

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

12 December 2024 (12.12.2024)



(10) International Publication Number

WO 2024/251598 A1

(51) International Patent Classification:

C09D 11/54 (2014.01) C09D 11/322 (2014.01)

C09D 11/107 (2014.01) C09D 11/102 (2014.01)

C09D 11/38 (2014.01) C09D 11/106 (2014.01)

C09D 11/40 (2014.01)

Published:

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(21) International Application Number:

PCT/EP2024/064862

(22) International Filing Date:

30 May 2024 (30.05.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

23177474.6 06 June 2023 (06.06.2023) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: PRE-TREATMENT LIQUID FOR INKJET PRINTING

(57) Abstract: An aqueous pre-treatment liquid and an ink set for inkjet recording. The aqueous pre-treatment liquid comprises comprising a multivalent metal salt and a carboxylic acid containing polymer or salt thereof or a carboxylic acid anhydride containing polymer, the polymer having an acid value equal to 950 mg KOH / g of polymer or less. A recording method including the above pre-treatment liquid is included.



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Description

Pre-treatment liquid for inkjet printing

Technical Field

[0001] The invention relates to pre-treatment liquids and ink sets suitable for inkjet recording, more specifically inkjet printing on liners for corrugated packaging, folding boards and corrugated card boards.

Background Art

[0002] Inkjet printing technology is a growing area of printing of liners for corrugated packaging and for corrugated card boards. In printing of liners for corrugated card boards, usually flexographic printing or offset printing is performed for applying a pre-coat or primer.

[0003] Nowadays, there is a growing area of digital printing of liners for corrugated packaging and corrugated card boards. Primers or pre-treatment liquids improve the image quality of the printed image. The possibility to apply a pre-treatment liquid, only on the parts which will carry the image, makes it possible to reduce the total consumption of the pre-treatment liquid in the printing job.

[0004] To obtain high quality images, the pre-treatment liquid is capable of receiving ink and holding or fixing colorants in the ink to a greater degree than a substrate not treated with a pre-treatment liquid. In particular, the pre-treatment liquid is capable of holding or fixing colorants at or near the surface of the substrate so that optical density and colour gamut of the printed image may be improved compared to a porous substrate that is not treated with the pre-treatment liquid.

[0005] US 2021/0187971 and EP 2 535 379 disclose pre-treatment liquids containing an organic acid and a water-soluble polymer and to be applied as a coating.

[0006] WO 2018/017089 describes a sprayable pre-treatment liquid for corrugated linerboard or containerboard packaging as packaging material. The pre-treatment liquid composition contains a polyvalent metal salt, a

wax, a dispersing agent, a latex and water. The latex includes monomers such as styrene, 1,3-butadiene, acrylonitrile or combinations thereof.

[0007] WO2019/013785 describes a treatment composition for a packaging liner including a fixing agent, a wax, and a latex. The latex is stabilized by means of anionic groups, for example originating from carboxylic groups. Image quality of images obtained by aqueous inks jetted onto the treatment composition still suffer from mottling and bad ink spreading of the aqueous inks resulting in an inhomogeneous colour density in the solid areas of the printed images.

[0008] WO2023/001650 discloses a jettable pre-treatment composition for corrugated printing including a water-soluble multi-valent metallic salt, a wax, a non-ionic dispersant and a resin particle,

[0009] In the pre-treatment liquids of both disclosures, the wax improves the ink durability during corrugation and has a positive effect on the image quality of the printed image. The wax is a particle consisting of hydrophobic material such as polyethylene, petroleum derivatives, paraffin, carnauba and polypropylene. These wax particles tend to clog filters in the liquid supply and filters in throughflow type of inkjet heads. In these heads the ink is circulated continuously through several filters. Due to this clogging recirculation issues can take place after a certain time (< 1000 min) of operating with this type of pre-treatment liquid.

Summary of invention

[0010] It is the objective of the present invention to provide a solution to the above stated problems. The objective has been achieved by providing a pre-treatment liquid as defined in claim 1.

[0011] It is another embodiment of the invention to provide an ink set containing an aqueous inkjet ink and a pre-treatment liquid of claim 1 as defined in Claim 7.

[0012] It is another embodiment of the invention to provide a printing method using the pre-treatment liquid of claim 1 as defined in Claim 11.

[0013] Other features, elements, steps, characteristics and advantages of the present invention will become more apparent from the following detailed

description of preferred embodiments of the present invention. Specific embodiments of the invention are also defined in the dependent claims.

Brief description of the figures

[0014] Fig. 1: Pattern used for inkjet printing during the evaluation of the image quality of images obtained with pre-treatment liquids. The pattern contains solid areas and negative text with different size ranging from 1 pt to 16 pt.

Description of embodiments

A. Aqueous pre-treatment liquid

A.1. Carboxylic acid containing polymer

[0015] The pre-treatment liquid for inkjet printing according to the invention comprises a carboxylic acid containing polymer or salt thereof or a carboxylic acid anhydride containing polymer. It is believed that carboxylic acid anhydrides are at least partially hydrolysed upon dissolving in the aqueous vehicle of the pre-treatment liquid to a carboxylic acid or salt thereof.

[0016] The effect of the use of carboxylic acid containing polymer or salt thereof or a carboxylic acid anhydride containing polymer in the pre-treatment liquid on image quality might be related to the interaction of these polymers with the fixing agent being multi valent metal ions or cationic polymers present in the pre-treatment liquid. The function of these fixing agents is to interact with the dispersed colorants from the ink such as dyes or pigments that are negatively charged such as to fix the colorants and avoid image bleed (see § A.2). Without being bound to a theory, it is believed that the activity of the fixing agent is better controlled when the carboxylic acid functionalized polymers are present and as such an optimum in image sharpness and ink spreading can be obtained.

[0017] The carboxylic acid containing polymer or salt thereof or the carboxylic acid anhydride containing polymer in the pre-treatment liquid, is not limited to a specific polymer, but should have an acid value equal to 950 mg KOH / g of polymer or less, more preferably having an acid value equal to 450 mg KOH / g of polymer or more and equal to 950 mg KOH / g of polymer or less, most preferably having an acid value equal to 346 mg KOH/g of

polymer or more and equal to 950 mg KOH / g polymer of less, assuming that the carboxylic acid or salt thereof or carboxylic acid anhydride containing polymer is in its acid form. If the acid value is above this range, i.e. for maleic acid and fumaric acid based homopolymers, the degree of polymerisation will be too low and consequently providing less interaction with the used multivalent salts leading to a poor ink spreading.

- [0018] Although no lower limit is specified in the first mentioned acid value range, the carboxylic acid containing polymer or salt thereof or the carboxylic acid anhydride containing polymer should have some acid groups, and hence have a small acid value, in order to solubilise the polymer in the pre-treatment liquid. If the acid value is below this value, solubility of the polymer in the pre-treatment liquid may be too low to give sufficient image quality.
- [0019] The acid number is defined in mg KOH/g polymer corresponding to the amount of carboxylic acid groups or carboxylate groups. The acid value can be determined either via titration or via calculation. An example of a titration method is described in ASTM D3644-06.
- [0020] When the monomer composition of the carboxylic acid containing polymer or salt thereof or carboxylic acid anhydride containing polymer is known, the acid value can be calculated. The molar composition of the carboxylic acid or salt thereof or carboxylic acid anhydride can be determined via analytical techniques such as NMR. In the calculation of the acid value the polymer end groups are neglected. The acid value of the polymer, assuming that the carboxylic acid or salt thereof or carboxylic acid anhydride is in its acid value, can be calculated via the wt.% of COOH and transferring this into mg KOH/g polymer. The wt.% COOH can be calculated by $(45/\text{molar mass of one repeating unit}) \times 100\%$. The acid value can be calculated from the wt.% COOH via $\text{wt.\% COOH}/15 \times 56,11 \times 10$ to get the acid value in mg KOH/g polymer. In polyacrylic acid the $\text{wt.\% COOH} = 15/72 \times 100\% = 20,83\%$. Consequently, the acid value for polyacrylic acid $= 20,83/15 \times 56,11 \times 10 = 779 \text{ mg KOH/g polymer}$.
- [0021] Preferable carboxylic acid containing polymers are homopolymers such as polyacrylic acid, polyitaconic acid, polycrotonic acid and polymethacrylic

acid and, poly(N-(2-hydroxyethyl)maleamic acid), poly(3-(aminocarbonyl)-3-butenic acid), poly(4-amino-2-methylene-4-oxobutanoic acid) and poly(maleamic acid) and salts of the corresponding homopolymers.

