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(54) **Method for printing on non-white absorbent materials**

(57) Method for printing on non-white absorbent materials, comprising the following steps:
(A) pre-treatment with a colourless aqueous formulation, comprising
(a) at least one water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:
M
is a metal ion with the charge +n, n being selected from 1 to 3,
X
is an anion with the charge -m, -m being selected from -1 to -3,
(b) a copolymer made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,
(c) optionally, at least one surfactant,

(B) printing a pattern or an image with a pigmented ink.

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Description

[0001] The present invention relates to a method for printing on non-white absorbent materials, comprising the following steps:

(A) pre-treatment with a colourless aqueous formulation, comprising

(a) at least one water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:

M is a metal ion with the charge +n, n being selected from 1 to 3,
X is an anion with the charge -m, -m being selected from -1 to -3,

(b) a copolymer made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,

(c) optionally, at least one surfactant,

(A) printing a pattern or an image with a pigmented ink.

[0002] Furthermore, the present invention relates to coloured absorbent materials that can be obtained by the inventive method. Furthermore, the present invention relates to a pre-treatment agent, which is particularly useful for performing the inventive method, and the present invention furthermore relates to a process for making the inventive pre-treatment agents.

[0003] Printing on materials including absorbent materials is a well-known method especially in the field of colouring textiles and paper including papier-mâché. It is particularly useful in many instances to perform said printing according to the ink-jet method. However, printing on non-white substrates, especially printing on dark substrates such as black, navy or dark green or even on intense coloured substrates such as yellow or red textiles leads to insufficient results.

[0004] In US 7,134,749 it has been suggested to apply a white ink layer including white pigments to a textile piece, to optionally cure said white ink layer and to then digitally print a coloured image on said white ink layer. The method according to US 7,134,749 includes several steps of ink-jet printing and can thus be rather time-consuming. Furthermore, due to the fact that in case the coloured image will be printed with a pigment-based ink, several layers of pigments will be applied to the textile which can affect the handle of the textile in an unpleasant way.

[0005] It was therefore an objective of the present invention to provide a method for printing on non-white absorbent materials which avoids the disadvantages of the prior art methods and which allows to create brilliant patterns or images without disadvantageously affecting the handle of the material. It was furthermore an objective to provide coloured materials with a non-white ground colour and a pleasant handle which are easily manufactured. Furthermore, it was an objective of the present invention to provide agents which are particularly suitable to perform a process for printing on non-white absorbent materials which avoids the disadvantages of the prior art methods and which allows to create brilliant patterns or images without disadvantageously affecting the handle of the material.

[0006] Accordingly, the method defined above was found.

[0007] The inventive method starts with a non-white absorbent material. Non-white in the context of the present invention refers to any colour which is not white but which may include black and grey. Included are colours like red, yellow, orange, pale blue, pale green and pink. Preferred are dark green, dark blue such as navy blue, magenta, burgundy, dark brown, grey, and black.

[0008] Absorbent materials in the context of the present invention refer to any material which can take up liquids, especially aqueous liquids such as inks. Examples may include sponges. Preferred are fibrous materials such as paper, papier-mâché, board, leather, artificial leather, and Alcantara. Particularly preferred are textiles.

[0009] Textiles for the purposes of the present invention are textile fibers, textile intermediate and end products and finished articles manufactured therefrom which, as well as textiles for the apparel industry, also comprise for example carpets and other home textiles and also textile constructions for industrial purposes. These include unshaped constructions such as for example staples, linear constructions such as twine, filaments, yarns, lines, strings, laces, braids, cordage and also three-dimensional constructions such as for example felts, wovens, nonwovens and waddings. Two-dimensional textiles such as knit wear and fabrics are preferred. Textiles for the purposes of the present invention can be of natural origin, examples being cotton, wool or flax, or synthetic, examples being polyamide, polyester, modified polyester, polyester blend fabrics, polyamide blend fabrics, polyacrylonitrile, triacetate, acetate, polycarbonate, polypropylene, polyvinyl chloride, polyester microfibres and glass fibre fabrics. Textiles composed of cotton are particularly

preferred.

[0010] Textiles in context of the present invention can be manufactured. For example, textiles in the context of the present inventions can be manufactured to be clothes, in particular t-shirts, pyjamas, or trousers.

[0011] Textile in the context of the present invention can be non-finished or preferably finished.

[0012] The inventive method comprises two steps. Step (A) is a pre-treatment step, and step (B) includes printing a pattern or an image with a pigmented ink.

[0013] Pre-treatment step (A) is performed before printing step (B).

[0014] Pre-treatment step (A) is performed by applying a colourless aqueous formulation to the non-white absorbent material. Said application can be performed on all sides of the non-white absorbent material or - preferably in case the non-white absorbent material is two-dimensional - on only one side, the other side being left non-pre-treated. Said pre-treatment can be performed by the use of a foulard (pad-mangle), by padding, drizzling, over-pouring or printing, especially by ink-jet printing, or preferably by single or multiple spraying, or roll-coating.

[0015] In the context of the present invention, the term "colourless aqueous formation" refers to aqueous formulations that contain neither dyestuffs nor pigments. The term "colourless aqueous formulations" refers to formulations that contain at least 20% by weight of water, preferably at least 50% by weight water, with the percentages referring to the continuous phase.

