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(54) **Title:** AUXILIARY FORMULATIONS FOR DIGITAL PRINTING

(57) **Abstract:** The technology disclosed herein provides pretreatment formulations for both wet-on- wet and wet-on-dry digital printing methods.

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AUXILIARY FORMULATIONS FOR DIGITAL PRINTING

TECHNOLOGICAL FIELD

The invention generally concerns pretreatment or auxiliary formulations for printing.

BACKGROUND

Fabrics and other textile materials have been used as substrates for inkjet printing and have proven to present a challenge due to their structure (e.g., presence of interstitial spaces between the fibers) and fibers' composition. Without the ability of an ink or a pigment to securely associate to or penetrate into the fabric, the resulting printed image may be deficient.

When using digital printing, including inkjet, to form patterns on fabrics and textiles, the image that is generated may appear to have a low color intensity, fuzziness, especially at the edges of the pattern or image, resulting mainly from penetration of the ink or pigment into the fibers.

Many technologies have been developed over the years in an attempt to at least partially overcome these difficulties. Some of these technologies offer the use of cationic polymers, fabric softeners or particles, while others offer improvements in the printing process rather than in treating the substrate, e.g., textile or fabric.

Thus, there still exists a need to provide a printed pattern that not only securely adheres to the fabric surface but which also presents a high print quality, wash-fastness, and mechanical durability, minimizing loss in tensile strength and enhancing tear resistance in case of resin finished fabrics.

BACKGROUND ART

[1] International Patent Publication NO. WO 2019/077615

GENERAL DESCRIPTION

The need to provide a coating material or a pretreatment material that can enhance receptivity of an ink to different fabric and textile surfaces has been met by the technology disclosed herein, which generally provides not only the means to enhance

receptivity of an ink to the substrate, but also by providing a continuum three-dimensional surface on which the ink may be applied. Such a continuum surface overcomes the difficulties associated with printing directly on a textile or a fabric, by filling up and thereby erasing interstitial spaces between the fibers and forming receptive surfaces that are better suited to receive the printed images.

The technology subject of the invention disclosed herein is based on the inventors' discovery that reactive polysiloxanes can be used in formulating pretreatment formulations for both wet-on-wet and wet-on-dry digital printing methods, for providing a 3D cushion or matrix onto which ink patterns may be formed. The pretreatment formulations of the invention may be used on any substrate on the surface of which printing or image forming is desired. The use of reactive polysiloxanes endows the surface with superior patterning capabilities, opening the door for using a vast variety of printing ink formulations, and forming patterns and images with an increased thermal or oxidative stability, increased adhesion, low viscosity change with temperature, high compressibility, low surface tension, low fire hazard, durability, water repellency (hydrophobicity), low abrasion and other superior characteristics.

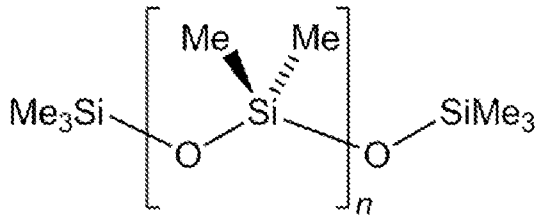
Thus, the present application provides a provision of pretreatment of a surface for digital printing. When applying, e.g., by printing or by any other means, the pretreatment formulations of the invention a pattern is provided which may be characterized by elastic properties and combined with permanent finishing properties of softness, smooth hand-feel, and mechanical durability, such as wet and dry abrasion resistance.

In a first aspect of the invention, there is provided a pretreatment formulation, optionally in the form of an aqueous dispersion or emulsion, which comprises at least one (unreactive) polysiloxane, at least one reactive polysiloxane, at least one humectant, at least one wetting agent, at least one pH adjuster, at least one rheology modifier, and at least one additive (e.g., a preservative and others as disclosed herein). The formulation is not an ink formulation and is free of any dye material, pigment or other coloring agent.

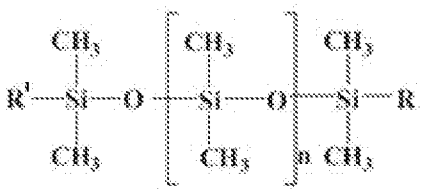
In some embodiments, formulations of the invention are free of acrylates of any form and composition. The formulations may also be free of acids or bases.

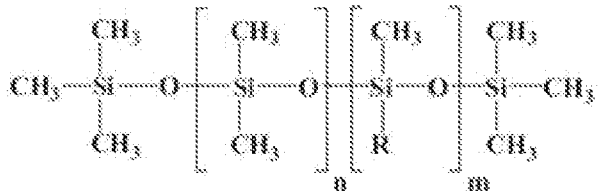
In some embodiments, formulations of the invention comprise at least one acid or base.

The polysiloxanes used in formulations of the invention are selected into two types. The first polysiloxane is an unreactive polysiloxane and the other is a reactive polysiloxane. The unreactive polysiloxanes, polydimethylsiloxane (PDMS) or a homologue thereof, is of the structure below, wherein n is between 10 and 20.



While the unreactive polysiloxane does not contain functionalities that permit self-crosslinking, or any cross-linking with another agent, the reactive polysiloxane may be any such material in which one of the methyl groups in any of the -Si-Me bonds or one of the -Si-Me groups has been replaced with a reactive functional group capable of crosslinking. Such reactive groups may be hydroxyl groups, amino groups and substituted amino groups, epoxide groups, which may be directly attached to the polymer backbone or to pendant groups. Other reactive groups include such groups as amide groups, carboxylic acid groups, activated esters and amides, epoxides, vinyl groups, alkenyl groups, acyl groups, and others. Non-limiting examples of reactive polysiloxanes are shown below, wherein each variant R is independently selected from hydroxyl, ether, amine, amide, carboxylic acid, activated ester, activated amide, epoxide, vinyl group, alkenyl, acyl and others, which are each directly bonded to the Si atom or via a linking moiety such as an alkyl. Where a reactive polysiloxane comprises more than one R group, each of the R groups (R and R') may be the same or different. In the structures shown below, each of n and m is an integer accounting for the number of repeating groups in the polysiloxane. Each of n and m, independently, may be selected from 1 to 60.





The unreactive polysiloxane may be fully or partially synthesized, as known in the art, or may be obtained from commercial sources. Such available sources include Rudolf (i.e., RUCOFIN HPU), WACKER, Momentive, and others.

