/cm at 25°C. Viscosity can be as high as 30 cP at 25°C, but is typically somewhat lower. The ink has physical properties are adjusted to the ejecting conditions and printhead design. The inks should have excellent storage stability for long periods so as not clog to a significant extent in an ink jet apparatus. Further, the ink should not corrode parts of the ink jet printing device it comes in contact with, and it should be essentially odorless and non-toxic. Preferred pH for the ink is in the range of from about 6.5 to about 8.

Ink Sets

The term “ink set” refers to all the individual inks or other fluids an inkjet printer is equipped to jet.

In one preferred embodiment, the ink set comprises at least two differently colored pigmented inkjet inks, and optionally one may be a white pigmented inkjet ink as described above.

In another preferred embodiment, the ink set comprises at least three differently colored pigmented inkjet inks, wherein at least one is a cyan pigmented inkjet ink, at least one is a magenta pigmented inkjet ink, and at least one is a yellow pigmented inkjet ink.

In addition to the colored inkjet inks just mentioned, it is also preferable to include a black pigmented inkjet ink in the ink set.

In addition to the CMYKW inks mentioned above, the ink sets may contain additional differently colored inks, as well as different strength versions of the CMYKW and other inks.

For example, the inks sets of the present invention can comprise full-strength versions of one or more of the inks in the ink set, as well as "light" versions thereof.

Additional colors for the inkjet ink set may include, for example, orange, violet, green, red and/or blue.

Printing Method

The present method relates to digitally printing a pretreated textile substrate. Typically, this involves the following steps:

(1) providing an inkjet printer that is responsive to digital data signals;

(2) loading the printer with the textile substrate to be printed, in this case the pretreated textile substrate;

(3) loading the printer with the above-mentioned inks or inkjet ink sets; and

(4) printing onto the substrate using the inkjet ink or inkjet ink set in response to the digital data signals.

Printing can be accomplished by any inkjet printer equipped for handling and printing fabric. Commercial printers include, for example, the DuPont™ Artistri™ 3210 and 2020 printers, and the Mimaki TX series of printers.

As indicated above, a variety of inks and ink sets are available for use with these printers. Commercially available ink sets include, for example, DuPont™ Artistri™ P700 and P5000 series inks.

The amount of ink laid down on the fabric can vary by printer model, by print mode (resolution) within a given printer and by the percent coverage need to achieve a given color. The combined effect of all these considerations is grams of ink per unit area of fabric for each color. In one embodiment, ink coverage is preferably from about 5 to about 17 grams of ink per square meter of fabric for colored inks (including black and white inks).

If, however, a white ink is used as a background for the digitally printed image, up to about twelve times more white ink (generally from about 5 to about 200 grams of ink per square meter of fabric) may be used to obtain an enhanced final image. In such case, the white ink is initially printed onto the substrate in at least a portion of the area to be covered by the final image (the underprint portion), then the final image is printed at least over the underprint portion.

The white ink can also be printed outside the boundaries of the final image (either as part of the initial background printing or subsequently as part of the image printing), for example, to generate a small, imperceptible boundary to the image, making the image appear to have a distinct boundary.

The use of the white ink for printing a background for an image is particularly useful when printed onto colored (non-white) textiles.

<u>Post Treatment of Fabric</u>

Fabric printed with colored inks will typically be post-treated according to procedures well-known in the textile printing art.

The printed textiles may optionally be post processed with heat and/or pressure, such as disclosed in US20030160851 (the disclosure of which is incorporated by reference herein for all purposes as if fully set forth). Upper temperature is dictated by the tolerance of the particular textile being printed. Lower temperature is determined by the amount of heat needed to achieve the desired level of durability. Generally, fusion temperatures will be at least about 80°C and preferably at least about 140°C, more preferably at least about 160°C and most preferably at least about 180°C.

Fusion pressures required to achieve improved durability can be very modest. Thus, pressures can be about 3 psig, preferably at least about 5 psig, more preferrable at least about 8 psig and most preferably at least about 10 psig. Fusion pressures of about 30 psi and above seem to provide no additional benefit to durability, but such pressures are not excluded.

The duration of fusion (amount of time the printed textile is under pressure at the desired temperature) is not believed to be particularly critical. Most of the time in the fusion operation generally involves bringing the print up to the desired temperature. Once the print is fully up to temperature, the time under pressure can be brief (seconds).