[0016] Colourless aqueous formulations can contain one or more organic solvents. Suitable organic solvents are, e.g., alcohols such as ethanol, Isopropanol or methanol, glycerol, ethylene glycol or diethylene glycol. Further suitable organic solvents are ethers such as 1,4-dioxane, 1,2-dimethoxy ethane, alkoxylated and particularly ethoxylated n-C_1-C_4-alkylalcohols.

[0017] The colourless aqueous formulations employed in step (A) comprises

(a) at least one water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:
M is a metal ion with the charge +n, n being selected from 1 to 3, for example +1 or +2, preferably +2,
X is an anion with the charge -m, -m being selected from -1 to -3, preferably as -1 or -2, particularly preferably -1.

[0018] Water soluble salts in the context of the present invention are salts which exhibit a solubility in distilled water at 25°C of at least 10 g/l, preferably at least 25 g/l.

[0019] Preferred examples for metal ions M are alkali metal ions such as Na^+, K^+, Rb^+, Cs^+ and particularly K^+ and Na^+, furthermore Zn^{2+} and alkaline earth metal ions such as Mg^{2+}, Ca^{2+}, preferably Ca^{2+}.M can refer to hydrate complex ions such as $[Mg(H_2O)_6]^{2+}$.

[0020] Preferred anions are inorganic anions such as sulphate, nitrate (NO_3^-), and halides such as F-, Cl^-, Br^- or I^-, preferred are Cl^-, Br^- and NO_3-.

[0021] CaF_2, $SrSO_4$ and $BaSO_4$ are not considered water-soluble salts.

[0022] Particularly preferred water-soluble salts are $CaCl_2$ and $Ca(NO_3)_2$.

[0023] The colourless aqueous formulation employed in step (A) further comprises (b) a copolymer made from at least two comonomers, briefly also referred to as copolymer (b), the comonomers being selected from
ethylenically unsaturated carboxylic acids, preferred are monoethylenically unsaturated C_3-C_{10}-monocarboxylic acids such as crotonic acid and particularly acrylic acid and methacrylic acid, and C_4-C_{10}-dicarboxylic acids and their anhydrides such as maleic acid, fumaric acid, itaconic anhydride, itaconic acid, citraconic anhydride, citraconic acid, metaconic acid or methylenemalonic anhydride, preferably itaconic anhydride and particularly preferably maleic anhydride;
C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl being substituted or non-substituted, preferred are C_1-C_{10}-alkyl esters of (meth)acrylic acid, such as methyl acrylate, methyl methacrylate, ethyl acrylate, methyl ethacrylate, n-propyl acrylate, n-propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylmethacrylate, 2-n-propylheptyl acrylate, 2-n-propylheptyl methacrylate, 2-isopropylheptyl acrylate, 2-isopropylheptyl methacrylate, n-decyl acrylate, n-decyl methacrylate;
examples for substituted C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids are hydroxyl-C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, in particular ω-hydroxy-C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids such as 2-hydroxyethyl (meth)acrylate and 3-hydroxypropyl (meth)acrylate,
vinyl aromatic compounds such as α-methyl styrene, para-methyl styrene and particularly styrene;
amides of ethylenically unsaturated carboxylic acids, especially acrylamide and methacrylamide;
(meth)acrylonitrile,
hydroxymethylamides of ethylenically unsaturated carboxylic acids, especially hydroxymethal acrylamide and hydroxymethyl methacrylamide,
and epoxy esters of ethylenically unsaturated carboxylic acids, especially glycidyl ester of (meth)acrylic acid.

[0024] In one embodiment of the present invention, copolymer (b) is employed in the form of an aqueous dispersion, especially in the form of an aqueous emulsion.

[0025] In one embodiment of the present invention, copolymer (b) has a molecular weight M_n in the range from 5,000

to 1,000,000 g/mol.

[0026] In one embodiment of the present invention, copolymer (b) is employed in the form of spherical particles with an average diameter in the range from 10 nm to 10 μm, preferably from 20 nm to 1 μm, determined by coulter counter.

[0027] In one embodiment of the present invention, copolymer (b) has a glass transition temperature from -40 to +40°C, preferably from -30 to -10°C, calculated according to the Fox equation.

[0028] In one embodiment of the present invention, the colourless aqueous formulation employed in step (A) can further contain at least one surfactant (c). Said surfactant (c) can be ionic, especially anionic, or non-ionic.

[0029] Suitable anionic surfactants are alkali metal or ammonium salts of fatty acids, of sulphates of C_{10}-C_{30}-alkanols, of sulphuric monoesters with ethoxylated C_{12}-C_{20}-alkanols (EO units: 4 to 30 per mole) or with ethoxylated alkylphenols (EO units: 4 to 50 per mole), of C_{10}-C_{30}-alkylsulfonic acids or of C_{10}-C_{30}-alkylarylsulfonic acids.

[0030] Suitable non-ionic surfactants are C_2-C_4-alkoxylated, especially propoxylated or ethoxylated fatty or oxo alcohols, i.e. PO or EO units: 3 to 100, C_{12}-C_{40}-alkyl.

[0031] In one embodiment of the present invention, surfactant (c) has been used for manufacturing copolymer (b).