The reactive polysiloxanes may similarly be partially or fully synthesized or may be obtained from commercial sources such as Rudolf (RUCOFIN MISP EXTRA), WACKER(i.e., POWERSOFT UP 68, POWERSOFT® AE 61, POWERSOFT® CF 20), Momentive (Magnasoft 68 reactive cross-linkable silicone emulsion) and others.

A reactive polysiloxane is selected to undergo self-crosslinking or crosslinking of two or more polysiloxanes, and further crosslinking with the substrate material (e.g., fabric or textile) and optionally also with components present in the ink formulation or any other formulation or component added thereto. The polysiloxanes are introduced to the substrate prior to ink deposition. The selection of reactive polysiloxane endows the pretreatment formulation of the invention with self-crosslinking or self-curing. Crosslinking of formulations of the invention may or may not require application of thermal energy or radiation to achieve full curing (for both the selected ink and pretreatment). Typically, energy in the form of heat or light may be applied, in some cases, after an ink formulation has been applied onto a surface pretreated with a formulation of the invention, as disclosed hereinbelow.

Generally, formulating a combination of reactive and unreactive polysiloxanes enables low-temperature curing. That means that crosslinking may be achieved in the presence of a chemical stimulus such as a catalyst, e.g., an acid or a base that may be included in the ink formulation. Pretreatment formulations of the invention may be absent of any such chemical stimuli so as to avoid undesired crosslinking before the ink

formulation is applied. However, acid, base or a pH adjuster may be added in order to achieve chemical compatibility to the printhead. Thus, in some embodiments, formulations of the invention may comprise latent acids or latent bases that can transform into the respective acid or base upon contact with e.g., a component in the ink formulation.

Thus, the latent acid or base may be selected amongst such compounds that decompose upon exposure to a stimulus such as heat or light or upon exposure to a suitable reaction condition, e.g., hydrolysis, or to a material (e.g., in the ink formulation) to provide an acid or a base. Exemplary latent acids include, but are not limited to, esters, sulfonic acid esters, fluorinated sulfonic acid esters, phosphonic acid esters and nitriles. The latent base may be selected amongst metal oxides which yields an alkaline material under suitable reaction conditions. Such latent bases may be selected from oxides of alkali or alkaline earth-metals such as barium oxide, calcium oxide, lithium oxide, or magnesium oxide.

Self-crosslinking occurs between the reactive functional groups present on the reactive polysiloxane and functional groups, such as (OH) or C=O groups on the substrate surface or in components of the ink formulation.

Where heat is needed to achieve a desired degree of curing, the reactive polysiloxane may be selected to undergo crosslinking upon exposure to heat, IR or UV radiation, or to any other means. Typically, temperatures ranging between room temperature (20-35°C) and 110°C may be used. According to some embodiments, the low temperatures are temperatures below 70°C, or below 60°C, or below 50°C, or below 40°C, or below 30°C or at a temperature between room temperature and 80°C.

The amount of the at least one unreactive polysiloxane is between 0.5 and 20 wt%. The amount of the at least one reactive polysiloxane is between 0.5 and 40 wt%. The total amount of the two polysiloxanes is between 1 and 60 wt%, relative to the total weight of the formulation.

Apart from the polysiloxanes, formulations of the invention comprise also at least one humectant, at least one wetting agent, at least one pH adjuster, at least one rheology modifier, and at least one additive (e.g., a preservative).

In some embodiments, the at least one humectant is a glycol, optionally selected from ethylene glycol (EG), glycerin, propylene glycol (PG), dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, propylene glycol n-butyl ether, propylene

glycol n-propyl ether, ethylene glycol hexyl ether, ethylene glycol propyl ether, diethylene glycol phenyl ether and ethylene glycol phenyl ether,. The amount of at least one humectant in formulations of the invention is, in some embodiments, between 20-45 wt %.

The at least one wetting agent may be BYK 348, Dynol 360 and others. The amount of at least one wetting agent in formulations of the invention is, in some embodiments, between 0.1-0.6 wt %.

The at least one pH adjuster may be triethanolamine. In some embodiments, the pH adjuster is a fatty acid. In some embodiments, the fatty acid may serve as a softening agent or as a softening enhancer. In some embodiments, the fatty acid is selected from lactic acid, butyric acid, lauric acid, myristic acid, palmitic acid, stearic acid, archidic acid, linolenic acid, linoleic acid, arachidonic acid, and oleic acid. The amount of at least one pH adjuster in formulations of the invention is, in some embodiments, between 0.1-5 wt %.

The at least one rheology modifier may be Joncryl 538. The amount of at least one rheology modifier in formulations of the invention is, in some embodiments, between 2-5 wt %.

In another aspect thereof, the invention further contemplates an aqueous pretreatment formulation (or a dispersion or an emulsion) comprising at least one metal salt and a copolymer, a polymer or a mixture thereof. The mixture may be a mixture of polymers, a mixture of copolymers or a mixture of polymers and copolymers.

The at least one metal salt may be provided alone or in combination with other salts such as an ammonium. In some embodiments, the at least one metal salt is provided in combination with an ammonium salt.

In some embodiments, the aqueous pretreatment formulation consists of at least one carbodiimide crosslinker that enhances the adhesion effect. The at least one carbodiimide crosslinker may be Stahl Picassian® XL-752.

In some embodiments, the aqueous pretreatment formulation comprises or consists at least one inorganic salt (i.e., metal salt) and a copolymer, a polymer or a polymer combination.

The at least one inorganic salt may be selected from monovalent metal salts, divalent metal salts, trivalent metal salts and combinations thereof. The metal may be sodium, calcium, aluminum, copper, zinc, cobalt, nickel, magnesium and others. In

other embodiments, the salt is an ammonium salt (an example of a suitable salt includes ammonium chloride that serves in some cases as an acidifying salt that is prompting the cationic characteristics of the pretreatment) or an organic salt.