- [0022] Other preferable carboxylic acid containing polymers are modified anhydride homopolymers which are hydrolysed by water or a base such as KOH, NaOH, or a water soluble organic base such as a water soluble mono-amine such as ethanol amine, ammonia and amine terminated polyethylene glycol, e.g. CAS registry number 65421-52-5, 171863-88-0, 33881-50-4 and 176703-83-6. Typical anhydride homopolymers or copolymers which can be used for a hydrolysis or post-modification are based on maleic anhydride and itaconic anhydride. When hydrolysed using a base, the carboxylic acid can be present as a salt.
- [0023] Other preferable carboxylic acid or carboxylic acid anhydride containing polymers are copolymers such as poly(ethylene-co-maleic anhydride), poly(isobutylene-co-maleic anhydride), poly(isobutene-co-anhydride), poly(vinyl methyl ether-co-maleic anhydride), poly(vinyl acetate-co-crotonic acid), poly(styrene-co-maleic anhydride), poly(acrylic acid-co-maleic acid) and maleic acid-methyl vinyl ether copolymer and salts of the corresponding copolymers.
- [0024] Further other preferable carboxylic acid or carboxylic acid anhydride containing polymers are copolymers of anhydride monoamine monomers such as maleamic acid = maleic acid monoamide, fumaric acid monoamide, 3-(carbamoyl)acrylic acid, 3-(aminocarbonyl)-3-butenic acid, 4-amino-2-methylene-4-oxobutanoic acid, N-(2-hydroxyethyl)maleamic acid and maleimide monomers such as 3-pyrroline-2,5-dione, 3-maleimidopropionic acid, N-(2-hydroxyethyl)maleimide, N-(2-aminoethyl)maleimide or salts of the corresponding copolymers, e.g. CAS registry numbers 183558-78-3, 60256-14-6, 30446-39-0, 28929-31-9, 89360-06-5, 89360-07-6 or reaction products of anhydride copolymers (e.g. maleic anhydride or itaconic anhydride) and a water soluble mono-amine such as ethanol amine, ammonia and amine terminated polyethylene glycol, e.g. CAS registry number 65421-52-5, 171863-88-0, 33881-50-4 and 176703-83-6.

- [0025] Preferably the carboxylic acid containing polymer or salts thereof or carboxylic acid anhydride containing polymers have an Mw equal to 5000 g/mol or more. The molecular weight is determined via GPC using universal calibration using polyethylene glycol standards. When the Mw is equal or higher than 5000 g/mol, a further improvement in image quality is observed, especially in the spreading of the ink in printing of solids.
- [0026] The amount of the carboxylic acid containing polymer or salt thereof or carboxylic acid anhydride containing polymer is preferably from 0.1 to 5 wt.%, more preferably from 0.2 to 4 wt.%. An amount below this range does show insufficiently an improvement of the image quality. An amount above this range can lead to (i) a decrease in jetting performance as a too high polymer content is present in the liquid, (ii) solubility issues leading to sedimentation, (iii) a decrease in image sharpness and an increase in bleeding and feathering.

A.2. Fixing agent

- [0027] The aqueous pre-treatment liquid according to the invention comprises a fixing agent. The fixing agent serves to crash, precipitate or destabilize the ink colorants such as dyes or pigments and hence fix them to the substrate. This leads to an improved image quality (less bleeding, less coalescence).
- [0028] The fixing agent is preferably a water-soluble multivalent metal salt or a cationic polymer.
- [0029] The multivalent metal salt may be present in the pre-treatment liquid to improve image quality of the inkjet printed image. Generally, the multivalent metal salt may be any water-soluble multivalent metal salt. In specific examples, the multivalent metal salt may include calcium chloride (CaCl_2), magnesium chloride (MgCl_2), magnesium sulfate (MgSO_4), aluminium chloride (AlCl_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), magnesium acetate ($\text{Mg}(\text{CH}_3\text{COO})_2$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), calcium propionate ($\text{Ca}(\text{C}_2\text{H}_5\text{COO})_2$), or a combination thereof. In further examples, the multivalent metal salt may include a metal

cation selected from calcium, copper, nickel, magnesium, zinc, barium, iron, aluminium, chromium, or another multivalent metal.

- [0030] Polymeric cationic polymers, suitable as fixing agent in the pre-treatment liquid contain either guanidinium or fully quaternized ammonium functionalities, such as quaternized polyamine copolymers. Generally, the weight average molecular weight (Mw) of the cationic polymer allows viscosity less than 25 cP at 25°C, as measured on a Brookfield viscometer. Typical Mw are less than 500.000, and in one aspect, less than 50.000.
- [0031] Suitable classes of cationic polymers that can be used include, but are not limited to, quaternized polyamines, dicyandiamide polycations, diallyldimethyl ammonium chloride copolymers, quaternized dimethylaminoethyl(meth)acrylate polymers, quaternized vinylimidazol polymers, alkyl guanidine polymers, alkoxyated polyethylene imines, and mixtures thereof.

A.3. Vehicle

- [0032] The aqueous medium of the pre-treatment liquid according to the invention contains water as a vehicle, but may include one or more water-soluble organic solvents.
- [0033] The one or more organic solvents may be added for a variety of reasons. For example, it can be advantageous to add a small amount of an organic solvent to improve the dissolution of a compound in the pre-treatment liquid to be prepared, to obtain better penetration in porous substrates or to prevent fast drying of the pre-treatment liquid at the nozzle of the inkjet head. Preferable water-soluble organic solvents are polyols (e.g., ethylene glycol, glycerin, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, tetraethylene glycol, triethylene glycol, tripropylene glycol, 1,2,4-butanetriol, diethylene glycol, propylene glycol, dipropylene glycol, butyleneglycol, 1,6-hexanediol, 1,2-hexanediol, 1,5-pentanediol, 1,2-pentanediol, 2,2-dimethyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,5-pentanediol, 3-methyl-1,3-butanediol, and 2-methyl-1,3-propanediol), N-hydroxyethyl-pyrrolidon, N-butyl-pyrrolidon, amines (e.g., ethanolamine,

and 2-(dimethylamino)ethanol), monohydric alcohols (e.g., methanol, ethanol, and butanol), alkyl ethers of polyhydric alcohols (e.g., diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monobutyl ether, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, and dipropylene glycol monomethyl ether), 2,2'-thiodiethanol, amides such as N,N-dimethylformamide, heterocycles such as 2-pyrrolidone and N-methyl-2-pyrrolidone, and acetonitrile. The humectant is preferably added to the pre-coat composition formulation in an amount of 0.1 to 35 wt.% based on the total weight of the liquid.

A.4. Resin particle

- [0034] The pre-treatment liquid according to the invention may comprise a resin particle which is dispersed in the aqueous medium of liquid. The resin particle may improve the mechanical and water resistance of the printed image. The resin is preferably selected from the group consisting of poly(urethanes) and copolymers thereof, acrylics and copolymers thereof, poly(esters) and copolymers thereof, poly(styrenes) and copolymers thereof, poly(vinyl amides) and copolymers thereof, poly(vinyl alcohol) derivatives and copolymers thereof, poly(acetals) and copolymers thereof, poly(ethers) and copolymers thereof, poly(vinyl ethers) and copolymers thereof, polyvinyl (esters) and copolymers thereof, poly(imides) and copolymers thereof, poly(imines) and copolymers thereof, polycarbonates and copolymers thereof, poly(vinyl chloride) and copolymers thereof, poly(vinylidene chloride) and copolymers thereof, poly(amic acids) and copolymers thereof, poly(saccharides) and derivatives thereof and cellulose and derivatives thereof. The resin particle is stabilized by a non-ionic group or a non-ionic or amphiphilic compound. Non-ionic groups are to be understood as groups which are covalently linked to the resin particle.
- [0035] In order to be compatible with multivalent metal salts or cationic polymers, the resin particle is preferably cationic or non-ionic and sterically stabilized.

- [0036] For poly(urethane) dispersions, a non-ionic stabilization can be accomplished by use of polyether diols in the preparation of the poly(urethane) resin. The polyether diol preferably used in the present invention, is Ymer N180, Ymer N120, Ymer N90 or Tegomer D 3403, i.e. α -[2,2-bis(hydroxymethyl)butyl]- ω -methoxy-Poly(oxy-1,2-ethanediyl). These diols can be prepared from trimethylol propane oxetane (TMPO). A possible synthesis procedure is described by Fock, J.; Möhring, V., Polyether-1,2- and -1,3-diols as macromonomers for the synthesis of graft copolymers, 1. Synthesis and characterization of the macromonomers. *Die Makromolekulare Chemie* 1990, 191 (12), 3045-3057. In general, also other polyether 1,2- or 1,3-diols can be used.
- [0037] For addition polymerization, e.g. preparation of polyacrylates, mono-methacrylate or mono-acrylate terminated polyethers can be used for the preparation of graft copolymers with polyether side chains. Examples of suitable macromers for addition polymerisations are listed [0022-0024] of WO2023/001650A.
- [0038] A preferred resin particle dispersion incorporated in the pre-treatment liquid according to the invention, is based on polyurethane particle dispersions. In the polyurethane synthesis one can implement different polyols for obtaining suitable physical, mechanical or optical properties, such as adhesion towards the substrate used, water resistance, solvent resistance, weather resistance, scratch resistance, gloss or opacity, ect... Regularly used polyols are: polyether polyols, polyester polyols, polycarbonate polyols, polyamide polyol, polyacrylate polyols and polyolefine polyols. Besides the polymeric polyols also low molar mass diols can be used and diols which could have affinity for the aqueous phase such as dimethylol propionic acid. In order to get a good compatibility with multivalent salts the use of water soluble polyether diols is preferred.
- [0039] The amount of the resin particle in the pre-coat composition is between 1 wt.%, and 50 wt.%, preferably between 5 wt.% and 45 wt.%, more preferably between 20 wt.% and 40 wt.% with respect to the total solids content of the pre-coat composition. An amount exceeding these values

has a negative effect on the jetting reliability of the pre-coat composition if it is applied via a jetting technique.