[0032] In a special embodiment of the present invention, the colourless aqueous formulations employed in step (A) comprises

2 to 20 % by weight, preferably 2.5 to 15 % by weight of water-soluble salt (a),

5 to 25 % by weight, preferably 10 to 15 % by weight of copolymer (b),

optionally, 0.1 to 2 % by weight, preferably up to 0.5 % by weight of surfactant (c).

[0033] Percentages refer to the complete colourless aqueous formulations employed in step (A).

[0034] In one embodiment of the present invention, the colourless aqueous formulations employed in step (A) has a solids content in the range from 8 to 30% by weight. A solids content in the range from 10 to 18% is preferred.

[0035] In one embodiment of the present invention, the colourless aqueous formulations employed in step (A) has a pH value in the range from 4.0 to 6.5, preferably in the range from 5.0 to 6.0.

[0036] In one embodiment of the present invention, the colourless aqueous formulation employed in step (A) can further comprise at least one cross-linking agent (d). Suitable cross-linking agents can be selected from melamine, melamine derivatives, mixtures of melamine or melamine derivatives with polyurethanes and especially with polyurethanes bearing hydrophobic and hydrophilic units.

[0037] Melamine derivatives are particularly selected from reaction products of melamine with one or more equivalent of aldehyde, especially formaldehyde, and optionally at least one equivalent of alcohol, suitable alcohols being selected from C_1-C_4-alkanols, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol and oligomers of ethylene glycol or propylene glycol with a molecular weight M_n in the range from 200 to 2,000 g/mole, glycerol, diglycerol and C_1-C_4-alkyl ethers of ethylene glycoldiethylene glycol, triethylene glycol, and oligomers of ethylene glycol or propylene glycol with a molecular weight M_n in the range from 200 to 2,000 g/mole.

[0038] Polyurethanes are known in the art. They can be manufactured by converting one or more diisocyanate with one or more diol. Polyurethanes in the context of the present invention can bear one or more urea or allophanate groups per molecule. Preferred polyurethanes bear one or more carboxylic acid groups or one or more sulfuric acid groups per mole. Such groups can be introduced by, e.g. converting dimethylol propionic acid or tartaric acid as diol component.

[0039] Particularly preferred polyurethanes bear hydrophobic and hydrophilic units. Hydrophilic units are those urethane units which bear at least one carboxylic acid group, free hydroxyl group, free NH_2 group or polyalkylenoxide groups. Hydrophobic units are, e.g., those urethane units with neither carboxylic acid groups nor free hydroxyl groups nor NH_2 groups nor polyalkylenoxide groups.

[0040] Examples for particularly preferred polyurethanes have been disclosed in US 7,074,850.

[0041] In one embodiment of the present invention, the colourless aqueous formulation employed in step (A) can contain in the range from 0.1 to 4, preferably 1 to 2.5 percent by weight of cross-linking agent (d).

[0042] In one embodiment of the present invention, the pre-treatment agent employed in step (A) can further comprise one or more auxiliaries (e). Examples of such auxiliaries (e) include degassers/defoamers such as for example ethoxylated acetylenediols, which typically comprise from 20 to 40 mol of ethylene oxide per mole of acetylenediol and may also have a dispersing effect. Substances also useful as defoamers are tri-alkyl phosphates such as tri-isobutyl phosphate.

[0043] In one embodiment of the present invention, 1 to 80 g/m^2 non-white absorbent material, preferably 5 to 50 g/m^2 of (a), (b), optionally (c) and optionally (d) are deposited in step (A). The amount of grams then refers to solids.

[0044] In step (B), a pattern or an image will be printed on the pre-treated material by using a pigmented ink. Preferably, step (B) will be performed according to the ink-jet method.

[0045] Pigmented inks according to the present invention are inks that contain at least one pigment. Pigments for the purposes of the present invention are virtually insoluble, finely dispersed, organic or inorganic colorants as per the definition in German standard specification DIN 55944.

[0046] Representative examples of pigments are

monoazo pigments such as C.I. Pigment Brown 25; C.I. Pigment Orange 5, 13, 36 and 67; C.I. Pigment Red 1, 2, 3, 5, 8, 9, 12, 17, 22, 23, 31, 48:1, 48:2, 48:3, 48:4, 49, 49:1, 52:1, 52:2, 53, 53:1, 53:3, 57:1, 63, 112, 146, 170, 184, 210,