The anion used as the counter ion can be, for example, a chloride, a fluoride, a bromide, an iodide, a nitride, a sulfate, acetate, a citrate, a propionate, a borate or phosphate. Examples of suitable salts of monovalent cations include, but are not limited to, lithium chloride, lithium acetate, lithium carbonate, lithium borate, lithium nitrate, lithium phosphate, sodium chloride, sodium acetate, sodium carbonate, sodium borate, sodium nitrate, sodium phosphate, potassium acetate, potassium chloride, potassium carbonate, potassium borate, potassium phosphate, potassium nitrate, copper chloride, copper nitride, copper sulfate, copper acetate, copper citrate, copper propionate, copper borate, copper phosphate, silver chloride, silver nitride, silver sulfate, silver acetate, silver citrate, silver propionate, silver borate, silver phosphate, gold chloride, gold nitride, gold sulfate, gold acetate, gold citrate, gold propionate, gold borate, and gold phosphate. Examples of suitable salts of divalent cations include, but are not limited to, magnesium chloride, magnesium acetate, magnesium carbonate, magnesium borate, magnesium nitrate, magnesium phosphate, calcium chloride, calcium acetate, calcium carbonate, calcium borate, calcium nitrate, calcium nitrate, calcium phosphate, zinc chloride, zinc acetate, zinc carbonate, zinc nitrate, zinc phosphate, copper chloride, copper acetate, copper carbonate, copper nitrate, copper phosphate, tin chloride, tin acetate, tin carbonate, tin nitrate, tin phosphate, ferrous chloride, ferrous acetate, ferrous carbonate, ferrous nitrate, ferrous phosphate, and combinations thereof. The anti-smear agent can include a combination of compounds having monovalent and/or divalent cations. For example, the anti-smear agent can include lithium and sodium, for example, in the form of lithium chloride and sodium acetate. Other combination of monovalent and/or divalent cations can also be included to provide the anti-migration combination.

In some embodiments, the salt is a calcium salt. Non-limiting examples of calcium salts include $CaCl_2$, CaF_2, $CaBr_2$, CaI_2, calcium carbonate and others.

In some embodiments, the at least one inorganic salt is provided alone or in combination with one other salt, wherein the at least one other salt may or may not be an organic salt. In some embodiments, the at least one organic salt is provided in combination with an ammonium salt, wherein the salt anion is selected from a chloride,

a fluoride, a bromide, an iodide, a nitride, a sulfate, acetate, a citrate, a propionate, or a borate.

In some embodiments, the copolymer, polymer or polymer mixture is provided as a dispersion which comprises as least one "***anti-migration polymer***", namely at least one polymeric material that when applied to a surface, it prevents migration or smearing of an ink pattern formed thereon. The anti-migration polymer may be selected to prevent migration or movement of the ink drop once applied, to thereby prevent distortion of a printed pattern, mixing of inks of different colors and loss of resolution and print quality. The anti-migration polymer may be a neutral polymer, an amphiphilic polymer, an anionic polymer, non-ionic or slightly cationic polymer, as known in the art. The anti-migration polymer dispersion may be selected to have a clear visuality and a low to high molecular weight. The molecular weight may be between 10 and 80 kDa, or may be between 20 and 60kDa or between 30 and 50 kDa or 40 and 50kDa, or generally selected to allow a better dispersibility in its medium.

The selection of specific polymer dispersions may depend on the ink formulation that is used, the nature of the substrate onto which the anti-migration polymer dispersion is to be applied, on the printing method (e.g., wet-on-dry or wet-on-wet) as well as on other parameters known to a person versed in the art. The polymer may thus be selected from a variety of polymer families. Non-limiting examples of such polymers include polyurethane polymers and copolymers, cellulosic materials, polymers and copolymers of polyacrylate (such as without limitation ethyl acrylate, propyl acrylate), polymers and copolymers of diallyldialkylammonium monomers, poly amide-epichlorohydrin copolymer, polypropylene polymers and copolymers (polypropylene glycol, propylene oxide), polyethylene copolymer (such as without limitation ethylene vinyl acetate copolymer (EVA), polyethylene glycol (PEG), copolymers of ethylene oxide) or butylene oxide, polyvinyl polymers (such as without limitation polyvinyl methyl ethers, polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA)) and others.

In some embodiments, the anti-migration polymer is at least one polyurethane polymer or a copolymer. In some embodiments, the anti-migration polymer is provided as a mixture of polymers or of polymer dispersions with one or more other components.

In some embodiments, the anti-migration polymer is a polymer or a copolymer of polyacrylate (such as ethyl acrylate and propyl acrylate).

In some embodiments, the anti-migration polymer is a polymer or a copolymer of diallyldialkylammonium.

In some embodiments, the anti-migration polymer is a polymer or a copolymer of poly amide-epichlorohydrin.

In some embodiments, the anti-migration polymer is a polymer or a copolymer of polypropylene (such as polypropylene glycol and propylene oxide).

In some embodiments, the anti-migration polymer is a polymer or a copolymer of polyethylene (such as ethylene vinyl acetate copolymer (EVA), polyethylene glycol (PEG), copolymers of ethylene oxide).

In some embodiments, the anti-migration polymer is a polymer or a copolymer of polyvinyl (such as polyvinyl methyl ethers, polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA)).

In some embodiments, the polyurethane is used in combination with at least one salt, such as a calcium salt. The combination may comprise the polyurethane or any other anti-migration polymer in an amount between 0.5 and 15wt%. The amount of the salt may be from 1 to about 6 wt%.

In some embodiments, the polymer mixture comprises one or more polymers selected from polyurethanes, cellulosic materials, polyacrylates, polypropylene, polyethylene and others. In some embodiments, the polymer mixture comprises a mixture of polyurethane. In some embodiments, the polymer mixture comprises one or more of the polymers mentioned herein, e.g., polymers selected from polyurethanes, ethyl acrylate, propyl acrylate, poly amide-epichlorohydrin, polypropylene glycol, propylene oxide, ethylene vinyl acetate copolymer (EVA), polyethylene glycol (PEG), butylene oxide, polyvinyl methyl ether, polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA)) and others.

In some embodiments, the polymer mixture, comprising, e.g., a polyurethane or a mixture of polyurethanes, is used in combination with at least one salt, such as a calcium salt. The combination may comprise the polyurethane or any other polymer, e.g., an anti-migration polymer in an amount between 0.5 and 18wt%. The amount of the salt may be from 0.5 to about 18 wt%.

In some embodiments, the formulation comprises epichlorohydrin-modified polyamide or epichlorohydrin polyamide copolymer. In some embodiments, the polyamide is utilized as a shrinking inhibitor.

In some embodiments, the aqueous pretreatment formulation, dispersion or emulsion comprises at least one metal salt, at least one ammonium salt, a copolymer, a polymer or polymer mixture, at least one crosslinker, e.g., carbodiimide, and epichlorohydrin (Epichlorohydrin polyamide copolymer).

In some embodiments, the copolymer, a polymer or polymer mixture is cationic.

In some embodiments, the aqueous pretreatment formulation, dispersion or emulsion is suitable for application onto fabrics as well as on plastic or polymeric substrates. In some embodiments, the aqueous pretreatment formulation, dispersion or emulsion provide a solid film onto which an ink composition may be applied (wet on dry application).