- [0040] Suitable commercially available PU dispersions are e.g. Vondic 2220, Vondic 1980NE supplied by Toyobo, Printrite DP375 and Printrite PD379 supplied by Lubrizol, Esacote PU3511 supplied by Lamberti, Neorez R9340 available from DSM and 2019WTT001-3 available from BASF.

A.5. Non-ionic dispersant

- [0041] The pre-treatment liquid of the invention may further include a non-ionic dispersant, preferably a non-ionic polymeric dispersing agent.
- [0042] Suitable non-ionic dispersants are polymeric dispersing agents, non-ionic surfactants and segmented polymers, such as graft-, block-, star-branched, comb- or gradient copolymers. These polymeric dispersing agents are preferably amphiphilic structures having at least one segment which is soluble, dispersible or compatible in water-based media. The medium is not necessarily only water but can also be a mixture with other solvents. In water-based inkjet inks, other water-soluble solvents can be added such as propylene glycol, glycerol, dipropylene glycol monomethyl ether, 2-hydroxyethyl pyrrolidone. At least one segment or part of the polymeric dispersing agent should be compatible with the solvent medium of the ink.
- [0043] Examples of suitable non-ionic surfactants as non-ionic dispersant are listed in [0033-0034] of WO2023001650.
- [0044] Examples of suitable polymeric dispersants are listed in [0035-0039] of WO2023001650.

A.6. Additives

- [0045] The pre-treatment liquid according to the invention may also contain humectants. Humectants are preferably incorporated in a pre-treatment liquid, especially if this liquid has to be applied by means of a jetting technique such as inkjet or valve jet. Humectants prevent the clogging of nozzles. The prevention is due to its ability to slow down the evaporation rate of the inkjet ink, especially the water in the liquid. The humectant is

preferably an organic solvent having a higher boiling point than water. Suitable humectants include triacetin, N-methyl-2-pyrrolidone, glycerol, urea, thiourea, ethylene urea, alkyl urea, alkyl thiourea, dialkyl urea and dialkyl thiourea, diols, including ethanediols, propanediols, propanetriols, butanediols, pentanediols, and hexanediols; glycols, including propylene glycol, polypropylene glycol, ethylene glycol, polyethylene glycol, diethylene glycol, tetraethylene glycol, and mixtures and derivatives thereof. A preferred humectant is glycerol.

[0046] The humectant is preferably added to the pre-treatment liquid formulation in an amount of 0.1 to 40 wt.% based on the total weight of the liquid.

[0047] The pre-treatment liquid may contain a surfactant. Any known surfactant may be used but preferably a non-ionic oxirane, mono(2-propylheptyl) ether is used.

[0048] A biocide may be added to the pre-coat composition to prevent unwanted microbial growth, which may occur over time. The biocide may be used either singly or in combination. Suitable biocides for the ink-jet ink of the present invention include sodium dehydroacetate, 2-phenoxyethanol, sodium benzoate, sodium pyridinethion-1-oxide, ethyl p-hydroxybenzoate and 1,2-benzisothiazolin-3-one and salts thereof.

[0049] Preferred biocides are Proxel™ GXL and Proxel™ Ultra 5 available from ARCH UK BIOCIDES and Bronidox™ available from COGNIS.

[0050] A biocide is preferably added to the aqueous medium in an amount of 0.001 to 3 wt.%, more preferably 0.01 to 1.0 wt. %, each based on the total weight of the liquid.

[0051] The pre-coat composition may further comprise at least one thickener for viscosity regulation in the liquid. Suitable thickeners include urea or urea derivatives, hydroxyethylcellulose, carboxymethylcellulose, hydroxypropylcellulose, derived chitin, derived starch, carrageenan, xanthan gum, pullulan, proteins, poly(styrenesulphonic acid), poly(styrene-co-maleic anhydride), poly(alkyl vinyl ether-co-maleic anhydride), polyacrylamid, partially hydrolyzed polyacrylamid, poly(acrylic acid), poly(vinyl alcohol), partially hydrolyzed poly(vinyl acetate), poly(hydroxyethyl acrylate), poly(methyl vinyl ether), polyvinylpyrrolidone,

poly(2-vinylpyridine), poly(4-vinylpyridine) and poly(diallyldimethylammonium chloride). Particular suitable thickeners are hydrophilically modified PU thickeners (HEUR) like Thijet 170 from Lamberti and Polyacrylic esters like BYK LP-R21675 from BYK.

[0052] The thickener is added preferably in an amount of 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.% based on the liquid.

B. Liquid ink set comprising a pre-treatment liquid and an aqueous inkjet ink.

[0053] The liquid set according to the invention comprises the pre-treatment liquid as described in §A. and an aqueous inkjet ink including a water-soluble organic solvent and a colorant. Optionally, the liquid ink set may comprise an aqueous varnish which is applied during or after the jetting of the aqueous inkjet ink.

B.1. Aqueous inkjet ink

[0054] The aqueous inkjet ink as part of the liquid set according to the invention, comprises colorants such as dyes and pigments. The pigments are preferably stabilized by anionic dispersing groups. The pigments can also be additionally stabilised by polymeric dispersants, surfactants or a combination thereof to achieve extra colloidal stability.

[0055] The aqueous medium of the ink contains water and one or more water-soluble organic solvents. Suitable water-soluble organic solvents are described in § A.3.

[0056] In a preferred embodiment of the invention, the aqueous inkjet ink comprises a resin and/or a wax.

[0057] The aqueous inkjet ink may further comprise a surfactant, a humectant, a biocide, a resin and a thickener as an additive.

B.1.1. Pigment

[0058] The pigments in the aqueous inkjet ink according to the invention may be black, white, cyan, magenta, yellow, red, orange, violet, blue, green, brown, mixtures thereof, and the like. A colour pigment may be chosen from those disclosed by HERBST, Willy, et al. Industrial Organic Pigments,

Production, Properties, Applications. 3rd edition. Wiley - VCH, 2004. ISBN 3527305769.

- [0059] Suitable pigments are disclosed in paragraphs [0128] to [0138] of WO 2008/074548.
- [0060] The pigment particles are dispersed in an aqueous medium using a polymeric dispersant, a surfactant or a combination thereof. Self-dispersible pigments can also be used. The latter prevents interaction of the polymeric dispersant with the dispersing groups of binders or capsules which may be included in the inkjet ink (see below).
- [0061] A self-dispersible pigment is a pigment having on its surface covalently bonded anionic hydrophilic groups or salt-forming groups, that allow the pigment to be dispersed in an aqueous medium without using a surfactant or a resin.
- [0062] The technology for making self-dispersible pigments is well-known. For example, EP1220879A discloses pigments having attached a) at least one steric group and b) at least one organic ionic group and at least one amphiphilic counterion, wherein the amphiphilic counterion has a charge opposite to that of the organic ionic group that are suitable for inkjet inks. Also EP906371A discloses suitable surface-modified coloured pigment having attached hydrophilic organic groups containing one or more ionic groups or ionizable groups. Suitable commercially available self-dispersible colour pigments are, for example, the CAB-O-JET™ inkjet colorants from CABOT.
- [0063] Pigment particles in inkjet inks should be sufficiently small to permit free flow of the ink through the inkjet-printing device, especially at the ejecting nozzles. It is also desirable to use small particles for maximum colour strength and to slow down sedimentation.
- [0064] The average pigment particle size is preferably between 0.050 and 1 µm, more preferably between 0.070 and 0.300 µm and particularly preferably between 0.080 and 0.200 µm. Most preferably, the numeric average pigment particle size is no larger than 0.150 µm. The average particle size of pigment particles is determined with a Brookhaven Instruments Particle Sizer BI90plus based upon the principle of dynamic light scattering.

- [0065] Suitable white pigments are given by Table 2 in [0116] of WO 2008/074548. The white pigment is preferably a pigment with a refractive index greater than 1.60. The white pigments may be employed singly or in combination. Preferably titanium dioxide is used as pigment with a refractive index greater than 1.60. Suitable titanium dioxide pigments are those disclosed in [0117] and in [0118] of WO 2008/074548.
- [0066] Also special colorants may be used, such as fluorescent pigments for special effects in clothing, and metallic pigments for printing a luxury look of silver and gold colours on textiles.
- [0067] Suitable polymeric dispersants are copolymers of two monomers but they may contain three, four, five or even more monomers. The properties of polymeric dispersants depend on both the nature of the monomers and their distribution in the polymer. Co-polymeric dispersants preferably have the following polymer compositions:
- statistically polymerized monomers (e.g. monomers A and B polymerized into ABBAABAB);
 - alternating polymerized monomers (e.g. monomers A and B polymerized into ABABABAB);
 - gradient (tapered) polymerized monomers (e.g. monomers A and B polymerized into AAABAABBABBB);
 - block copolymers (e.g. monomers A and B polymerized into AAAAABBBBBB) wherein the block length of each of the blocks (2, 3, 4, 5 or even more) is important for the dispersion capability of the polymeric dispersant;
 - graft copolymers (graft copolymers consist of a polymeric backbone with polymeric side chains attached to the backbone); and
 - mixed forms of these polymers, e.g. blocky gradient copolymers.
- [0068] Suitable dispersants are DISPERBYK™ dispersants available from BYK CHEMIE, JONCRYL™ dispersants available from BASF and SOLSPERSE™ dispersants available from Lubrizol. Other suitable dispersants are Edaplan 482 from Münzing. A detailed list of non-polymeric as well as some polymeric dispersants is disclosed by MC

CUTCHEON. Functional Materials, North American Edition. Glen Rock, N.J.: Manufacturing Confectioner Publishing Co., 1990. p.110-129.