245 and 251; C.I. Pigment Yellow 1, 3, 73, 74, 65, 97, 151 and 183;
disazo pigments such as C.I. Pigment Orange 16, 34 and 44; C.I. Pigment Red 144, 166, 214 and 242; C.I. Pigment Yellow 12, 13, 14, 16, 17, 81, 83, 106, 113, 126, 127, 155, 174, 176 and 188;
anthanthrone pigments such as C.I. Pigment Red 168 (C.I. Vat Orange 3);
anthraquinone pigments such asC.I. Pigment Yellow 147 and 177; C.I. Pigment Violet 31;
anthraquinone pigments such as C.I. Pigment Yellow 147 and 177; C.I. Pigment Violet 31;
anthrapyrimidine pigments such as C.I. Pigment Yellow 108 (C.I. Vat Yellow 20);
quinacridone pigments such as C.I. Pigment Red 122, 202 and 206; C.I. Pigment Violet 19;
quinophthalone pigments such as C.I. Pigment Yellow 138;
dioxazine pigments such as C.I. Pigment Violet 23 and 37;
flavanthrone pigments such as C.I. Pigment Yellow 24 (C.I. Vat Yellow 1);
indanthrone pigments such as C.I. Pigment Blue 60 (C.I. Vat Blue 4) and 64 (C.I. Vat Blue 6);
isoindoline pigments such as C.I. Pigment Orange 69; C.I. Pigment Red 260; C.I. Pigment Yellow 139 and 185;
isoindolinone pigments such as C.I. Pigment Orange 61; C.I. Pigment Red 257 and 260; C.I. Pigment Yellow 109, 110, 173 and 185;
isoviolanthrone pigments such as C.I. Pigment Violet 31 (C.I. Vat Violet 1);
metal complex pigments such as C.I. Pigment Yellow 117, 150 and 153; C.I. Pigment Green 8;
perinone pigments such as C.I. Pigment Orange 43 (C.I. Vat Orange 7); C.I. Pigment Red 194 (C.I. Vat Red 15);
perylene pigments such as C.I. Pigment Black 31 and 32; C.I. Pigment Red 123, 149, 178, 179 (C.I. Vat Red 23), 190 (C.I. Vat Red 29) and 224; C.I. Pigment Violet 29;
phthalocyanine pigments such as C.I. Pigment Blue 15, 15:1, 15:2, 15:3, 15:4, 15:6 and 16; C.I. Pigment Green 7 and 36;
pyranthrone pigments such as C.I. Pigment Orange 51; C.I. Pigment Red 216 (C.I. Vat Orange 4);
thioindigo pigments such as C.I. Pigment Red 88 and 181 (C.I. Vat Red 1); C.I. Pigment Violet 38 (C.I. Vat Violet 3);
triarylcarbonium pigments such as C.I. Pigment Blue 1, 61 and 62; C.I. Pigment Green 1; C.I. Pigment Red 81, 81:1 and 169; C.I. Pigment Violet 1, 2, 3 and 27; C.I. Pigment Black 1 (aniline black);
C.I. Pigment Yellow 101 (aldazine yellow);
C.I. Pigment Brown 22.

[0047] Examples of inorganic pigments are:

white pigments: titanium dioxide (C.I. Pigment White 6), zinc white, pigment grade zinc oxide; zinc sulfide, lithopone; lead white, barium sulphate;

black pigments: iron oxide black (C.I. Pigment Black 11), iron manganese black, spinell black (C.I. Pigment Black 27); carbon black (C.I. Pigment Black 7);

chromatic pigments: chromium oxide, chromium oxide hydrate green; chrome green (C.I. Pigment Green 48); cobalt green (C.I. Pigment Green 50); ultramarine green; cobalt blue (C.I. Pigment Blue 28 and 36); ultramarine blue; iron blue (C.I. Pigment Blue 27); manganese blue; ultramarine violet; cobalt violet, manganese violet; iron oxide red (C.I. Pigment Red 101); cadmium sulfoselenide (C.I. Pigment Red 108); molybdate red (C.I. Pigment Red 104); ultramarine red;

iron oxide brown, mixed brown, spinell and corundum phases (C.I. Pigment Brown 24, 29 and 31), chrome orange;

iron oxide yellow (C.I. Pigment Yellow 42); nickel titanium yellow (C.I. Pigment Yellow 53; C.I. Pigment Yellow 157 and 164); chrome titanium yellow; cadmium sulfide and cadmium zinc sulfide (C.I. Pigment Yellow 37 and 35); chrome yellow (C.I. Pigment Yellow 34), zinc yellow, alkaline earth metal chromates; Naples yellow; bismuth vanadate (C.I. Pigment Yellow 184);

interference pigments: metallic effect pigments based on coated metal platelets; pearl luster pigments based on mica platelets coated with metal oxide; liquid crystal pigments.

[0048] It is preferred that at least one pigment used in the ink(s) in step (B) has a colour that differs from the non-white absorbent material to be treated.

[0049] Non-white pigments are preferred. Preferred pigments in this context are monoazo pigments (especially laked BONS pigments, naphthol AS pigments), disazo pigments (especially diaryl yellow pigments, bisacetoacetanilide pigments, disazopyrazolone pigments), quinacridone pigments, quinophthalone pigments, perinone pigments, phthalocyanine pigments, triarylcarbonium pigments (alkali blue pigments, laked rhodamines, dye salts with complex anions), isoindoline pigments and carbon blacks.

[0050] Specific examples of particularly preferred pigments are: C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3 and 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 5, 38 and 43 and C.I. Pigment Green 7.

[0051] The pigments recited above are advantageously useful for preparing ink-jet ink sets based on the recording fluids of the present invention. The level of the particular pigments in the individual recording fluids or inks must be adapted to the particular requirements (trichromatic colouration, for example), i.e., cyan, magenta, yellow and black pigments have to be coordinated with each other with regard to content.

[0052] The following pigment combinations are particularly useful for trichromatic requirements:

C.I. Pigment Yellow 138, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3 and C.I. Pigment Black 7;

C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4 and C.I. Pigment Black 7;

C.I. Pigment Yellow 138, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3, C.I. Pigment Black 7, C.I. Pigment Orange 43 and C.I. Pigment Green 7;

C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 5 and C.I. Pigment Green 7;

C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 38 and C.I. Pigment Green 7;

C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 43 and C.I. Pigment Green 7.