Formulations of the invention may also comprise a variety of additives such as preservatives, crosslinking agents, viscosity modifiers, film forming agents, pH adjuster agents, ink receptive materials, bleeding inhibitors, migration inhibitors, color enhancers and adhesion promoting agents.

While formulations of the invention are suitable for forming ink receptive films or substrates, at times an ink receptive material may be required. These materials, which are designed to enhance the printing surface, are known in the art and may be selected amongst those known in the art.

The ink receptive material is typically a component of the formulation of the invention. However, in some embodiments, a film of the ink receptive material may be formed on top of a film formed of a formulation of the invention.

In some embodiments, the pretreatment formulation comprising at least one ink receptive material that may be a polyurethane polymer dispersion, not limited to such owning silanol functional groups, forming siloxane bonding. The polyurethane polymer may be ether-based, ester based, or carbonate-based.

In some embodiments, the pretreatment formulation comprises at least one anti-migration agent, such as fumed silica. The anti-migration agent may be Evonik Aerodisp G 1220.

In some embodiments, the pretreatment formulation possesses a softening effect. Thus, as used herein, the pretreatment formulation, dispersion or emulsion of the invention may also be regarded a softening formulation, dispersion or emulsion. The softening effect may be associated with the collection of materials making up a formulation of the invention, or may be endowed by one or more of the materials

present in the formulation. In some examples, the polysiloxanes, pH adjusters and other components may enhance or contribute to the softening effect of formulations of the invention. The softening effect is allowed by association of the pretreatment formulation to the functional groups within the substrates and in turn the bonding of the functional groups within the pretreatment formulations to the ink formulations. This activity is linked to the textile or fabric ability to withstand various conditions while preserving a durable pattern formed on the substrate. Among others, two important measurements are known in the art and performed to assess the fastness of the material.

-Rub-fastness, or 'crock resistance,' is measured by evaluating the transference of color onto white (wet or dry) fabric when rubbed back and forth against a printed pattern for a set number of times under a given weight. The grades range of these measurements is between 1 and 5, while the lowest rank is 1. Manufacturers target a minimum of grade 3, but usually aim for a grade equal or above 4.

-Wash-fastness is measured via sequential or non-sequential set number of laundry cycles. The resistance of a material to change in any of its color characteristics is evaluated while stimulating rubbing-fastness, withstanding changes in pH and temperature parameters and exposing to water.

As noted herein, pretreating of the substrate results in higher ranking scores of both rubbing (wet and dry) as well as washing fastness evaluations. This stands to show that the pretreatment allows an enhanced resistance to external forces, reflecting on the bonding of the substrate-pretreatment formulations-ink formulations that mediates the softening effect as well.

Table 1: Enhanced reactivity of formulations of the invention

Sample	Wet rubbing	Dry rubbing	Wash-fastness
Non-pretreated textile or fabric (reference)	3	3.5	3.5
Pretreated textile or fabric according to the invention	4	4.5	4-4.5

In place of the ink receptive material or in addition thereto, the formulation may comprise a bleeding inhibitor or a migration inhibitor.

Non-limiting examples of formulations of the invention include, in addition to those already mentioned:

Formulation 1 comprising:
A carrier such as water
An antimigration polymer
A metal salt
An ammonium salt
Epichlorohydrin polyamide copolymer.

Formulation 2 comprising:
A carrier such as wate
An antimigration polymer
A metal salt
An ammonium salt
Epichlorohydrin polyamide copolymer
An adhesion promoter (or a crosslinker), such as a polycarboimmide crosslinker.

Formulation 3 comprising:
A carrier
An unreactive polysiloxane
A reactive polysiloxane
An antimigration polymer
A metal salt
An ammonium salt
Epichlorohydrin polyamide copolymer
A humectant
A wetting agent
A softening agent.

Formulation 4 comprising:
A carrier
A polyurethane

A humectant

A wetting agent

An antimigration material such as fumed silica.

Formulation 5 comprising:

A carrier such as water

An unreactive polysiloxane

A reactive polysiloxane

A silane coupling agent

An antimigration polymer

A metal salt

An ammonium salt

Epichlorohydrin polyamide copolymer

A humectant

A wetting agent

A softening agent.

Formulation 6 comprising:

water

An antimigration polymer, as defined herein

A metal salt, such as calcium chloride

An ammonium salt

Epichlorohydrin polyamide copolymer.

Formulation 7 comprising:

water

An antimigration polymer, as defined herein

A metal salt, such as calcium chloride

An ammonium salt

Epichlorohydrin polyamide copolymer

polycarboimmide crosslinker.

Formulation 8 comprising:

water

PDMS

RUCOFIN MISP EXTRA

Ruco-print PPB (from Rudolf)

A metal salt, such as calcium chloride

An ammonium salt

Epichlorohydrin polyamide copolymer

glycol

BYK 348

A fatty acid.

Formulation 9 comprising:

water

A polyurethane polymer dispersion

glycol

BYK 348

fumed silica.

Formulation 10 comprising:

water

PDMS

RUCOFIN MISP EXTRA

KBM-403 (from ShinEtsu)

Ruco-print PPB (from Rudolf)

A metal salt, such as a calcium chloride

An ammonium salt

Epichlorohydrin polyamide copolymer

glycol

BYK 348

A fatty acid.

Formulation 11 comprising:

A carrier such as water- 58-97% w/w

An antimigration polymer- 0.5-18 %w/w

A metal salt- 0.5-18% w/w

An ammonium salt- 0.005-2% w/w

Epichlorohydrin polyamide copolymer- 0.005-2% w/w.

Formulation 12 comprising:

A carrier such as water- 58-97% w/w

An antimigration polymer- 0.5-18% w/w

A metal salt- 0.5-18% w/w

An ammonium salt- 0.005- 2% w/w

Epichlorohydrin polyamide copolymer- 0.005%- 2% w/w

An adhesion promoter (or a crosslinker), such as a polycarboimmide crosslinker- 0.5%-6% w/w.

Formulation 13 comprising:

A Carrier- 15%-55% w/w

An unreactive polysiloxane- 0.5%- 20% w/w

A reactive polysiloxane- 0.5%-40% w/w

An antimigration polymer- 0%-25 % w/w

A metal salt- 0.5%-18% w/w

An ammonium salt- 0.005%-2% w/w

Epichlorohydrin polyamide copolymer- 0.005%-2% w/w

A humectant- 20%-45% w/w

A wetting agent- 0.1-0.6% w/w

A softening agent- 0.1-2% w/w.

Formulation 14 comprising:

A carrier- 5%-50% w/w

A polyurethane- 30%-80% w/w

A humectant- 10%-30% w/w

A wetting agent- 0.1-0.6% w/w

An antimigration material such as fumed silica- 0.1-4% w/w.