## EXAMPLES

### Preparation of Nonionic Latex Polymers

The following ingredients and abbreviations were used to describe the chemical components of the nonionic latex polymers
DBTL = dibutyltindilaurate
DMPA = dimethylol propionic acid
EDA = ethylene diamine
IPDI = isophoronediisocyanate
TEA = triethylamine
TETA = triethylenetetramine
LHT = polypropylene glycol triol, from Bayer and Desmophen C 1200 - a polyester carbonate diol from Bayer (Pittsburgh, PA)
MPEG500 – Methyoxypolyethlene glycol from Dow Chemical (Midland, MI)
Tegomer D-3403 – Polyether diol from Tego Chemie (Essen Germany)

### Synthesis of polyether diol with polyethylene glycol side chain.

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line was added 400 g MPEG500 from Dow Chemical, 160.8 g (0.72) mole IPDI and 3 drops DBTDL. The mixture was reacted at room temperature until NCO was 5.4% or less. 476 g LHT-240, polypropylene triol from Bayer and 10 drops DBTDL was added to the flask. Then the solution was heated to 70 °C and held between 65 and 70 °C until NCO% reached 0%. This polyether diol was called PDiol-1.

### Preparation of nonionic latex polymer, a polyurethane, Inv Ex 1.

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line, was added 150.5 g Desmophen C 1200, a 2000MW polycarbonate/ester diol, 180 g PDiol-1, 100 g acetone and 0.03g DBTL. The contents were heated to 40°C and mixed well. 72 g IPDI was then added to the flask via the addition funnel at 40°C over 60 min, with any residual IPDI being rinsed from the addition funnel into the flask with 10 g acetone.

The flask temperature was raised to 50°C, then held at 50°C until NCO % was less than 2.03 %.

700 g deionized (DI) water at 50 °C was added over 10 minutes, followed by 24.4 g EDA 75 g TETA (as a 6.25% solution in water) over 5 minutes, via the addition funnel, which was then rinsed with 40.0g water. The mixture was held at 50°C for 1 hr, then cooled to room temperature.

Acetone (-310.0 g) was removed under vacuum, leaving a final dispersion of polyurethane with about 35.0% solids by weight and pH around 7.5. This polymer has 17 wt% or 0.39 meq. ethylene oxide unit.

Preparation of nonionic latex polymer, a polyurethane, Inv Ex 2.

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line, was added 200 g Desmophen C 1200, 150 g PDiol-1, 123 g acetone and 0.03g DBTL. The contents were heated to 40°C and mixed well. 80 g IPDI was then added to the flask via the addition funnel at 40°C over 60 min, with any residual IPDI being rinsed from the addition funnel into the flask with 10 g acetone.

The flask temperature was raised to 50°C, then held for 30 minutes. 10 g DMPA followed by 7.5 g TEA was added to the flask via the addition funnel, which was then rinsed with 10 g acetone. The flask temperature was then raised again to 50°C and held at 50°C until NCO % was less than 1.25 %.

740 g deionized (DI) water at 50 °C was added over 10 minutes, followed by 46.3 g EDA (as a 6.25% solution in water) over 5 minutes, via the addition funnel, which was then rinsed with 40.0g water. The mixture was held at 50°C for 1 hr, then cooled to room temperature.

Acetone was removed under vacuum, leaving a final dispersion of polyurethane with about 35.0% solids by weight and pH around 7.5. This polymer has 13wt% or 0.30 meq. ethylene oxide unit and 0.017 meq. COOH group.

Preparation of nonionic latex polymer, a polyurethane, Inv Ex 3

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line, was added 265 g Desmophene C 1200, 50 g Tegomer D3403, a polyether diol from Tego Chemie , 110 g acetone and 0.03g DBTL. The contents were heated to 40°C and mixed well. 75 g IPDI was then added to the flask via the addition funnel at 40°C over 60 min, with any residual IPDI being rinsed from the addition funnel into the flask with 10 g acetone.

The flask temperature was raised to 50°C, then held for 30 minutes. 10 g DMPA followed by 7.5 g TEA was added to the flask via the addition funnel, which was then rinsed with 10 g acetone. The flask temperature was then raised again to 50°C and held at 50°C until NCO % was less than 1.47 %.

654 g deionized (DI) water at 50 °C was added over 10 minutes, followed by 59.2 g TETA (as a 6.25% solution in water) over 5 minutes, via the addition funnel, which was then rinsed with 40.0g water. The mixture was held at 50°C for 1 hr, then cooled to room temperature.