[0053] Inks used in step (B) are preferably aqueous ink-jet inks.

[0054] Inks used in step (B) may contain additional ingredients. Examples of such additional ingredients include erythritol, pentaerythritol, pentitols such as arabitol, adonitol and xylitol and hexitols such as sorbitol, mannitol and dulcitol. Further examples are polyethylene glycols having an M_w in the range from more than 200 g/mol to about 10,000 g/mol and preferably up to 800 g/mol. Further examples are preservatives such as for example 1,2-benzisothiazolin-3-one and its alkali metal salts, degassers or defoamers such as for example ethoxylated acetylenediols, which typically comprise from 20 to 40 mol of ethylene oxide per mole of acetylenediol and may also have a dispersing effect, viscosity regulators, flow agents, wetting agents (examples being wetting surfactants based on ethoxylated or propoxylated fatty or oxo alcohols, propylene oxide-ethylene oxide block copolymers, ethoxylates of oleic acid or alkylphenols, alkylphenol ether sulfates, alkylpolyglycosides, alkylphosphonates, alkylphenylphosphonates, alkyl phosphates, alkylphenyl phosphates, or preferably polyethersiloxane copolymers, especially alkoxylated 2-(3-hydroxypropyl)heptamethyltrisiloxanes, which generally have a block of 7 to 20 and preferably 7 to 12 ethylene oxide units and a block of 2 to 20 and preferably 2 to 10 propylene oxide units and may be present in the colorant preparations in amounts from 0.05% to 1% by weight), anti-settlers, luster improvers, lubricants, adhesion promoters, anti-skinning agents, delusterants, emulsifiers, stabilizers, hydrophobicizers, light control additives, antistats, bases such as for example K_2CO_3, or acids, specifically carboxylic acids such as for example lactic acid or citric acid to adjust the pH value. When these agents are part of ink-jet inks used in step (B), their maximum total amount will generally be 2% by weight and especially 1% by weight, based on the weight of the ink-jet inks used in step (B).

[0055] Inks used in step (B) are preferably aqueous inks but can contain one or more organic solvents such as glycerol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, polyethylene glycol with an average molecular weight M_n in the range from 150 to 1,000 g/mol, 1,2-pentanediol, 1,2-hexanediol and polytetramethylene ether (poly-THF) with an average molecular weight M_n in the range from 200 to 2,000 g/mol. The majority of the continuous phase of aqueous ink-jet inks is preferably water.

[0056] Said pattern or image can be mono-coloured or multi-coloured. Preferably, said pattern or image is not exclusively white but includes at least one more colour.

[0057] After having performed the printing step, the pattern or image printed can be cured. Curing can be performed by thermal curing or by radiation curing. Thermal curing can be performed under conventional conditions, e.g., temperatures ranging from 30 to 120°C for a period from 1 minute to 24 hours, preferably up to 30 min, more preferably up to 5 min. For radiation curing, actinic radiation having a wavelength range from 200 nm to 450 nm is useful for example. Actinic radiation having an energy in the range from 70 mJ/cm^2 to 2000 mJ/cm^2 is useful for example. Actinic radiation may advantageously be applied continuously or in the form of flashes for example. Useful radiation also includes for example IR radiation in a wave region above 800 nm. Radiation curing can be improved if a curing agent or a photoinitiator is added to the ink.

[0058] In a special embodiment, radiation curing is supported by having an infrared absorbent added to the ink-jet ink. Particularly preferred infrared absorbents are substituted phthalocyanines and carbon nanoparticles konwn per se.

[0059] In a special embodiment of the present invention, a drying step (C) is performed between step (A) and step (B). Said drying step (C) is preferably a thermal drying step. Drying step (C) can be, e.g., carried out by drying at ambient temperature for a period of 15 minutes up to 24 hours. In another version of step (C), drying can be carried out at elevated temperature such as 35°C to 180°C for a period of 10 seconds up to 1 hour, preferably at a temperature in the range from 50 to 150°C for a period of 20 seconds up to 15 minutes.

[0060] In a preferred embodiment of the present invention, drying step (C) is performed in way that the pre-treated non-white absorbent material is not dried completely but a residual humidity is left, e.g., a residual humidity of 0.1 to 10% by weight, based on the non-pre-treated non-white absorbent material.

[0061] Another aspect of the present invention are coloured absorbent materials obtainable by the inventive method, which has been described above. Inventive coloured absorbent materials exhibit brilliant colours and a very pleasant handle. Inventive coloured absorbent materials and especially inventive coloured textiles furthermore exhibit excellent properties such as rubfastness, and wet rubfastness.

[0062] Another aspect of the present invention is a pre-treatment agent, comprising

(a) 2 to 20 % by weight of water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:

M is a metal ion with the charge +n, n being selected from 1 to 3 such as +1 or +2, preferably +2,
X is an anion with the charge -m, -m being selected from -1 to -3, preferably -1 or -2, particularly preferably-1

(b) 1 to 15 % by weight copolymer, made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,

(c) optionally, 0.1 to 2% by weight surfactant.

[0063] The inventive pre-treatment agent is usually in the form of a colourless aqueous formulation.