Formulation 15 comprising:

A carrier such as water- 15%-55% w/w

An unreactive polysiloxane- 0.5%-20% w/w

A reactive polysiloxane- 0.5%-40% w/w

A silane coupling agent- 0.1-4% w/w

An antimigration polymer- 0%-25 % w/w

A metal salt- 0.5%-18% w/w

An ammonium salt- 0.005%-2% w/w

Epichlorohydrin polyamide copolymer- 0.005%-2% w/w

A humectant- 20%-45% w/w

A wetting agent- 0.1-0.6% w/w

A softening agent- 0.1-2% w/w.

Formulation 16 comprising:

water- 58-97% w/w

An antimigration polymer, as defined herein- 0.5-18 %w/w

A metal salt, such as calcium chloride- 0.5-18% w/w

An ammonium salt- 0.005-2% w/w

Epichlorohydrin polyamide copolymer- 0.005-2% w/w.

Formulation 17 comprising:

water- 58-97% w/w

An antimigration polymer, as defined herein- 0.5-18% w/w

A metal salt, such as calcium chloride- 0.5-18% w/w

An ammonium salt- 0.005- 2% w/w

Epichlorohydrin polyamide copolymer- 0.005%- 2% w/w

polycarboimmide crosslinker- 0.5%-6% w/w.

Formulation 18 comprising:

water- 15%-55% w/w

PDMS- 0.5%- 20% w/w

RUCOFIN MISP EXTRA- 0.5%-40% w/w

Ruco-print PPB (from Rudolf)- 0.5%-25 % w/w

A metal salt, such as calcium chloride- 0.5%-18% w/w

An ammonium salt- 0.005%-2% w/w

Epichlorohydrin polyamide copolymer- 0.005%-2% w/w

glycol- 20%-45% w/w

BYK 348- 0.1-0.6% w/w

A fatty acid- 0.1-2% w/w.

Formulation 19 comprising:

water- 5%-50% w/w

A polyurethane polymer dispersion- 30%-80% w/w

glycol- 10%-30% w/w

BYK 348- 0.1-0.6% w/w

fumed silica- 0.1-4% w/w.

Formulation 20 comprising:

water- 15%-55% w/w

PDMS- 0.5%-20% w/w

RUCOFIN MISP EXTRA - 0.5%-40% w/w

KBM-403 (from ShinEtsu)- 0.1-4% w/w

Ruco-print PPB (from Rudolf)- 0.5%-25 % w/w

A metal salt, such as a calcium chloride- 0.5%-18% w/w

An ammonium salt- 0.005%-2% w/w

Epichlorohydrin polyamide copolymer- 0.005%-2% w/w

glycol- 20%-45% w/w

BYK 348- 0.1-0.6% w/w

A fatty acid- 0.1-2% w/w.

Formulations of the invention are typically aqueous formulations that in addition to water may further comprise at least one liquid carrier selected not only to formulate a homogenous and stable formulation, but optionally also to modify the viscosity of the formulations. Typically, the formulations disclosed herein exhibit low viscosities,

thereby permitting their application by a variety of means ranging from manual (hand) applications (e.g., wiping, immersing, padding, spraying) to application by an inkjet printer.

In some embodiments, the aqueous formulations comprise or consist a water-miscible organic solvent that may be selected amongst humectants and coalescing agent. Non-limiting examples of humectants include ethylene glycol (EG) and/or glycerin (20-40 wt. %). The coalescing agent may be propylene glycol (PG). Additional examples include dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, ethylene glycol hexyl ether, ethylene glycol propyl ether, diethylene glycol phenyl ether,ethylene glycol, and phenyl ether.

As stated herein, formulations of the invention may be adapted for a variety of applications. The viscosity of the formulation may thus be adjusted based, inter alia, the intended mode of application, e.g., inkjet printing. The formulations viscosity parameters (at a typical jetting temperature ranging from room temperature (25°C) and 35°C) and surface tension parameters may further be adapted per a specific inkjet printhead technology for a stable jetting at a wide range of frequencies. Formulations of the invention exhibit viscosities ranging between 4 and 20 mPa·s (jetting temperatures range: 25-35 °C) and a surface tension ranging from 20 and 35 dyne/cm^2.

Where application of the pretreatment formulation is by padding or spraying accurate patterning with the formulation may be more difficult to achieve. Padding and spraying may completely cover the surface region, and where fibers are to receive pretreatment, pretreating the fibers may be tuned to completely cover each fiber. Pretreating a surface by inkjet printing, for example, allows a a selective deposition of the pretreatment formulation right under the patterned ink formulation ensuring precision, frugality, and a better hand-feel.

According to methods of the invention, a pretreatment formulation of the invention may be applied to a surface region of a substrate prior to application of an ink or pigment formulation. The substrate may be any substrate selected, in some embodiments, from absorptive or non-absorptive materials, natural or synthetic materials (e.g., fabrics and textiles), paper materials (e.g., paper, paperboard, wallpaper), polymeric materials (e.g., made from a polyester, a polyethylene, a

polypropylene, vinyl & acrylic banners, PVC banners, leather, metal, wood, corrugated plastic signs, plasticized nylon and blends thereof) and others.

Application of a pretreatment formulation is generic to all types of surfaces; however, it may be more selective towards textile and fabric substrates. Such textile and fabric substrate may be a woven or a non-woven textile material, which may or may not be formed of a natural fiber, a synthetic fiber or a combination of the two.

A pretreated surface, either wet or dry, may receive an ink formulation by any means and methods known in the art. While common ink printing methods include digital printing, such as inkjet printing may be typically used (i.e., direct to garment (DTG), and roll-to-roll for textile and fabric substrates), transfer printing processes,flexo, roto gravure, direct to film (DTF), offset and screen printing may be similarly used.

The ink formulations may be any such known in the art. The ink formulation may be applied onto any part of the pretreated surface region. Application may proceed wet-on-wet, whereby the ink formulation is applied while the pretreatment formulation is still wet and uncured, or wet-on-dry, whereby the applied pretreatment is first allowed to dry. Where the pretreatment formulation is patterned on the surface by printing, e.g., inkjet printing, it may be patterned only where application of the ink is intended.

The invention further provides a pattern formed of a formulation according to the invention. In some embodiments, the pattern is formed on a surface of a substrate, may be intercalated within or absorbed into the substrate, the substrate being selected from absorptive or non-absorptive materials, natural or synthetic materials, paper materials and polymeric materials. In some embodiments, the substrate is a fabric or a textile.