Acetone was removed under vacuum, leaving a final dispersion of polyurethane with about 35.0% solids by weight pH around 7.5. This polymer has 11.3wt% or 0.26 meq. ethylene oxide unit and 0.019 meq. COOH group.

<u>Preparation of a comparative nonionic latex polymer, a polyurethane, Comp Prep Ex 1</u>

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line, was added 235 g Desmophen C 1200, 80 g PDiol-1, 112 g acetone and 0.03g DBTL. The contents were heated to 40°C and mixed well. 82 g IPDI was then added to the flask via the addition funnel at 40°C over 60 min, with any residual IPDI being rinsed from the addition funnel into the flask with 10 g acetone.

The flask temperature was raised to 50°C, then held for 30 minutes. 15 g DMPA followed by 10 g TEA was added to the flask via the addition funnel, which was then rinsed with 10 g acetone. The flask temperature was then raised again to 50°C and held at 50°C until NCO % was less than 3.2 %.

687 g deionized (DI) water at 50 °C was added over 10 minutes, followed by 46.3 g EDA (as a 6.25% solution in water) over 5 minutes, via the addition funnel, which was then rinsed with 40.0g water. The mixture was held at 50°C for 1 hr, then cooled to room temperature.

Acetone was removed under vacuum, leaving a final dispersion of polyurethane with about 35.0% solids by weight and pH around 7.5. This polymer has 7.4wt% or 0.17 meq. ethylene oxide unit and 0.026 meq. COOH group.

Preparation of a comparative nonionic latex polymer, a polyurethane, Comp Prep Ex 2

This polymer has 3.9wt% or 0.09 meq. ethylene oxide unit and 0.042 meq. COOH group.

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line, was added 330 g Desmophene C 1200, 55 g PDiol-1, 112 g acetone and 0.03g DBTL. The contents were heated to 40°C and mixed well. 120 g IPDI was then added to the flask via the addition funnel at 40°C over 60 min, with any residual IPDI being rinsed from the addition funnel into the flask with 10 g acetone.

The flask temperature was raised to 50°C, then held for 30 minutes. 30 g DMPA followed by 20 g TEA was added to the flask via the addition funnel, which was then rinsed with 10 g acetone. The flask temperature was then raised again to 50°C and held at 50°C until NCO % was less than 4.3 %.

900 g deionized (DI) water at 50 °C was added over 10 minutes, followed by 62.1 g EDA (as a 6.25% solution in water) over 5 minutes, via the addition funnel, which was then rinsed with 40.0g water. The mixture was held at 50°C for 1 hr, then cooled to room temperature.

Acetone was removed under vacuum, leaving a final dispersion of polyurethane with about 35.0% solids by weight pH around 7.5. This polymer has 3.9wt% or 0.09 meq. ethylene oxide unit and 0.042 meq. COOH group.

Preparation of a comparative latex polymer, a polyurethane, Comp Prep Ex 3

To a dry, alkali- and acid-free flask, equipped with an addition funnel, a condenser, stirrer and a nitrogen gas line, was added 699.2 g Desmophen C 1200, 280.0 g acetone and 0.06g DBTL. The contents were heated to 40°C and mixed well. 189.14 g IPDI was then added to the flask via the addition funnel at 40°C over 60 min, with any residual IPDI being rinsed from the addition funnel into the flask with 15.5 g acetone.

The flask temperature was raised to 50°C, then held for 30 minutes. 44.57 g DMPA followed by 25.2 g TEA was added to the flask via the addition funnel, which was then rinsed with 15.5 g acetone. The flask temperature was then raised again to 50°C and held at 50°C until NCO % was less than 1.23 %. This polymer has 0.036 meq. COOH group and no nonionic components.

Testing

The Inventive Examples and Comparative Examples were tested for stability with a multivalent cationic salt solution. An amount of latex polymer to obtain 10 wt % in the final aqueous solution/emulsion was put into a beaker, the mixture stirred, then a 15 wt % calcium nitrate aqueous solution was added over about 5 minutes The dry polymer and the calcium nitrate tetrahydrate weight ratio was 10/15. The mixture was stirred for an additional 5 minutes. After 10 minutes and 24 hours, the solution/emulsion was observed for coagulation, gelling or other signs of instability. . If no coagulation was observed, it is rated compatible or stable. If the test solution was coagulated after 10 minutes or 24 hours, the combination of latex polymer and calcium nitrate test solution is judged to be not an inventive combination.