- [0069] The polymeric dispersant has preferably a number average molecular weight M_n between 500 and 30000, more preferably between 1500 and 10000.
- [0070] The polymeric dispersant has preferably a weight average molecular weight M_w smaller than 100,000, more preferably smaller than 50,000 and most preferably smaller than 30,000.
- [0071] The pigments are preferably present in the range of 0.01 to 15 %, more preferably in the range of 0.05 to 10 % by weight and most preferably in the range of 0.1 to 5 % by weight, each based on the total weight of the inkjet ink. For white inkjet inks, the white pigment is preferably present in an amount of 3% to 40% by weight of the inkjet ink, and more preferably 5% to 35%. An amount of less than 0.01% by weight cannot achieve sufficient covering power.
- [0072] In a preferred embodiment of the invention the aqueous ink comprises a pigment which is encapsulated by means of a cross-linked polymeric shell. Encapsulated pigments provide printed images having improved physical properties such as water resistance and dry rub resistance with respect to pigments dispersed by means of un-cross-linked polymers.
- [0073] Suitable encapsulated pigments are provided by Lubrizol as Diamond HSDX-dispersions and by Fujifilm as RxD pigment dispersions such as APD1000 and APD4000 premium dispersions.

B.1.2. Resin

- [0074] The ink jet ink composition according to the invention may comprise a resin. The resin is often added to the ink jet ink formulation to achieve a good adhesion of the pigment to the recording medium. The resin is preferably a polymer and suitable resins can be an acrylic based resin, a urethane resin or a wax.
- [0075] The polyurethane resin is to be incorporated in the ink formulation as a dispersion and may be selected from the group consisting of aliphatic polyurethane dispersions, aromatic polyurethane dispersions, anionic polyurethane dispersions, non-ionic polyurethane dispersions, aliphatic

polyester polyurethane dispersions, aliphatic polycarbonate polyurethane dispersions, aliphatic acrylic modified polyurethane dispersions, aromatic polyester polyurethane dispersions, aromatic polycarbonate polyurethane dispersions, aromatic acrylic modified polyurethane dispersions, for example, or a combination of two or more of the above.

- [0076] A preferred urethane resin to be used as dispersion in the ink of the invention is a polyester resin including a structural unit containing a urethane bond. Among such resins, a water-soluble or water-dispersible urethane-modified polyester resin is preferred. It is preferable that the urethane-modified polyester resin include at least one structural unit derived from a hydroxyl group-containing polyester resin (polyester polyol) and at least one structural unit derived from an organic polyisocyanate.
- [0077] Furthermore, the hydroxyl group-containing polyester resin is a resin formed by an esterification reaction or transesterification reaction between at least one polybasic acid component and at least one polyhydric alcohol component.
- [0078] A preferred polyurethane resin to be included in the ink of the invention is a polyurethane resin obtainable by reacting a polyester polyol, a polyether diol, a polyol containing an anionic group and a polyisocyanate. A particular preferred polyurethane resin is a polyurethane resin obtainable by reacting a polyester polyol, a polyether diol, a polyol containing an anionic group and a polyisocyanate, and wherein the polyester polyol is obtained by reacting an aromatic polycarboxylic acid and a polyol. Examples of suitable polyurethane resins and their preparations are disclosed in the patent application EP3532545A.
- [0079] Some examples of suitable polyurethane dispersions are NEOREZ R-989, NEOREZ R-2005, and NEOREZ R-4000 (DSM NeoResins); BAYHYDROL UH 2606, BAYHYDROL UH XP 2719, BAYHYDROL UH XP 2648, and BAYHYDROL UA XP 2631 (Covestro); DAOTAN VTW 1262/35WA, DAOTAN VTW 1265/36WA, DAOTAN VTW 1267/36WA, DAOTAN VTW 6421/42WA, DAOTAN VTW 6462/36WA (Allnex); and SANCURE 2715, SANCURE 20041, SANCURE 2725 (Lubrizol Corporation), for example, or a combination of two or more of the above.

- [0080] Acrylic based resins include polymers of acrylic monomers, polymers of methacrylic monomers, and copolymers of the aforementioned monomers with other monomers. These resins are present as a suspension of particles having an average diameter of about 30 nm to about 300 nm. The acrylic latex polymer is formed from acrylic monomers or methacrylic monomer residues. Examples of monomers of the acrylic latex polymer include, by way of illustration, acrylic monomers, such as, for example, acrylate esters, acrylamides, and acrylic acids, and methacrylic monomers, such as, for example, methacrylate esters, methacrylamides, and methacrylic acids. The acrylic latex polymer may be a homopolymer or copolymer of an acrylic monomer and another monomer such as, for example, a vinyl aromatic monomer including, but not limited to, styrene, styrene butadiene, p-chloromethylstyrene, divinyl benzene, vinyl naphthalene and divinyl naphthalene.
- [081] Some examples of suitable acrylic latex polymer suspensions are, JONCRYL 537 and JONCRYL 538 (BASF Corporation, Port Arthur TX); CARBOSET GA-2111, CARBOSET CR-728, CARBOSET CR-785, CARBOSET CR-761, CARBOSET CR-763, CARBOSET CR-765, CARBOSET CR-715, and CARBOSET GA-4028 (Lubrizol Corporation); NEOCRYL A-1110, NEOCRYL A-1131, NEOCRYL A-2091, NEOCRYL A-1127, NEOCRYL XK-96, and NEOCRYL XK-14 (DSM); and BAYHYDROL AH XP 2754, BAYHYDROL AH XP 2741, BAYHYDROL A 2427, and BAYHYDROL A2651 (Bayer), for example, or a combination of two or more of the above.
- [082] The concentration of the resin in the ink jet ink according to the invention is at least 1 wt.% and preferably lower than 30 wt.%, more preferably lower than 20 wt.%.
- [083] The aqueous inkjet ink of the invention may also comprise a wax. The wax in the ink improves wet rub or wet scratch resistance of the printed layer.
- [084] Generally, any suitable wax may be used in the ink and varnish composition. As such, the wax may be polyethylene waxes, petroleum waxes, paraffin waxes, carnauba waxes, polypropylene waxes, crystalline and microcrystalline waxes, amide waxes (oleamide, stearamide,

erucamide, cyclic amide, etc...), and combinations thereof. In an aspect of the invention, the wax may be a high density polyethylene wax.

- [085] In an aspect of the invention, the wax may be a polyethylene wax or modified paraffin wax. An example of polyethylene wax includes high density polyethylene (HDPE) wax, which has a density ranging from about 0.93 g/mL to 0.97 g/mL.
- [086] An example of modified paraffin wax particles includes paraffin wax that has been modified to improve dispersibility in water, e.g., via emulsification. The modified paraffin wax may be surface modified, chemically modified, etc.
- [087] Some specific examples of wax that may be used include those of the JONCRYL Wax series (such as JONCRYL Wax 22, JONCRYL Wax 26, and JONCRYL Wax 120 available from BASF Corp.), those of the AQUACER series (such as AQUACER 498, AQUACER 501, AQUACER 505, AQUACER 513, AQUACER 530, AQUACER 531, AQUACER 535, AQUACER 537, AQUACER 539, and AQUACER 552 available from BYK-Gardner, Columbia, Md.) and Liquilube 404E from Lubrizol .
- [088] The wax may have i) a high melting temperature T and/or ii) a small average particle size. In an example, the wax may have a high melting T such as one that is equal to or greater than 90°C. Further, the wax may have an average particle size (in terms of effective diameter assuming that the individual wax particles are not perfectly spherical) ranging from 0.03 μm to 1.5 μm , more preferably from 0.05 μm to 1 μm (D50). If the particle size exceeds these upper limits, jetting reliability problems of the varnish are likely to occur.
- [089] The wax may be present in the ink in an amount ranging from 3 to 30 wt. %, more preferably from 5 to 25 wt. %, relative to the total solids weight of the ink.
- [090] The ink jet ink composition according to the invention may comprise a capsule. Capsules, more preferably, nanocapsules are often incorporated in ink jet ink formulations to encapsulate colouring agents (US2009227711A, JP2004075759) or to encapsulate reactive ingredients which can cross-link. Particularly useful are the nanocapsules disclosed in

WO2015158649 [0037-0110]: The nanocapsules have a polymeric shell surrounding a core containing reactive chemistry. The shell material includes polyureas, polyurethanes, polyesters, polycarbonates, polyamides, melamine based polymers and mixtures thereof, with polyureas and polyurethanes being especially preferred. Other particularly useful nanocapsules are disclosed in WO2016165970 [0051-0138]: the nanocapsules are selfdispersable and include a dispersing group covalently coupled to the shell polymers. The core of the nanocapsules in WO2015158649 [0037-0110] and WO2016165970 [0051-0138] comprise reactive chemistry which is able to form a reaction product upon application of heat and/or light, allowing a wide variety of substrates to be addressed. Other suitable reactive chemistry is the one which is activated upon radiation as described in WO2015158649 [0068-0110].