In some embodiments, the pattern is in a form configured to receive an ink formulation. The pattern may be in a wet form or a dry form. The pattern may be in a form of a wet uncross-linked or partially cross-linked form, or a cross-linked dry pattern.

The invention further provides a method of forming an ink pattern on a surface, the method comprising coating a surface region of a substrate with a pretreatment formulation according to the invention, and patterning an ink formulation on at least a portion of the surface region coated with the pretreatment formulation.

In some embodiments, the ink formulation is patterned on a wet coat of the pretreatment formulation. In some embodiments, the ink formulation is patterned on a dry coat of the pretreatment formulation.

Also provided is a method of forming an ink pattern on a surface, the method comprising obtaining a substrate having at least part of its surface region coated with a pretreatment formulation according to the invention, and patterning an ink formulation on at least a portion of the surface region coated with the pretreatment formulation. In some embodiments, coating with the pretreatment formulation is patterning of a surface region of the substrate.

In some embodiments, the ink formulation is patterned by a means selected from digital printing, transfer printing and screen printing.

The invention further provides a method of forming a pattern on a surface region by digital printing, the method comprises patterning a pretreated surface region of a substrate (namely a surface region having received a layer of a pretreatment formulation of the invention) with an ink formulation.

In some embodiments, the method comprises obtaining a pretreatment formulation according to the invention.

In some embodiments, the pretreatment formulation is applied onto the surface region by inkjet printing. In some embodiments, the pretreatment formulation is patterned on the surface region.

In some embodiments, the ink formulation is applied onto a region which previously received a pretreatment formulation, while wet (following a wet-on-wet method, as known in the art). In some embodiments, the film or layer or pattern of a pretreatment formulation is allowed to dry before receiving an ink.

In some embodiments, the method is carried out using an in-line printing system. Such an in-line system may comprise a plurality of printing stations, each is selected and operable to advance image forming on a substrate. In such an in-line system, at least one of the stations is operable to apply or pattern a pretreatment formulation onto the surface region, at least one another station is operable to apply or pattern an ink formulation on a region having received the pretreatment formulation, and at least one further station for promoting crosslinking of the formed patterns. Other stations may also be included. The stations may be associated and operated via a

conveyer on which the surface (article or product) to be patterned is moved from one station to another.

As noted herein, a pretreated surface may receive any ink for forming a pattern on an image. The inks may be selected, for example, from reactive inks, acid inks, disperse inks, sublimation inks, pigment inks and others.

DETAILED DESCRIPTION OF EMBODIMENTS

In the following, non-limiting examples of pretreatment formulations according to the invention are provided:

Table 2: A digital wet-on-dry pretreatment formulation according to the invention.

Ingredient	**Function**	**Amount**
Deionized water	Carrier	58% - 97% w/w
RUCO-PRINT PPB (from Rudolf)	Ink receptive, anti- migration polymer	0.5% - 18% w/w
Metal salt	Cationic charge adjuster	0.5% - 18% w/w
Ammonium salt	Cationic charge adjuster	0.005% - 2% w/w
Epichlorohydrin polyamide copolymer	Shrinking inhibitor	0.0051% - 2% w/w

Table 3: A digital wet-on-dry pretreatment formulation according to the invention.

Ingredient	**Function**	**Amount**
Deionized water	Carrier	58% - 97% w/w
RUCO-PRINT PPB (from Rudolf)	Ink receptive, anti- migration polymer	0.5% - 18% w/w
Metal salt	Cationic charge adjuster	0.5% - 18% w/w
Ammonium salt	Cationic charge adjuster	0.u005% - 2% w/w
Epichlorohydrin polyamide copolymer	Shrinking inhibitor	0.005% - 2% w/w
Polycarbodiimide crosslinker	Adhesion promoter	0.5% - 6% w/w

Table 4: A digital pretreatment formulation according to the invention. The glycol and fatty acid are as selected herein.

Ingredient	Function	Amount
PDMS	Unreactive polysiloxane	0.5% - 20% w/w
RUCOFIN MISP EXTRA	Reactive polysiloxane	0.5% - 40% w/w
Ruco-print PPB (from Rudolf)	Ink receptive, anti- migration polymer	0.5% - 25 % w/w
Metal salt	Cationic charge adjuster	0.5% - 18% w/w
Ammonium salt	Cationic charge adjuster	0.005% - 2% w/w
Epichlorohydrin polyamide copolymer	Shrinking inhibitor	0.005% - 2% w/w
Glycol	Humectant	20% - 45% w/w
Deionized water	Carrier	15% - 55% w/w
BYK 348	Wetting agent	0.1-0.6% w/w
Fatty acid	Softening effect enhancer	0.1-2% w/w

Table 5: A digital pretreatment wet-on-wet formulation according to the invention. The glycol is as selected herein.

Ingredient	Function	Amount
Polyurethane polymer dispersion	Ink receptive component	30% - 80% w/w
Glycol	Humectant	10% - 30% w/w
Deionized water	Carrier	5% - 50% w/w
BYK 348	Wetting agent	0.1-0.6% w/w
Fumed Silica	Anti-migration additive	0.1-4% w/w

Table 6: A Digital Pretreatment Formulation According to the Invention. The glycol and fatty acid are as selected herein.

Ingredient	**Function**	**Amount**
PDMS	Unreactive polysiloxane	0.5% - 20% w/w
RUCOFIN MISP EXTRA	Reactive polysiloxane	0.5% - 40% w/w
KBM-403 (from ShinEtsu)	Silane coupling agent	0.1-4% w/w
Ruco-print PPB (from Rudolf)	Ink receptive, anti-migration polymer	0.5% - 25 % w/w
Metal salt	Cationic charge adjuster	0.5% - 18% w/w
Ammonium chloride	Cationic charge adjuster	0.005% - 2% w/w
Epichlorohydrin polyamide copolymer	Shrinking inhibitor	0.005% - 2% w/w
Glycol	Humectant	20% - 45% w/w
Deionized water	Carrier	15% - 55% w/w
BYK 348	Wetting agent	0.1-0.6% w/w
Fatty acid	Softening effect enhancer	0.1-2% w/w

Also provided is a kit comprising one or more receptacles or containers, at least one of which comprising a formulation according to the invention, and instructions of use. In some embodiments, the further comprises an ink formulation.

CLAIMS:

1. An aqueous pretreatment formulation, dispersion or emulsion comprising at least one metal salt and a copolymer, a polymer or a mixture thereof.

2. The formulation according to claim 1, wherein the at least one metal salt is provided alone or in combination with at least one other salt.