[0064] Water soluble salts in the context of the present invention are salts which exhibit a solubility in distilled water at 25°C of at least 10 g/l, preferably at least 25 g/l.

Preferred examples for metal ions M are alkali metal ions such as Na^+, K^+, Rb^+, Cs^+ and particularly K^+ and Na^+, furthermore Zn^{2+} and alkaline earth metal ions such as Mg^{2+}, Ca^{2+}, preferably Ca^{2+}. M can refer to a complex ions such as $[Mg(H_2O)_6]^{2+}$.

[0065] Preferred anions are inorganic anions such as sulphate, nitrate (NO_3^-), and halides such as F-, Cl^-, Br^- or I^-, preferred are Cl^-, Br^- and NO_3-.

[0066] CaF_2, $SrSO_4$ and $BaSO_4$ are not considered water-soluble salts.

[0067] Particularly preferred water-soluble salts are $CaCl_2$ and $Ca(NO_3)_2$.

[0068] The inventive pre-treatment agent further comprises

(b) a copolymer made from at least comonomers, briefly also referred to as copolymer (b), the comonomers being selected from

ethylenically unsaturated carboxylic acids, preferred are monoethylenically unsaturated C_3-C_{10}-monocarboxylic acids such as crotonic acid and particularly acrylic acid and methacrylic acid, and C_4-C_{10}-dicarboxylic acids and their anhydrides such as maleic acid, fumaric acid, itaconic anhydride, itaconic acid, citraconic anhydride, citraconic acid, metaconic acid or methylenemalonic anhydride, preferably itaconic anhydride and particularly preferably maleic anhydride;

C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl being substituted or non-substituted, preferred are C_1-C_{10}-alkyl esters of (meth)acrylic acid, such as methyl acrylate, methyl methacrylate, ethyl acrylate, methyl ethacrylate, n-propyl acrylate, n-propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylmethacrylate, 2-n-propylheptyl acrylate, 2-n-propylheptyl methacrylate, 2-isopropylheptyl acrylate, 2-isopropylheptyl methacrylate, n-decyl acrylate, n-decyl methacrylate;

examples for substituted C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids are hydroxyl-C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, in particular ω-hydroxy-C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids such as 2-hydroxyethyl (meth)acrylate and 3-hydroxypropyl (meth)acrylate,

vinyl aromatic compounds such as α-methyl styrene, para-methyl styrene and particularly styrene;

amides of ethylenically unsaturated carboxylic acids, especially acrylamide and methacrylamide;

(meth)acrylonitrile,

hydroxymethylamides of ethylenically unsaturated carboxylic acids, especially hydroxymethal acrylamide and hy-

droxymethyl methacrylamide,
and epoxy esters of ethylenically unsaturated carboxylic acids, especially glycidyl ester of (meth)acrylic acid.

[0069] In one embodiment of the present invention, copolymer (b) is comprised in the form of an aqueous dispersion, especially in the form of an aqueous emulsion.

[0070] In one embodiment of the present invention, copolymer (b) has a molecular weight M_n in the range from 5,000 to 1,000,000 g/mol.

[0071] In one embodiment of the present invention, copolymer (b) is the form of spherical particles with an average diameter in the range from 10 nm to 10 μm, preferably from 20 nm to 1 μm, determined by coulter counter.

[0072] In one embodiment of the present invention, copolymer (b) has a glass transition temperature in the range from -40 to +40°C, preferably from -30 to -10°C, calculated according to the Fox equation.

[0073] In one embodiment of the present invention, the inventive pre-treatment agent can further contain at least one surfactant (c). Said surfactant (c) can be ionic, especially anionic, or non-ionic.

[0074] Suitable anionic surfactants are alkali metal or ammonium salts of fatty acids, of sulphates of C_{10}-C_{30}-alkanols, of sulphuric monoesters with ethoxylated C_{12}-C_{20}-alkanols (EO units: 4 to 30 per mole) or with ethoxylated alkylphenols (EO units: 4 to 50 per mole), of C_{10}-C_{30}-alkylsulfonic acids or of C_{10}-C_{30}-alkylarylsulfonic acids.

[0075] Suitable non-ionic surfactants are C_2-C_4-alkoxylated, especially propoxylated or ethoxylated fatty or oxo alcohols, i.e. PO or EO units: 3 to 100, C_{12}-C_{40}-alkyl.

[0076] In a special embodiment of the present invention, the inventive pre-treatment agents comprise
2 to 20 % by weight, preferably 2.5 to 15 % by weight of water-soluble salt (a),
5 to 25 % by weight, preferably 10 to 15 % by weight of copolymer (b),
optionally, 0.1 to 2 % by weight, preferably up to 0.5 % by weight of surfactant (c).

[0077] Percentages refer to the complete inventive pre-treatment agent.

[0078] In one embodiment of the present invention, the colourless aqueous formulations employed in step (A) has a solids content in the range from 8 to 30% by weight. A solids content in the range from 10 to 18% is preferred.

[0079] In one embodiment of the present invention, the colourless aqueous formulations employed in step (A) has a pH value in the range from 4.0 to 6.5, preferably in the range from 5.0 to 6.0.