- [0091] The capsules are preferably present in the inkjet ink in an amount of no more than 30 wt.%, preferably between 5 and 25 wt.% based on the total weight of the ink.

B.1.3. Additives

- [0092] The ink composition may contain a surfactant. Any known surfactant may be used but preferably a glycol surfactant and/or an acetylene alcohol surfactant and /or a polysiloxane surfactant is used. The use of the acetylene glycol surfactant and/or the acetylene alcohol surfactant and/or the polysiloxane surfactant further reduces bleeding to improve printing quality, and also improves the drying property in printing to allow high-speed printing.
- [093] The acetylene glycol surfactant and/or the acetylene alcohol surfactant is preferably one or more selected from 2, 4, 7, 9-tetramethyl-5-decine-4, 7-diol, alkylene oxide adducts of 2,4,7,9-tetramethyl-5-decine-4, 7-diol, 2,4-dimethyl-5-decin-4-ol, and alkylene oxide adducts of 2,4-dimethyl-5-decin-4-ol. These are available, for example, from Air Products (GB) or from Nissin Chemical Industry, e.g. Olfine series (registered trademark) such as Olfine E1010 and Surfynol (registered trademark) series, as Surfynol 465, Surfynol 104H and Surfynol 61.

- [094] A biocide may be added to the ink composition to prevent unwanted microbial growth, which may occur over time. Suitable biocides are listed in § A.6.
- [095] A biocide is preferably added to the aqueous medium in an amount of 0.001 to 3 wt.%, more preferably 0.01 to 1.0 wt. %, each based on the total weight of the ink.
- [096] The one or more optothermal converting agents are preferably present in the range of 0.1 to 10 wt.% based on the total weight of the ink.

B.2. Over print varnish

- [097] The varnish as part of the liquid ink set according to the invention is used to protect the inkjet printed image against wet & dry rubbing, scratches and solvents. The varnish therefor, comprises water and resin particles.
- [098] The varnish as comprised in the liquid set according to the invention may comprise a wax. The wax may improve the durability of the printed image. Generally, any suitable wax may be used in the varnish composition. Suitable waxes are described in § B.1.

Resin particles

- [099] Examples of the resin particles included in the varnish include well-known resins such as a urethane-based resin, an acrylic resin, a fluorene-based resin, a polyolefin-based resin, a rosin modified resin, a terpene-based resin, a poly-ester-based resin, a polyamide-based resin, an epoxy-based resin, and a vinyl chloride-based resin. The vinyl chloride-based resin includes a vinyl chloride copolymer such as a vinyl chloride-vinyl acetate copolymer. These resins may be used alone, or two or more thereof may be used in combination.
- [0100] Among the aforementioned resin particles, the resin included in the varnish is preferably a urethane-based resin, an acrylic resin, a styrene-acrylic resin or a polyolefin-based resin.
- [0101] As the urethane-based resin, commercially available products may be used, for example, commercially available products such as SUPER FLEX 460, 460s, 840, E-4000 (trade name, manufactured by DKS Co., Ltd.), RESAMINE D-1060, D-2020, D-4080, D-4200, D-6300, D-6455 (trade

name, manufactured by Dainichiseika Color & Chemicals Mfg.Co., Ltd.), TAKELAC WS-6021, W-512-A-6 (trade name, manufactured by Mitsui Chemicals Polyurethanes INC.), SUNCURE 2710 (trade name, manufactured by LUBRIZOL Corporation), and PermalinUA-150 (trade name, manufactured by Sanyo Chemical Industries, Ltd.) may be used.

- [0102] The acrylic resin is a general name of a polymer obtained by polymerizing at least an acrylic monomer such as (meth)acrylic acid and (meth)acrylate, and the examples thereof include a (meth)acryl resin obtained from the acrylic monomer, and a copolymer of the acrylic monomer and monomers other than the acrylic monomer (for example, a vinyl based monomer such as styrene). Acrylamide and acrylonitrile can be also used as the acrylic monomer. The acrylic resin can be non-reactive or self-cross linking. As a resin emulsion using the acrylic resin as a raw material, commercially available products may be used, and the examples thereof include FK-854 (trade name, manufactured by CHIRIKA.Co., Ltd.), Mowinyl 952B, 718A (trade name, manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.), Nipol LX852, and LX874 (trade name, manufactured by ZEON Corporation).
- [0103] Examples of styrene-acrylic resins include poly(styrene-alkyl acrylate), polystyrene-1, 3-diene), poly(styrene-alkyl methacrylate), poly(styrene-alkyl acrylate-acrylic acid), poly(styrene-1, 3-diene-acrylic acid), poly(styrene-alkyl methacrylate-acrylic acid), poly(styrene-alkylacrylate-acrylonitrile-acrylic acid), and poly(styrene-1, 3-diene-acrylonitrile-acrylic acid). Other examples include poly(styrene-propyl acrylate), poly(styrene-butylacrylate), poly(styrene-butadiene-acrylic acid), poly(styrene-butadiene-methacrylic acid), poly(styrene-butadieneacrylonitrile-acrylic acid), poly(styrene-butyl acrylateacrylic acid), poly(styrene-butyl acrylate-methacrylic acid),poly(styrene-butyl acrylate-acrylonitrile), poly(styrenebutyl acrylate-acrylonitrile-acrylic acid). Commercial styrene-acrylic resins are Neocryl D2101 (Covestro) and Bonron PS001 and Bonron PS002 (Mitsui).
- [0104] Other suitable resins include Esajet acrylic latices from Lamberti such as Esajet AC 20, Esajet AC22, Esajet AC 29, Esajet AC31 and Esajet AC03.

- [0105] The varnish contains the resin in an amount from 1 wt.% to 30 wt.% with respect to the total mass of the liquid. When the content of the resin in the varnish is within the aforementioned range, the effect of improving rub resistance of the image tends to become more excellent. More preferably the varnish contains the resin in an amount from 3 wt.% – 15 wt.% with respect to the weight of the liquid. Most preferably the varnish contains the resin in an amount from 5 wt.% to 12 wt.% with respect to the weight of the liquid.
- [0106] The varnish may contain a surfactant. Suitable surfactants are listed in § B.1.3, but polyether siloxane surfactants are preferable.
- [0107] The varnish may further comprise a water soluble polymer selected from the group of linear PPO-PEO copolymers and aryloxyphenyl polyglycol ethers as described in unpublished patent application EP23161106.2 A.
- [0108] The varnish may further comprise a crosslinking agent. Any water soluble or water dispersible crosslinking agent can be used, but preferably the crosslinking agent is a carbodiimide such as described in the unpublished patent application EP23164057.4 A.

C. Recording method

C.1. Application method of the pre-treatment liquid

- [0109] The pre-treatment liquid according to the present invention is suitable for treating different substrates, absorbing and non-absorbing ones. A substrate is characterized as absorbing, when the amount of absorbed water after a contact time of 60 s is at least 10 g/m². Absorbing substrates include paper, card board, white lined chipboard, corrugated board, packaging board, folding board, wood, ceramics, stone, leather and textile. Non-absorbing substrates include metal, glass, polypropylene, polyvinylchloride, PET, PMMA, polycarbonate, polyamide, polystyrene or co-polymers thereof.
- [0110] The pre-treatment liquid is particularly suited for being coated or jetted onto papers intended for packaging applications, more preferably packaging applications including absorbing substrate such as card board,

paper lines, corrugated board, packaging board, folding board and paper. The paper can be a single layer of a multilayer paper.

- [0111] The paper may be brown Kraft, White Top or bleached board. The paper may be manufactured from chemical, wood, or recycled fibre. As an example, the paper may be a liner intended for printing on page wide web presses and converted into corrugated boxes. In this aspect, the liner paper may be used as a double face liner and may be converted directly in a corrugator or laminated onto a double face liner after corrugation. The paper may also be boards used for boxes and other packaging applications.
- [0112] All well-known conventional methods can be used for coating or impregnating the pre-treatment liquid on a substrate. Examples of the method include air knife coating, blade coating, roll coating, gravure coating and spraying. More preferably the pre-treatment liquid is applied by means of a jetting technique.
- [0113] The pre-treatment liquid is then applied using an ink jet head or valve jet head. This means of applying the pre-treatment liquid, which is preferably according to an image, has the advantage that the amount of required pre-treatment liquid is substantially lower than with the other application methods. By means of a jetting head, it is possible to apply the pre-treatment liquid onto areas of the substrate where the image should be printed. Suitable ink jet head types for applying the pre-treatment liquid are piezoelectric type, continuous type, thermal print head type, Memjet-type, valve jet type or through-flow heads as described in §C.2.
- [0114] After applying the pre-treatment liquid onto a substrate, the liquid is preferably at least partially dried before printing the image onto the treated substrate such as to form a pre-coat layer.
- [0115] Substrates to which the pre-treatment liquid has been applied may be dried and optionally undergo a heat treatment, before the subsequent ink jetting step with the colorant containing ink onto the formed pre-coat layer. Examples of the heating process include, but are not limited to, heat press, atmospheric steaming, high-pressure steaming, and THERMOFIX. Any

heat source can be used for the heating process; for example, an infrared ray lamp is employed.