3. The formulation according to claim 2, wherein the at least one other salt is an ammonium salt.

4. The formulation according to claim 3, wherein the ammonium salt is selected to have an anion selected from a chloride, a fluoride, a bromide, an iodide, a nitride, a sulfate, acetate, a citrate, a propionate, a borate and a phosphate

5. The formulation according to any one of claims 1 to 4, further comprising at least one carbodiimide crosslinker.

6. The formulation according to any one of the preceding claims, wherein at least one inorganic salt is selected from monovalent metal salts, divalent metal salts, trivalent metal salts and combinations thereof.

7. The formulation according to claim 6, wherein the metal is sodium, calcium, aluminum, copper, zinc, cobalt, nickel, or magnesium.

8. The formulation according to claim 1, wherein the at least one metal salt has an anion selected from a chloride, a fluoride, a bromide, an iodide, a nitride, a sulfate, acetate, a citrate, a propionate, a borate and a phosphate.

9. The formulation according to claim 1, wherein the at least one metal salt is selected from lithium chloride, lithium acetate, lithium carbonate, lithium borate, lithium nitrate, lithium phosphate, sodium chloride, sodium acetate, sodium carbonate, sodium borate, sodium nitrate, sodium phosphate, potassium acetate, potassium chloride, potassium carbonate, potassium borate, potassium phosphate, potassium nitrate, copper chloride, copper nitride, copper sulfate, copper acetate, copper citrate, copper propionate, copper borate, copper phosphate, silver chloride, silver nitride, silver sulfate, silver acetate, silver citrate, silver propionate, silver borate, silver phosphate, gold chloride, gold nitride, gold sulfate, gold acetate, gold citrate, gold propionate, gold borate, gold phosphate, magnesium chloride, magnesium acetate, magnesium carbonate, magnesium borate, magnesium nitrate, magnesium phosphate, calcium chloride, calcium acetate, calcium carbonate, calcium borate, calcium nitrate, calcium nitrate, calcium phosphate, zinc chloride, zinc acetate, zinc carbonate, zinc nitrate, zinc

phosphate, copper chloride, copper acetate, copper carbonate, copper nitrate, copper phosphate, tin chloride, tin acetate, tin carbonate, tin nitrate, tin phosphate, ferrous chloride, ferrous acetate, ferrous carbonate, ferrous nitrate, ferrous phosphate, and combinations thereof.

10. The formulation according to any one of the preceding claims, wherein the copolymer, polymer or mixture thereof is provided as a dispersion.

11. The formulation according to claim 10, wherein the dispersion is an anti-migration dispersion.

12. The formulation according to any one of the preceding claims, wherein the copolymer or polymer is a neutral polymer, an amphiphilic polymer, an anionic polymer, non-ionic or a cationic polymer.

13. The formulation according to any one of the preceding claims, wherein the copolymer or polymer has a molecular weight between 10 and 80 kDa, or between 20 and 60kDa, or between 40 and 50 kDa.

14. The formulation according to any one of the preceding claims, wherein the copolymer or polymer is selected amongst polyurethane polymers and copolymers, cellulosic materials, polymers and copolymers of polyacrylate, polymers and copolymers of diallyldialkylammonium, poly amide-epichlorohydrin copolymers, polypropylene polymers and copolymers, polyethylene copolymer and polyvinyl polymers.

15. The formulation according to any one of the preceding claims, wherein the mixture of polymers and/or copolymers comprises polyurethane polymers and copolymers, cellulosic materials, polymers and copolymers of polyacrylate, polymers and copolymers of diallyldialkylammonium, poly amide-epichlorohydrin copolymers, polypropylene polymers and copolymers, polyethylene copolymer and polyvinyl polymers.

16. The formulation according to claim 14 or 15, wherein the polymer is a polyurethane.

17. The formulation according to any one of the preceding claims, wherein the copolymer or polymer is cationic.

18. An aqueous pretreatment formulation, dispersion or emulsion consisting at least one metal salt, at least one ammonium salt, a copolymer, a polymer or polymer mixture, at least one crosslinker and epichlorohydrin polyamide copolymer.

19. A formulation according to any one of claims 1 to 18, for use in a method of printing.

20. The formulation according to claim 19, for forming a pretreatment solid film on a substrate.

21. The formulation according to claim 20, for forming an ink pattern on the solid film.

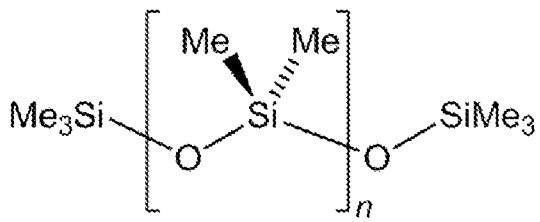
22. The formulation according to any one of the preceding claims, comprising at least one polysiloxane.

23. The formulation according to claim 1, wherein the at least one metal salt is a pH adjuster.

24. A pretreatment formulation, in the form of an aqueous dispersion or emulsion, comprising at least one unreactive polysiloxane, at least one reactive polysiloxane, at least one humectant, at least one wetting agent, at least one pH adjuster, at least one rheology modifier, and at least one additive, wherein the formulation is not an ink formulation.

25. A pretreatment formulation, in the form of an aqueous dispersion or emulsion, comprising at least one unreactive polysiloxane, at least one reactive polysiloxane, at least one humectant, at least one wetting agent, at least one pH adjuster, at least one rheology modifier, and at least one additive, wherein the formulation is free of a dye, a pigment, a coloring agent, acrylates, acids and bases.

26. The formulation according to claim 24 or 25, wherein the at least one unreactive polysiloxane is polydimethylsiloxane (PDMS) or a homologue thereof, optionally having the structure:



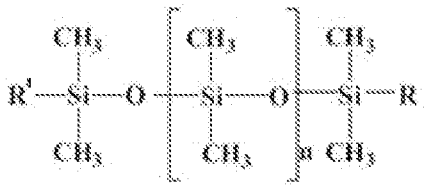
wherein n is between 10 and 20.

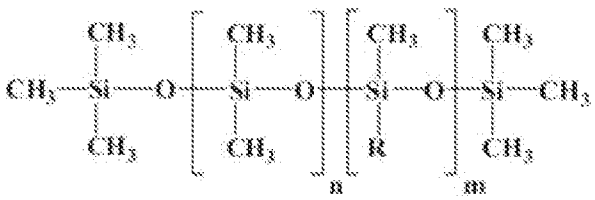
27. The formulation according to claim 24 or 25, wherein the at least one reactive polysiloxane having a reactive functional group capable of crosslinking.