Table 1: Stability Test for Nonionic Latex Polymers with Multivalent Cationic Solution

| | Inv Ex 1 | Inv Ex 2 | Inv Ex 3 | Comp Ex 1 | Comp Ex 2 | Comp Ex 3 |
|---|---|---|---|---|---|---|
| Stability with Calcium nitrate | Compatible | Compatible | Compatible | Coagulated | Coagulated | Coagulated |
| Nonionic EO meq. | 0.39 | 0.30 | 0.26 | 0.17 | 0.09 | 0 |
| Anionic acid meq. | 0 | 0.017 | 0.019 | 0.026 | 0.042 | 0.036 |

Printing Conditions

The examples described below were done using an Epson 3000 ink jet printer, a Fast T-Jet™ from US Screen Printing Institute (Tempe, AZ), the and prints were made on various substrates. The textile substrates used were 419 100 % cotton and 7409 65/35 polyester/cotton blend from Testfabrics Hanes Beefy T 100% cotton t-shirts, Hanes Heavy weight 100% cotton t-shirts, Hanes 50/50 polycotton cotton t-shirts, and a black fabric from Joann's Fabric (woven 100% cotton tweed). All test prints were fused at about 170°C for about 1 minute.

Pigmented Inks were used for testing the nonionic latex polymer and multivalent cation pretreatment solution and comparison pretreatment formulations. The inks used were DuPont™ Artistri™ P700 and P5000 series inks. The white ink used was described in IJ0132 and IJ0196.

Colorimetric measurements were done using a Minolta Spectrophotometer CM-3600d using Spectra Match software.

Where indicated the printed textile was tested for washfastness according to methods developed by the American Association of Textile Chemists and Colorists, (AATCC), Research Triangle Park, NC. The AATCC Test Method 61-1996, "Colorfastness to Laundering, Home and Commercial: Accelerated", was used. In that test, colorfastness is described as “the resistance of a material to change in any of its color characteristics, to transfer of its colorant(s) to adjacent materials or both as a result of the exposure of the material to any environment that might be encountered during the processing, testing, storage or use of the material.” Tests 2A and 3A were done and the color washfastness and stain rating were recorded. The ratings for these tests are from 1-5 with 5 being the best result, that is, little or no loss of color and little or no transfer of color to another material, respectively. Crock measurements were made using methodology described in AATCC Test Method 8-1996.

Pretreatment Solutions

Reagent grade calcium nitrate tetrahydrate (Aldrich) was mixed with deionized water until the calcium nitrate was completely in solution. Six pretreatment solutions were prepared, and a comparative solution with only a multivalent cation present was also prepared.

Table 2: Pretreatment Solutions 1-6

| | Component (Wt%) | |
|---|---|---|
| | as Calcium Nitrate Tetrahydrate | as Calcium Nitrate |
| Pretreatment Solution 1; Nonionic Latex Polymer Inv Ex 1 | 15 | 10.45 |
| Pretreatment Solution 2; Nonionic Latex Polymer Inv Ex 2 | 15 | 10.45 |
| Pretreatment Solution 3; Nonionic Latex Polymer Inv Ex 3 | 15 | 10.45 |
| Pretreatment Solution 4* | 15 | 10.45 |
| Pretreatment Solution 5** | 15 | 10.45 |
| Pretreatment Solution 6*** | 15 | 10.45 |
| Comparative Pretreatment Solution 1 | 10 | 6.95 |

* Pretreatment Solution 4 contains 10 % by weight (solids)of Printrite™ 2003, a nonionic polymer.
** Pretreatment Solution 5 contains 10 % by weight (solids) of Airflex™ 4530.
*** Pretreatment Solution 6 contains 10 % by weight (solids) of Permax™ 200.

Print Testing of Pretreatment

Print Test Set A: A 419 white cotton was printed with DuPont™ Artistri™ P5000 CMYK Inks with various pretreatment conditions. Each example was pretreated by spraying the textile in an area about the same as the intended image to be printed, dried and printed with the Epson 3000 printer. The estimated amount of calcium nitrate hydrate on the T-shirt prior to printing was about 7.5 grams/square meter. 5 grams of nonionic latex polymer. Then the printed textile was fused at 170°C for 1 minute. The printed textile were tested for optical density, 2A and 3A wash fastness and wet and dry crock. Table 3 shows the results of this printing.