[00116] In another preferred embodiment of the invention, the pre-treatment liquid, is not substantially dried before the image is printed by means of an aqueous ink jetting step.

C.2. Ink jetting & drying

[0117] After the application of the pre-treatment liquid to the substrate, the aqueous inkjet ink as part of the ink set according to the invention is applied to obtain a printed image preferably at least upon the areas where the pre-treatment liquid has been applied. The inkjet ink comprises a colorant, more preferably a pigment. A preferred method of applying the aqueous inkjet ink is by means of an ink jetting technique.

[0118] A preferred ink jet head for the jetting of the pre-treatment liquid printing system is a piezoelectric ink jet head. Piezoelectric inkjet jetting is based on the movement of a piezoelectric ceramic transducer when a voltage is applied thereto. The application of a voltage changes the shape of the piezoelectric ceramic transducer in the print head creating a void, which is then filled with aqueous inkjet ink. When the voltage is again removed, the ceramic expands to its original shape, ejecting a drop of pre-treatment liquid from the ink jet head. However, the jetting of the ink according to the present invention is not restricted to piezoelectric inkjet printing. Other inkjet print heads can be used and include various types, such as a continuous type, a thermal print head type, a Memjet-type of head and a valve jet type.

[0119] In a preferred embodiment, the printing system may be configured to recirculate the aqueous ink prior to printing. A particularly useful inkjet head to print the aqueous inkjet inks of the liquid set of the invention, is from the type that includes a recirculation of the ink within the head such as through-flow heads as disclosed in WO 2006/030235 A2 and WO 2006/064036 A1. This type of inkjet head is very suitable to be incorporated in a printing system comprising a through-flow print head having one or more nozzles for ejecting drops of a pre-treatment liquid

and/or aqueous ink. The ink circulation system for feeding and circulating the pre-treatment liquid and/or the ink through the print head, comprises an ink tank for containing the pre-treatment liquid and/or ink, a supply buffer tank for receiving the pre-treatment liquid and/or ink from the main tank and supplying the ink to the through-flow print head, a return manifold for receiving the pre-treatment liquid and/or ink from the through-flow print head and returning pre-treatment liquid and/or ink to the main ink tank via a pump.

- [0120] After having applied the aqueous inkjet ink onto at least a part of the pre-treatment liquid or pre-coat layer such that an image is formed, the image is dried.
- [0121] The drying step of the image can be performed by applying an air flow and or apply heating. The heating step must be performed by using heat sources; examples include equipment for forced-air heating, radiation heating such as IR-radiation, including NIR-, CIR- and SWIR radiation, conduction heating, high-frequency drying, and microwave drying.
- [0122] Examples of the heating process include, but are not limited to, heat press, atmospheric steaming, high-pressure steaming, and THERMOFIX. Any heat source can be used for the heating process; for example, an infrared ray lamp is employed.

C.3. Application of the varnish

- [0123] After having at least partially dried the image obtained by printing the aqueous inkjet ink, the varnish which makes part of the liquid set according to the invention, is applied onto at least a part of the image.
- [0124] In one of the embodiments of the invention, the varnish is applied on non-image areas, more specifically on non-image areas which contain a pre-treatment liquid or a pre-coat layer.
- [0125] All well-known conventional methods can be used for coating or printing the varnish onto at least a part of the image. Examples of the method include air knife coating, blade coating, roll coating, gravure coating and spraying. The advantage of the coating or printing technique is that thick

varnish layers in one pass of the recording medium can be obtained to assure sufficient rub resistance of the image.

[00126] The varnish is preferably applied via a jetting technique which allows to apply the varnish selectively onto the image. This means of applying the varnish composition, which is preferably according to an image, has the advantage that the amount of required varnish material is substantially lower than with the other application methods. The jetting heads suitable for jetting the varnish are the same as described in § C.2.

[0127] Finally, the applied varnish is dried according to one of the ways described above for drying the pre-treatment liquid or the aqueous inkjet ink.

D.1. Materials

[0128] All materials used in the following examples were readily available from standard sources such as Aldrich Chemical Co. (Belgium) and Acros (Belgium) unless otherwise specified. Where used, water is demineralised water (D.I. water).

- **Proxel** is a 5 wt. % aqueous solution of 1,2-benzisothiazolin-3-one available as Proxel™ K from YDS CHEMICALS NV.
- **Surfynol 104PG50** is a 50 wt.% solution of 2,4,7,9-Tetramethyl-5-decyne-4,7-diol in propylene glycol from Evonik
- **Printrade DP379** is an aqueous 30 wt.% dispersion of a polyether based polyurethane from Lubrizol
- **Aquacer 530** is an aqueous dispersion containing 32 wt.% oxidized HDPE wax from BYK
- **Kauropal K933** is a non-ionic oxirane, mono(2-propylheptyl) ether from BASF
- **Pluronic PE10500** is a 100 wt.% of a block copolymer of ethylene oxide and propylene oxide, with 50% EO and a Mw of 6500 from BASF
- **Tego Foamex 822** is a polyether siloxane copolymer from Evonik
- **Mg(NO₃)₂·6H₂O** is Magnesium nitrate hexahydrate from Merck Group
- **PG** is propylene glycol from Merck

- **HC 327 (HPMA)** is hydrolysed poly(maleic acid) having a Mw of 300 g/mole or more and a calculated acid value of 967 mg KOH/g polymer from Changzhou Wujin Honggunang Chemical Co Ltd.
- **SMA 3000H** is poly(styrene-co-maleic anhydride) having a Mn from 3500 g/mole and Mw 8500 g/mole, a calculated acid value of 346 mg KOH/g from Aurorium
- **ZEMAC E10** is poly(ethylene-co-maleic anhydride) having a Mw from 10.000 g/mole, a calculated acid value of 779 mg KOH/g from Aurorium
- **ZEMAC E60** is poly(ethylene-co-maleic anhydride) having a Mw from 60.000 g/mole a calculated acid value of 779 mg KOH/g of from Aurorium
- **Itaconix DSP5K** is a linear polyitaconic acid partially neutralized with sodium salt, a calculated acid value of 863 mg KOH/g from Itaconix
- **ITACONIX® DSP 2K™** is a linear polyitaconic acid partially neutralized with sodium salt, an acid value of 863 mg KOH/g from Itaconix
- **Sokalan CP12S** is a 50% solution of poly(acrylic acid-co-maleic acid) having a Mw of 3000 g/mole, a calculated acid value of 826 mg KOH/g from BASF
- **KOH 30PCT** is a 30% solution of Potassium hydroxide from VWR
- **PAA-1800** is a polyacrylic acid having a Mw of 1800 g/mole from Sigma-Aldrich
- **PAA-30000** is a 25 % polyacrylic acid solution under the commercial name of ALCOTAC CB9 having a Mw of 30000 g/mole from BASF
- **Ultralube GA1042** is a from Keim additec surface GmbH, obtained via Grolman Benelux BV
- **BYK3450** is a polyether siloxane from BYK-Chemie GmbH
- **HSD X1 series cyan dispersion** is a cyan pigment dispersion from Lubrizol
- **HSD X1 series magenta dispersion** is a magenta pigment dispersion from Lubrizol

- **HSD Y1 series yellow dispersion** is a yellow pigment dispersion from Lubrizol

D.2. Evaluation methods

D.2.1. Sample preparation

- [0129] The samples are made by coating a pre-treatment liquid onto a coated Ensocoat liner (coated solid bleached sulphate board by Stora Enzo (<https://www.storaenso.com/en/products/paperboard-materials/folding-cartons/ensocoat>), using a 4 µm spiral bar. The coated liner was dried at 60°C in an oven for 2 minutes.
- [0130] To obtain an image having a cyan colour, a cyan aqueous inkjet ink was jetted onto the coated liner using a Samba G3L print head, at a resolution of 1200 dpi x 1200dpi and a drop size of about 4.5 pL. To obtain an image having a magenta colour, magenta aqueous inkjet ink was jetted onto the coated liner using a Samba G5L print head, at a resolution of 800 dpi x 1200 dpi and a drop size of about 8 pL.
- [0131] The printed images were dried at 60°C for 5 minutes in an oven. The pattern of the print is shown in **Figure 1**.
- [0132] To obtain an image having a composite colour (green), a solid area of yellow ink was printed onto the coated liner first, followed by printing the image according to Fig. 1 onto the yellow solid with a cyan ink. Both inks were printed by means of a Ricoh Gen 5S inkjet head in single pass mode at a resolution of 1200 dpi x 1200 dpi and a drop size of about 6 pL.
- [0133] The printed images were dried for 5 minutes in an oven at 60°C.

D.2.2. Image quality

- [0134] The image quality of the print was evaluated by visually analysing the following properties: 1) ink spreading; and 2) ink fixing.
- [00135] Ink spreading: the ink should completely cover the solids in the printed image. A lack of ink spreading is demonstrated by the appearance of white lines in the solid areas. The evaluation was conducted by visually observing the solid areas and by giving a score from 0 (excellent ink

spreading, complete coverage) to 3 (poor ink spreading, more than 20 white lines visible in the solid area).