28. The formulation according to claim 27, wherein the reactive functional groups is selected from hydroxyl groups, amino groups, substituted amino groups, epoxide

groups, amide groups, carboxylic acid groups, activated esters and amides, vinyl groups, alkenyl groups and acyl groups, each of which being directly bonded to a silicon atom or indirectly via a linker moiety.

29. The formulation according to claim 28, wherein the at least one reactive polysiloxane having a structure:





wherein each of R and R', independently from the other, is selected from hydroxyl, ether, amine, amide, carboxylic acid, activated ester, activated amide, epoxide, vinyl group, alkenyl and acyl, each being directly bonded to the Si atom or indirectly via a linking moiety; each of n and m, independently, is an integer between 1 and 60.

30. The formulation according to any one of the preceding claims, wherein the at least one reactive polysiloxane is selected to undergo self-crosslinking or crosslinking with at least one another reactive polysiloxane.

31. The formulation according to any one of the preceding claims, wherein the at least one reactive polysiloxane is selected to undergo crosslinking with a substrate material.

32. The formulation according to any one of the preceding claims, configured and operable for low-temperature curing.

33. The formulation according to claim 24 or 25, comprising at least one latent acid or latent base enabling acid or base catalyzed cross-linking.

34. The formulation according to claim 33, wherein the at least one latent acid is selected amongst esters, sulfonic acid esters, fluorinated sulfonic acid esters, phosphonic acid esters and nitriles.

35. The formulation according to claim 33, wherein the at least one latent base is selected amongst metal oxides, optionally selected from oxides of alkali or alkaline earth-metals.

36. The formulation according to claim 24 or 25, wherein crosslinking of the at least one reactive polysiloxane is achievable by exposure to heat, IR or UV radiation.

37. The formulation according to claim 36, wherein crosslinking is achievable thermally by exposure to a temperature ranging between room temperature (20-35°C) and 110°C.

38. The formulation according to claim 24 or 25, wherein the amount of the at least one unreactive polysiloxane is between 0.5 and 20 wt%.

39. The formulation according to claim 24 or 25, wherein the amount of the at least one reactive polysiloxane is between 0.5 and 40 wt%.

40. The formulation according to claim 24 or 25, wherein the total amount of the at least one unreactive polysiloxane and the at least one reactive polysiloxane is between 1 and 60 wt%, relative to the total weight of the formulation.

41. The formulation according to claim 24 or 25, wherein the at least one humectant is a glycol, optionally selected from ethylene glycol (EG), glycerin, propylene glycol (PG), dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, ethylene glycol hexyl ether, ethylene glycol propyl ether, diethylene glycol phenyl ether, ethylene glycol phenyl ether, dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, propylene glycol n-butyl ether and propylene glycol n-propyl ether.

42. The formulation according to claim 24 or 25, wherein the at least one wetting agent is BYK 348 or Dynol 360.

43. The formulation according to claim 24 or 25, wherein the at least one pH adjuster is an amine or a fatty acid.

44. The formulation according to claim 43, wherein the fatty acid is selected from lactic acid, butyric acid, lauric acid, myristic acid, palmitic acid, stearic acid, archidic acid, linolenic acid, linoleic acid, arachidonic acid and oleic acid.

45. The formulation according to claim 24 or 25, wherein the at least one additive is selected from preservatives, crosslinking agents, viscosity modifiers, film forming agents, pH adjuster agents, ink receptive materials, bleeding inhibitors, migration inhibitors, color enhancers and adhesion promoting agents.

46. The formulation according to any one of the preceding claims, having a viscosity allowing ink jetting.

47. The formulation according to claim 46, wherein the viscosity is between 4 and 20 mPa·s, at a jetting temperature between 25 and 35°C.

48. The formulation according to any one of the preceding claims, having a surface tension ranging between 20 and 35 dyne/cm^2.

49. The formulation according to any of claims 24 to 45, configured for application by wiping, immersing, padding, spraying and by an inkjet printer.

50. The formulation according to any one of the preceding claims, for application onto a surface of a substrate, the substrate being selected from absorptive or non-absorptive materials, natural or synthetic materials, paper materials and polymeric materials.

51. The formulation according to claim 50, wherein the substrate is a fabric or a textile.

52. A pattern formed of a formulation according to any one of claims 1 to 51.

53. The pattern according to claim 52, formed on a surface of a substrate, the substrate being selected from absorptive or non-absorptive materials, natural or synthetic materials, paper materials and polymeric materials.

54. The pattern according to claim 53, wherein the substrate is a fabric or a textile.

55. The pattern according to claim 52 to 53, in a form configured to receive an ink formulation.

56. The pattern according to claim 55, wherein the form is a wet or dry form.

57. The pattern according to claim 55, in a form of a wet uncross-linked or partially cross-linked form.

58. The pattern according to claim 55, being a cross-linked dry pattern.

59. A method of forming an ink pattern on a surface, the method comprising coating a surface region of a substrate with a pretreatment formulation according to any one of claims 1 to 51, and patterning an ink formulation on at least a portion of the surface region coated with the pretreatment formulation.

60. The method according to claim 59, wherein the ink formulation is patterned on a wet coat of the pretreatment formulation.

61. The method according to claim 59, wherein the ink formulation is patterned on a dry coat of the pretreatment formulation.

62. A method of forming an ink pattern on a surface, the method comprising obtaining a substrate having at least part of its surface region coated with a pretreatment formulation according to any one of claims 1 to 51, and patterning an ink formulation on at least a portion of the surface region coated with the pretreatment formulation.

63. The method according to any one of claims 59 to 62, wherein coating with the pretreatment formulation is patterning of a surface region of the substrate.

64. The method according to any one of claims 59 to 63, wherein the ink formulation is patterned by a means selected from digital printing, transfer printing and screen printing.

65. A method for forming a pattern on a surface region by digital printing, the method comprises patterning a pretreated surface region of a substrate with an ink formulation, wherein the pretreated surface region is patterned with a formulation according to any one of claims 1 to 51.

66. The method according to claim 65, the method comprising obtaining a pretreatment formulation according to any one of claims 1 to 51.

67. The method according to claim 65, wherein the pretreatment formulation is applied onto the surface region by inkjet printing.

68. The method according to any one of claims 52 to 67, the method being carried out using an in-line printing system.

69. A kit comprising one or more receptacles or containers, at least one of which comprising a formulation according to any one of claims 1 to 51, and instructions of use.

70. The kit according to claim 69, further comprising an ink formulation.