Table 3: Print Testing of Pretreatment Conditions Set A

| Treatment | Color | OD | 2A | 3A | Dry | Wet |
|---|---|---|---|---|---|---|
| No pretreat | Black | 1.13 | 4.4 | 3.7 | 4.6 | 1.9 |
| Pretreatment Solution 1 | Black | 1.24 | ND | 1.5 | 3.8 | 1.1 |
| Pretreatment Solution 3 | Black | 1.25 | ND | 1.8 | 3.5 | 1.4 |
| Pretreatment Solution 4 | Black | 1.24 | ND | 1.8 | 2.9 | 1.5 |
| Pretreatment Solution 5 | Black | 1.37 | 3.9 | 2.5 | 4.7 | 1.3 |
| Pretreatment Solution 6 | Black | 1.35 | ND | 2.2 | 4 | 1 |
| Comparison Pretreatment Solution | Black | 1.23 | ND | 0.5 | 2.1 | 1.3 |
| No pretreat | Cyan | 1.09 | 3.6 | 2.8 | 4.0 | 2.1 |
| Pretreatment Solution 4 | Cyan | 1.12 |  | 2.2 | 4.7 | 1.2 |
| Pretreatment Solution 5 | Cyan | 1.17 | 4.4 | 3.3 | 4.6 | 1.6 |
| No pretreat | Magenta | 1.02 | 4.5 | 4.2 | 4.3 | 2.6 |
| Pretreatment Solution 5 | Magenta | 1.16 | 4.6 | 3.8 | 4.6 | 2.1 |
| No pretreat | Yellow | 1.12 | 4.8 | 4.3 | 3.0 | 2.1 |
| Pretreatment Solution 5 | Yellow | 1.31 | 4.8 | 3.9 | 3.5 | 1.7 |

ND not determined

Each pretreatment inventive example shows an improvement in optical density(OD), over the non pretreated sample and an improved washfastness and crock over the Comparison Pretreatment Solution example.

Print Test Set B: A 7409 polyester/cotton blend was printed with DuPont™ Artistri™ P5000 CMYK Inks with various pretreatment conditions. Each example was pretreated by spraying the textile in an area about the same as the intended image to be printed, dried and printed with the Epson 3000 printer. The estimated amount of calcium nitrate hydrate on the T-shirt prior to printing was about 7.5 grams/square meter. 5 grams of nonionic latex polymer. Then the printed textile was fused at 170°C for 1 minute. The printed textile were tested for optical density, 2A and 3A wash fastness and wet and dry crock. Table 4 shows the results of this printing.

Table 4: Print testing of Pretreatment Conditions Set B

| Treatment | Color | OD | 2A | 3A | Dry | Wet |
|---|---|---|---|---|---|---|
| No pretreat | Black | 0.96 | 3.3 | 2.5 | 4.7 | 2.1 |
| Pretreatment Solution 5 | Black | 1.30 | 2.3 | 1.2 | 4.6 | 1.1 |
| Pretreatment Solution 4 | Black | 1.27 | 2.6 | ND | 4.0 | 1.2 |
| Pretreatment Solution 3 | Black | 1.27 | 1.8 | ND | 4.2 | 1.2 |
| Comparison Pretreatment Solution | Black | 1.26 | 1 | ND | 4.2 | 1 |
| No pretreat | Cyan | 0.95 | 2.7 | 2.1 | 4.0 | 2.4 |
| Pretreatment Solution 5 | Cyan | 0.99 | 3.0 | 2 | 4.4 | 1.8 |
| No pretreat | Magenta | 0.85 | 3.1 | 2.3 | 4.6 | 3.0 |
| Pretreatment Solution 5 | Magenta | 1.09 | 4.7 | 2.2 | 4.6 | 2.0 |
| No pretreat | Yellow | 0.96 | 4.1 | 3.6 | 3.3 | 2.8 |
| Pretreatment Solution 5 | Yellow | 1.27 | 3.7 | 1.7 | 3.0 | 1.9 |

Each pretreatment inventive example shows an improvement in optical density(OD), over the non pretreated sample and an improved washfastness and crock over the Comparison Pretreatment Solution example.