[00136] Ink fixing: the ink should homogeneously and intensely cover the solids in the printed image. A lack of ink fixing is demonstrated by the appearance of uneven patterns in the solid areas. The ink fixing was evaluated by visually observing the solid areas and by giving a score from 0 (excellent ink fixing, homogeneous coverage) to 3 (poor ink fixing, strong unevenness observable).

D.2.3. Pre-treatment liquid recirculation test

[0137] A recirculation test is carried out to test the suitability of the pre-liquid to be used in a printhead equipped with a recirculating ink system.

To conduct a recirculation test, a device constantly drives an amount of 3.5 – 4 L of pre-treatment liquid within a loop and through a filter mesh of 10 µm size at a flow rate of 1.0 – 1.3 L/min. at a temperature of 32 °C. The pressures of the pre-treatment liquid before and after the filter mesh are monitored throughout the complete testing period. The pressure drop across the filter is calculated according to following equation:

Pressure drop = Pressure (before entering the filter) - Pressure (after exiting the filter)

Over time, an increase in pressure drop can be observed indicating the clogging of the filter mesh. A suitable pre-treatment liquid demonstrates less than 15% pressure drop increase after 10,000 minutes of recirculation.

C.3. Preparation of the aqueous pre-treatment liquids

C.3.1. Preparation of aqueous pre-treatment liquids including resin particles

[0138] Comparative and inventive pre-treatment liquids were prepared by mixing the ingredients given in Table 1. The weight percentages are relative to the total weight of the pre-treatment liquid. The raw materials were used as supplied without any further treatments.

Table 1: Composition of comparative and inventive pre-treatment liquids including resin particles.

Compound	COMP-PL-1	COMP-PL-2	INV-PL-1	INV-PL-2	INV-PL-3
Printrite DP379	14.61	12.45	14.61	14.61	8.70
Mg(NO ₃) ₂ ·6H ₂ O	13.36	7.88	13.36	13.36	9.82
Pluronic PE10500	1.0	0.7	1.0	1.0	0.7
Kauropal K933	0.04	0.03	0.04	0.04	0.03
TegoFoamex 822	0.04	0.03	0.04	0.04	0.03
PG	16	25	16	16	32
1,2 hexane diol	-	2.85	-	-	-
n-BuOH	2.85	-	2.85	2.85	2.85
Aquacer 530	-	5.6	-	-	—
HC 327 (HPMA)	0.5	-	-	-	-
SMA 3000H	-	-	1.0	-	-
ZEMAC E60	-	-	-	0.5	0.35
D.I. water	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %

Table 1 (continued)

Compound	INV-PL-4	INV-PL-5	INV-PL-6	INV-PL-7
Printrite DP379	14.61	14.61	14.61	14.61
Mg(NO ₃) ₂ ·6H ₂ O	13.36	13.36	13.36	13.36
Pluronic PE10500	1	1	1	1
Kauropal K933	0.04	0.04	0.04	0.04
TegoFoamex 822	0.04	0.04	0.04	0.04
PG	16	16	16	16
n-BuOH	2.85	2.85	2.85	2.85
ZEMAC E10	0.5	-	-	-

Itaconix DSP5K	-	1.5	-	-
ITACONIX® DSP 2K™	-	-	1.5	-
Sokalan CP12S	-	-	-	3.0
D.I. water	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %

C.3.2. Preparation of aqueous pre-treatment liquids without resin particles

[0139] Comparative and inventive pre-treatment liquids were prepared by mixing the ingredients given in Table 2. The weight percentages are relative to the total weight of the pre-treatment liquid. The raw materials were used as supplied without any further treatments.

Table 2: Composition of comparative and inventive pre-treatment liquids without resin particles

Compound	COMP- PL-3	COMP- PL-4	COMP- PL-5	INV- PL-8	INV- PL-9	INV- PL-10
Mg(NO ₃) ₂ ·6H ₂ O	9.82	-	-	9.82	9.82	9.82
Citric acid	-	11.4	11.4	-	-	-
Malonic acid	-	10.9	10.9	-	-	-
KOH 30PCT	-	24.3	24.3	-	-	-
Pluronic PE10500	0.7	-	-	0.7	0.7	0.7
Kauropal K933	0.03	-	0.04	0.03	0.03	0.03
TegoFoamex 822	0.03	-	0.04	0.03	0.03	0.03
PG	32	-	32	32	32	32
n-BuOH	2.85	-	2.85	2.85	2.85	2.85
PAA-30000	-	4.0	8.0	-	-	-
HC 327 (HPMA)	0.5	-	-	-	-	-
ZEMAC E60	-	-	-	0.5		-
ZEMAC E10	-	-	-	-	0.5	-

Itaconix DSP5K	-	-	-	-	-	0.5
D.I. water	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %

Table 2 (continued): Composition of comparative and inventive pre-treatment liquids without resin particles

Compound	INV-PL-11	INV-PL-12	INV-PL-13	INV-PL-14	INV-PL-15
Mg(NO ₃) ₂ ·6H ₂ O	9.82	9.82	15	15	15
Pluronic PE10500	0.7	0.7	-	-	-
Hydropalat WE3120	-	-	-	1	1
Kauropal K933	0.03	0.03	-	0.04	0.04
TegoFoamex 822	0.03	0.03	-	0.04	0.04
PG	32	32	-	32	32
n-BuOH	2.85	2.85	-	2.85	2.85
Sokalan CP12S	1.0	-	-	-	4.0
PAA-1800	-	0.5	-	-	-
PAA-30000	-	-	4	8	-
Acetic acid	-	-	-	To pH 2.1	0.03
Sodium acetate trihydrate	-	-	-	-	1.28
KOH 30PCT	-	-	To pH 3.8	-	-
D.I. water	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %

C.4. Preparation of the aqueous inkjet inks

[0140] Aqueous inks INVINK-1 to INVINK-5 were prepared by adding the ingredients from Table 3 into a recipient. All ingredients according to Table 3 are expressed in wt. % based on the total weight of the ink. Water was added to complete the ink to the desired pigment concentration.

[0141] Aqueous inks INVINK-1 to INVINK-3 were prepared by first diluting the wax followed by adding the other ingredients from Table 3.

Table 3: Composition of aqueous inkjet inks of the inventive liquid set.

Compound	INV- INK-1	INV- INK-2	INV- INK-3	INV- INK-4	INV- INK-5
Ultralube GA1042	1.43	1.43	1.43	-	-
PG	42	25	41.5	40.5	33.5
n-Butanol	2.95	2.95	2.95	2.95	2.95
Surfynol 104PG50	0.4	0.4	-	2	0.7
BYK3450	-	0.1	0.6	-	-
Pluronic PE10500	-	1.0	-	-	-
Proxel	0.2	0.2	0.2	-	-
HSD X1 series cyan dispersion	13.16	-	13.16	9.5	-
HSD X1 series magenta dispersion	-	23.68	-	-	-
HSD Y1 series yellow dispersion	-	-	-	-	19.59
DI water	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %	To 100 wt. %

C.5. Results of evaluation of image quality

[00142] The performance of the pre-treatment liquids containing resin particles onto the image quality of inkjet printed images with INV-INK-1 (except INV-PL-3 was combined with INV-INK-3) as obtained in § D.2.1. and as described in § D.2.2., is listed in Table 4.

Table 4: Image quality of printed images onto different liner pre-treatments containing resin particles.

Pre-treatment liquid	Ink spreading	Ink fixing
COMP-PL-1	3	2
INV-PL-1	0	0

INV-PL-2	0	0
INV-PL-3*	1	0
INV-PL-4	1.5	0
INV-PL-5	0	0
INV-PL-6	1.5	0
INV-PL-7	0	0

*: performance of INV-PL-3 onto the image quality of inkjet printed image with INV-INK-3.

[0143] The performance of the pre-treatment liquids without resin particles onto the image quality of inkjet printed images with INV-INK-2 as obtained in § D.2.1. and as described in § D.2.2., are listed in Table 5.

Table 5: Image quality of printed images onto different liner pre-treatments without resin particles.

Pre-treatment liquid	Ink spreading	Ink fixing
COMP-PL-3	2	2.5
INV-PL-8	1	1.5
INV-PL-9	1	1.5
INV-PL-10	0.5	0.5
INV-PL-11	0.5	0.5
INV-PL-12	1.5	1.5

[0144] The performance of the pre-treatment liquids without resin particles onto the image quality of inkjet printed images having a composite colour (green) with INV-INK-4 and INV-INK-5 as obtained in § D.2.1. and described in § D.2.2., are listed in Table 6.

Table 6: Image quality of printed images having a composite colour onto different liner pre-treatments without resin particles

Pre-treatment liquid	Ink spreading	Ink fixing
COMP-PL-4	3	0
COMP-PL-5	2	0
INV-PL-13	1	0
INV-PL-14	0	1
INV-PL-15	0	0

[0145] From Table 4, Table 5 and Table 6, it can be concluded that the pre-treatment liquids according to the invention were able to improve the image quality of the image printed onto the liner.

C.6. Results of evaluation of recirculation behaviour of pre-treatment liquid

[0146] The recirculation behaviours of the pre-treatment liquids COMP-PL-2 and INV-PL-3 were tested for recirculation according to § D.2.3. After 10,000 minutes of recirculation, the wax containing pre-treatment liquid COMP-PL-2 showed a pressure drop increase of more than 15%; the inventive pre-treatment liquid did not show any pressure drop increase throughout the 10,000 minutes of recirculation.