[0080] In one embodiment of the present invention, the inventive pre-treatment agents further comprise at least one cross-linking agent (d). Suitable cross-linking agents can be selected from melamine, melamine derivatives, mixtures of melamine or melamine derivatives with polyurethanes and especially with polyurethanes bearing hydrophobic and hydrophilic units. Examples of suitable cross-linking agents have been described above.

[0081] In one embodiment of the present invention, the inventive pre-treatment agents contain in the range from 0.1 to 4, preferably 1 to 2.5 percent by weight of cross-linking agent (d).

[0082] In one embodiment of the present invention, the pre-treatment agent employed in step (A) can further comprise one or more auxiliaries (e). Examples of such auxiliaries (e) include degassers/defoamers such as for example ethoxylated acetylenediols, which typically comprise from 20 to 40 mol of ethylene oxide per mole of acetylenediol and may also have a dispersing effect.

[0083] Inventive pre-treatment agents are particularly useful to carry out step (A) of the inventive method described above.

[0084] A further aspect of the present invention is a process for making inventive pre-treatment agents, briefly also being referred to as inventive manufacturing process. The inventive manufacturing process can be carried out by mixing

(a) 2 to 20 % by weight of water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:

M is a metal ion with the charge +n, n being selected from 1 to 3,
X is an anion with the charge -m, -m being selected from -1 to -3,

(b) 1 to 15 % by weight copolymer, made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,

(c) optionally, 0.1 to 2% by weight surfactant.

[0085] If desired, cross-linking agent (d) and/or one or more auxiliaries (e) can be added as well.

[0086] The order of addition is not critical. In a preferred version of the inventive manufacturing process, however, in a first step an aqueous dispersion of copolymer (b) can be made in the presence of surfactant (c). Then, water-soluble salt (a) is added. Then, cross-linking agent (d) and/or one or more auxiliaries (e) can be added as well.

[0087] The present invention is further illustrated by examples.
Unless explicitly mentioned otherwise, percentages refer to percentages by weight. Parts refer to parts per weight unless explicitly mentioned otherwise.

I. Manufacturing of an Inventive Pre-Treatment Agent

[0088] In a flask, the following ingredients were mixed by stirring:

120 g of $CaCl_2$ (salt a.1)
500 g of a copolymer dispersion, pH value 6.8, solids content 40 %, of a random emulsion copolymer of 1 part N-Methylolacrylamid, 1 part acrylic acid, 24 parts ethyl acrylate, 26 parts styrene, 48 parts n-butyl acrylate, parts per weight refer to the total solids, average particle diameter (weight average) 172 nm, determined by Coulter Counter, copolymer (b.1), manufactured in the presence of n-$C_{12}H_{25}$-O(CH_2CH_2O)$_3SO_3Na$, surfactant (c.1),

distilled water was added to 1 liter.
Inventive pre-treatment Agent (A.1) was obtained.

II. Manufacturing of Ink-Jet Inks

II.1 Manufacturing of a magenta-coloured ink-jet ink

General procedure:

[0089] Inks were produced by a two-step method: Firstly, a mix component was made by dispersing pigment, water and various auxiliaries according to table 1 in a ball-mill. For this purpose, a ball mill (with a volume of 1200ml) was filled with 2 kg of beads (zirconium dioxide, 0.3 to 0.4 mm in diameter), and the ingredients according to table 1. All the ingredients with exception of the pigment were added first and premixed for 5 minutes, then the pigment was added and mixing was continued for 1 hour. The mixture was placed in the ball-mill and the milling was performed over a period of 4 hours at 2,750 rpm (revolutions per minute) with cooling. Said mix component was then mixed with further ink ingredients in a beaker, filtered and filled into a cartridge.

Table 1: Composition of mix components M1 and M2

	M1	M2
C.I. Pigment Red 122	10	-
C.I. Pigment Yellow 138	-	10
Binder 1	5.4	5.4
Dispersing binder D1	15	15
Melamine derivative 1, 90 % by weight in iso-Butanol	6	6
Polyethylene glycol, M_n 400 g/mol	5	5
Biocide 1	2.6	2.0
Tri-n-butyl phosphate	0.4	0.4
Triethanolamine	0.2	0.2

[0090] All amounts reported in g/100 g mix component. In case formulations were used, amounts in g are tell quelle. 300 g of mix component M1 and M2 were produced in each case.

Table 2: Composition of inks T1 and T2

	T1	T2
Wetting agent 1	0.35	
Wetting agent 2		2
Urea	2.0	2.0

(continued)

	T1	T2
Biocide 1	2.5	2.5
Glycerol	16.0	13.0
Polyethylene glycol, M_n 250 g/mol	2	5
1,2-pentanediol	4.5	9
Mix component M1	26	
Mix component M2		26
Distilled water	Add 100	Add 100

[0091] All use levels reported in g/100 ml. 100 ml of ink T1, T2 and T3 were produced in each case.

II.2 Manufacturing of the ingredients of mix components M1 and M2, and of ink-jet inks T1 and T2

Manufacture of Dispersing binder D1:

[0092] 6.85 g of neopentylglycol, 7.03 g of dimethylpropionic acid, 51.95 g of polyesterdiol and 53.01 g of 4,4'-diphenyl diisocyanate were dissolved in 118.74 g of tetrahydrofuran previously distilled over sodium/benzophenone by a standard laboratory method. A drop of di-n-butyltin dilaurate was added and the reaction solution was brought to the boil. It was heated under reflux until free isocyanate was no longer detectable (titrimetrically in accordance with German standard specification DIN 53 185). The reaction solution was then cooled down by means of an ice bath and admixed with a solution of 6.25 g of diethanolamine in 6.25 g of distilled tetrahydrofuran and thereafter with 5.4 g of triethylamine. 315 g of water were added and the tetrahydrofuran was distilled off to leave dispersing binder D3 in aqueous solution, solids content 33% by weight.