Print Test Set C: The test shows the use of a white ink used after the inventive pretreatment, but prior to the image printing. A black t shirt was printed with DuPont® Artistri® P5000 CMY inks. Pretreatment Solution # 4 was used for all of the white ink tests

Table 9 Printing on Black T Shirt: Inventive Example Set 7

| | | | D65/10° | | | | | | Max. |
|---|---|---|---|---|---|---|---|---|---|
| | | | L* | a* | b* | C* | h° | OD | K/S |
| Cyan | Pretreated White ink Black T-shirt | C | 48.27 | 16.89 | 29.94 | 34.37 | 240.56 | 1.16 | 6.28 |
| Magenta | Pretreated White ink Black T-shirt | M | 39.07 | 37.62 | 10.56 | 39.07 | 344.32 | 1.26 | 8.17 |
| Yellow | Pretreated White ink Black T-shirt | Y | 66.27 | -2.86 | 63.64 | 63.70 | 92.58 | 1.40 | 11.49 |
| unprinted T-Shirt | Std Black T-Shirt | | 16.91 | -0.59 | -0.55 | 0.81 | 223.09 | 1.71 | 24.39 |
| Comp Example Cyan | No Pretreatment White ink black T-shirt | C | 18.35 | -1.80 | -5.88 | 6.15 | 253.02 | 1.69 | 23.28 |
| Comp Example Magenta | No Pretreatment White ink black T-shirt | M | 18.92 | 4.74 | -3.67 | 6.00 | 322.30 | 1.62 | 19.93 |
| Comp Example Yellow | No Pretreatment White ink black T-shirt | Y | 21.89 | -3.40 | 4.75 | 5.84 | 125.58 | 1.59 | 18.62 |

The inventive examples have significantly improved Chroma and L* relative to the comparative examples.

# CLAIMS

1. A method of digitally printing a textile comprising the steps of:

(a) pretreating the textile with an aqueous pretreatment solution comprising a nonionic latex polymer and a multivalent cationic salt solution,

(b) drying the pretreated textile,

(c) digitally printing the dried, pretreated textile with a colored ink jet ink,

whter the nonionic latex polymer has sufficient nonionic components such that the nonionic latex polymer is stable in the presence of the multivalent cationic salt solution.

2. The method of claim 1 where the nonionic latex polymer comprises one or more nonionic components selected from the group of ethylene oxide derivatives, acrylamide, hydroxyethyl, vinylpyrrolidone, and ethyleneimine.

3. The method of claim 1 where the nonionic latex polymer comprises one or more polymer components selected from the group of urethanes, vinylacetates, ethylene-vinylacetates, acrylates, acylamides, styrenes, and styrene-acrylate polymers.

4. The method of claim 3 wherein the polymer component of the nonionic latex polymer is selected from the group urethanes, acrylates, and acylamides.

5. The method of claim 4 where the polyurethane has a nonionic component derived from ethylene oxide components.

6. The method of claim 5 where the ethylene oxide components are at least 15 milliequivalents/gram of nonionic latex polymer.

7 The method of claim 1, wherein the multivalent cation is selected from one or more of the group of multivalent cations of elements Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, V, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Cu, Au, Zn, Al, Ga, In, Sb, Bi, Ge, Sn and Pb.

8. The method of claim 1, wherein the multivalent cation is calcium.

9. The method of claim 8, wherein the pretreatment solution comprises a solution of a multivalent cationic salt in water, wherein the multivalent cationic salt is selected from the group consisting of calcium nitrate, calcium nitrate hydrate, calcium chloride, calcium hydrate and mixtures thereof.

10. The method of claim 1, wherein the textile is pretreated with the pretreatment solution in a wet pick-up of from about 0.20 to about 7.5 grams of multivalent cationic salt per 100 grams of fabric.

11. The method of claim 1, wherein the textile is printed with a colored inkjet ink set comprises at least two differently colored inkjet inks.

12. The method of claim 11 where the colored inkjet ink is a pigmented ink.

13. The method of claim 11, wherein at least one of the pigmented inkjet inks is white.

14. The method of claim 12, wherein the ink set comprises at least three differently colored pigmented inkjet inks, wherein at least one is a cyan pigmented inkjet ink, at least one is a magenta pigmented inkjet ink, and at least one is a yellow pigmented inkjet ink.

15. The method of claim 14, wherein the ink set further comprises a black pigmented inkjet ink.

16. The method of claim 14 or 15, wherein the textile is printed with the at least two differently colored inkjet ink to an ink coverage of between about 5 to about 17 grams of ink per square meter of fabric.

17. The method claim 14 or 15, wherein the pigmented inkjet ink comprises, or each the pigmented inkjet inks in the inkjet set individually comprise, an anionically stabilized pigment in an aqueous vehicle.

18. The method of claim 1, further comprising the step of post-treating the printed textile with heat and/or pressure.

19. The pretreated textile of claim 1, wherein the fabric comprises a cotton or cotton blend.

20. The pretreated textile of claim 1 which, subsequent to application of the textile pretreatment solution, has been dried to equilibrium moisture at ambient temperature.