[0147] It can be concluded that the inventive pre-treatment liquids do show excellent image quality when combined with aqueous inkjet inks and at the same time do not result in filter clogging when used in recirculation type inkjet heads.

Claims

- Claim 1. An aqueous pre-treatment liquid for inkjet recording comprising a multivalent metal salt and a carboxylic acid containing polymer or salt thereof or a carboxylic acid anhydride containing polymer, the polymer having an acid value equal to 950 mg KOH / g of polymer or less.
- Claim 2. The aqueous pre-treatment liquid according to claim 1 wherein the polymer has a molecular weight equal to 5000 g/mol or more, the molecular weight is measured with respect to a polyethylene standard via a GPC-method using universal calibration using polyethylene glycol standards
- Claim 3. The aqueous pre-treatment liquid according to any of the preceding claims further containing a water-soluble organic solvent.
- Claim 4. the polymer having an acid value equal to 346 mg KOH / g of polymer or more and equal to 950 mg KOH / g of polymer or less.
- Claim 5. The aqueous pre-treatment liquid according to any of the preceding claims further containing a resin particle, the resin is selected from the group consisting of poly(urethanes) and copolymers thereof, acrylics and copolymers thereof, poly(esters), poly(styrenes) and copolymers thereof, poly(vinyl amides) and copolymers thereof, poly(vinyl alcohol) derivatives and copolymers thereof, poly(acetals) and copolymers thereof, poly(ethers) and copolymers thereof, poly(vinyl ethers) and copolymers thereof, polyvinyl (esters) and copolymers thereof, poly(imides) and copolymers thereof, poly(imines) and copolymers thereof, polycarbonates and copolymers thereof, poly(vinyl chloride) and copolymers thereof, poly(vinylidene chloride) and copolymers thereof poly(amic acids) and copolymers thereof, poly(saccharides) and derivatives thereof and cellulose and derivatives thereof.
- Claim 6. The aqueous pre-treatment liquid according to any of the preceding claims further containing a non-ionic dispersant being a PPO/PEO copolymer, an aryethylphenyl polyglycolether or fatty acid derivatives with EO/PO moieties.
- Claim 7. An ink set for inkjet recording, the set comprising an aqueous pre-treatment liquid and an aqueous ink, the pre-treatment liquid comprises a multivalent metal salt and a carboxylic acid containing polymer or salt thereof

or a carboxylic acid anhydride containing polymer, the polymer having an acid value equal to 400 mg KOH / g of polymer or more and equal to 950 mg KOH / g of polymer or less, the aqueous ink comprising a colorant and a water-soluble organic solvent.

Claim 8. The ink set for inkjet recording according to Claim 7 wherein the colorant is a pigment.

Claim 9. The ink set for inkjet recording according to Claim 7 to Claim 8 wherein the aqueous inkjet ink comprises a resin particle.

Claim 10. The ink set for inkjet recording according to Claim 7 to Claim 9, the set further comprising an aqueous varnish comprising a resin particle, the resin is selected from the group consisting of a urethane-based resin, an acrylic resin, a fluorene-based resin, a polyolefin-based resin, a rosin modified resin, a terpene-based resin, a poly-ester-based resin, a polyamide-based resin, an epoxy-based resin, a vinyl chloride-based resin and a wax.

Claim 11. A recording method comprising the steps of:

- a) applying the pre-treatment liquid as defined in Claim 1 to Claim 6 to a substrate; and
- b) optionally at least partially dry the applied pre-treatment liquid; and
- c) jetting onto the applied pre-treatment liquid an aqueous inkjet ink containing a colorant; and
- d) applying heat to dry the applied pre-treatment liquid and the jetted aqueous inkjet ink .

Claim 12. The recording method according to Claim 11 wherein the application of the pre-treatment liquid is done by means of an inkjet head, and the liquid is recirculated in the head or the liquid supply system of the inkjet head.

Claim 13. The recording method according to Claim 11 to Claim 12 wherein a varnish is applied during or after the jetting of the aqueous inkjet ink, the varnish comprising water and a resin particle.

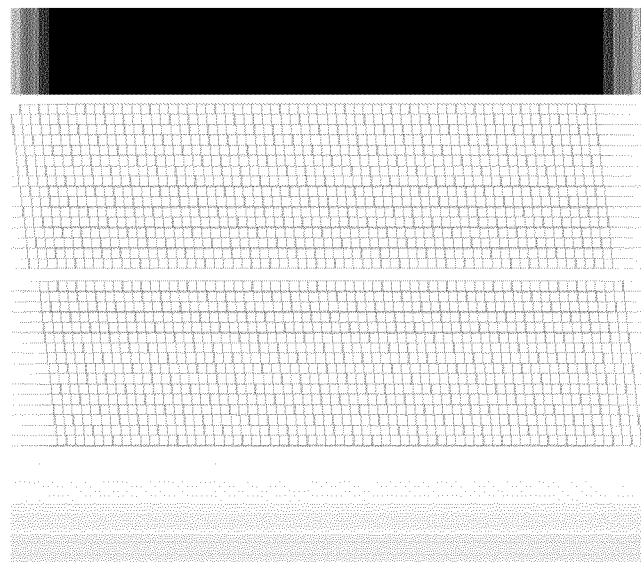


Figure 1: Pattern used for image quality evaluation of pre-treatment liquids.

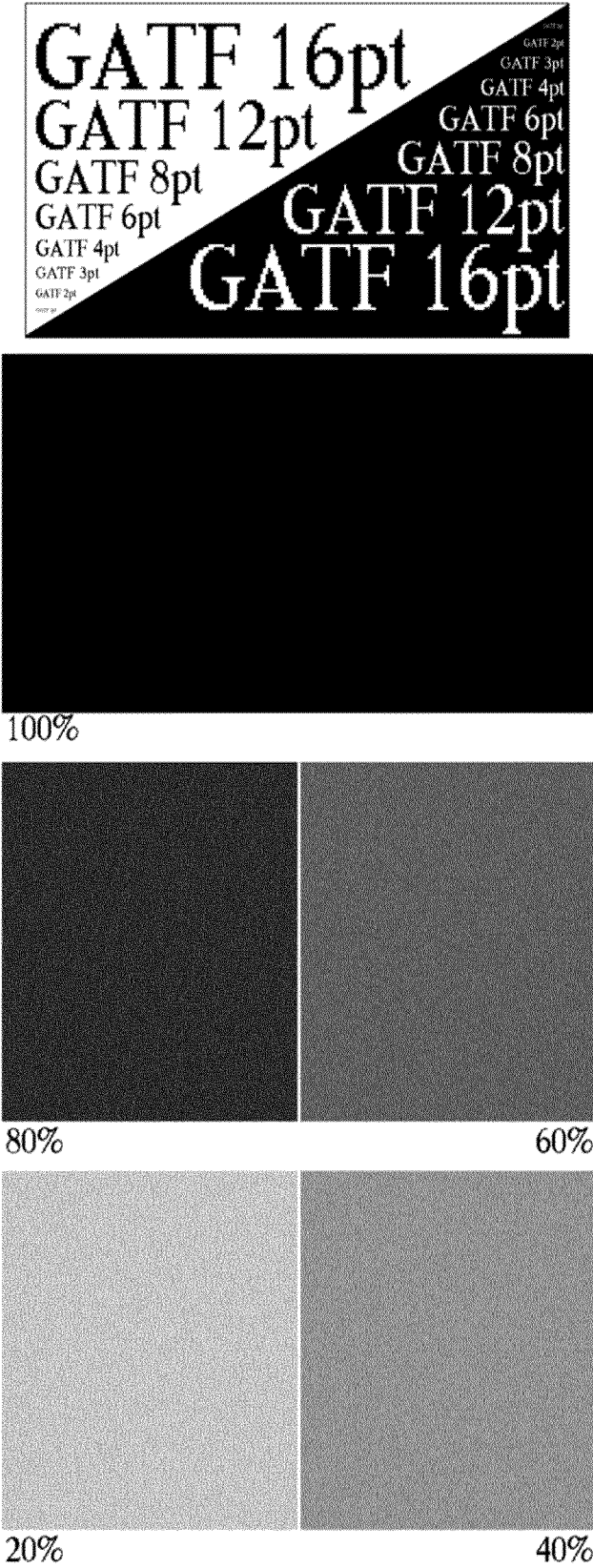


Figure 1 (continued): Pattern used for image quality evaluation of pre-treatment liquids.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/064862

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C09D11/54	C09D11/107	C09D11/38	C09D11/40	C09D11/322
	C09D11/102	C09D11/106			
ADD.					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) C09D					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
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X	EP 2 535 379 A1 (FUJIFILM CORP [JP]) 19 December 2012 (2012-12-19) claims; examples 6,8,9; table 2 -----				1 - 13
X	WO 2018/016141 A1 (SAKATA INX CORP [JP]) 25 January 2018 (2018-01-25) examples -----				1 - 13
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.					
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Date of the actual completion of the international search 19 August 2024			Date of mailing of the international search report 03/09/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Schmitz, Volker		

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International application No

PCT/EP2024/064862

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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