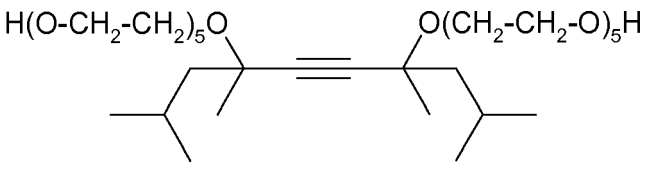
[0093] The polyesterdiol used was a polyesterdiol having a hydroxyl number of 140 mg of KOH/g of polyesterdiol, determined according to German standard specification DIN 53240, obtained from isophthalic acid, adipic acid and 1,4-cyclohexanedimethanol in a molar ratio of 1:1:2.2.

[0094] Melamine derivative 1: reaction product of 1 mole of melamine, 3 moles of formaldehyde and 3 moles of methanol
Biocide 1: 20% solution of 1,2-benzisothiazolin-3-one in dipropylene glycol

Binder 1: copolymer of maleic anhydride with styrene

[0095]

Wetting agent 1: $[(CH_3)_3Si]_2Si(CH_3)[CH_2]_3\text{-}O\text{-}(CH_2CH_2O)_3H$
Wetting agent 2:



11.3 Inventive Pre-treating and printing

[0096] The outer surface of black cotton t-shirts were sprayed with pre-treatment agent (A.1) so that 25 g/m^2 of solids were deposited on the t-shirt. The pre-treated cotton t-shirts were dried at 60°C for 10 minutes.

[0097] After drying, the pre-treated t-shirts were directly printed with ink T1 and T2 using an ink-jet printer with an Epson 4800 printhead, 100% or more colour strength, bidirectional, 1440 x 1440 dpi, directly producing a bright coloured image.

[0098] After printing, thermal curing was performed at a temperature of 150°C for 2 minutes. Inventive black cotton t-shirts with yellow or red printed patterns were obtained. The handle was extremely pleasant. Rubfastness and wetrub-

fastness were excellent.

Claims

1. Method for printing on non-white absorbent materials, comprising the following steps:

   (A) pre-treatment with a colourless aqueous formulation, comprising

   (a) at least one water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:

   M is a metal ion with the charge +n, n being selected from 1 to 3,
   X is an anion with the charge -m, -m being selected from -1 to -3,

   (b) a copolymer made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,
   (c) optionally, at least one surfactant,

   (B) printing a pattern or an image with a pigmented ink.

2. Method according to claim 1 wherein M is selected from alkali metal ions and alkaline earth metal ions.

3. Method according to claim 1 or 2 wherein X is selected from halides.

4. Method according to any of the preceding claims wherein step (B) is performed according to the ink-jet process.

5. Method according to any of the preceding claims wherein the pre-treatment (A) is performed with an aqueous formulation, comprising

   (a) 2 to 20 % by weight of salt M_mX_n,
   (b) 5 to 25 % by weight of copolymer, and
   (c) optionally, 0.1 to 2% by weight surfactant.

6. Method according to any of the preceding claims wherein absorbent materials are selected from textiles.

7. Method according to any of the preceding claims wherein between step (A) and step (B) a drying step is performed.

8. Method according to any of the preceding claims wherein no extra printing step with a white pigmented ink is performed before step (B).

9. Method according to any of the preceding claims wherein the pre-treatment is performed by spraying, roll-coating or padding.

10. Method according to any of the preceding claims wherein the pre-treatment is performed with a pigment-free formulation.

11. Coloured absorbent materials obtainable by a method according to any of claims 1 to 9.

12. Pre-treatment agent, comprising

   (a) 2 to 20 % by weight of water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:

   M is a metal ion with the charge +n, n being selected from 1 to 3,
   X is an anion with the charge -m, -m being selected from -1 to -3,

(b) 1 to 15 % by weight copolymer, made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,
(c) optionally, 0.1 to 2% by weight surfactant.

13. Process for making a pre-treatment agent according to claim 12 by mixing

(a) 2 to 20 % by weight of water-soluble salt according to the formula M_mX_n, wherein the variables are defined as follows:

M is a metal ion with the charge +n, n being selected from 1 to 3,
X is an anion with the charge -m, -m being selected from -1 to -3,

(b) 1 to 15 % by weight copolymer, made from at least two comonomers, selected from ethylenically unsaturated carboxylic acids, C_1-C_{10}-alkyl esters of ethylenically unsaturated carboxylic acids, vinyl aromatic compounds, amides of ethylenically unsaturated carboxylic acids, (meth)acrylonitrile, hydroxymethylamides of ethylenically unsaturated carboxylic acids, epoxy esters of ethylenically unsaturated carboxylic acids,
(c) optionally, 0.1 to 2% by weight surfactant.

REFERENCES CITED IN THE DESCRIPTION

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