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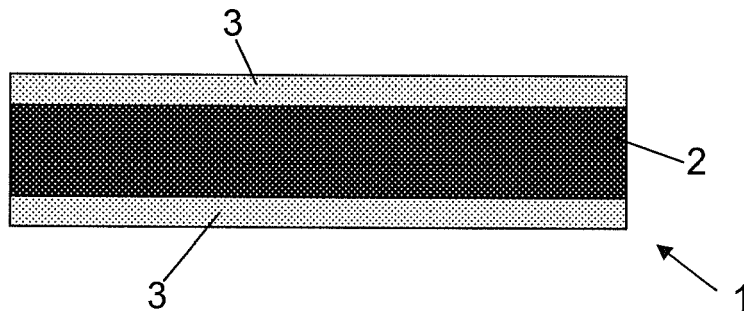
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(54) **Substrate for ink-jet printing**

(57) An inkjet printable substrate (1) with an essentially unpigmented sizing layer (3) on at least one surface of a raw cellulosic substrate (2) is proposed, wherein the sizing layer (3) essentially consists of a combination of a polyaluminium hydroxychloride compound with at least

one organic cationic polydimethylammonium compound, applied as an aqueous formulation at a pH of less than 6 in which the polyaluminium hydroxychloride is in solution and the cationic polydimethylammonium compound is in dispersion.



**FIG. 1**

**EP 2 392 467 A1**

**Description**

## TECHNICAL FIELD

5 **[0001]** The present invention relates to the field of uncoated inkjet substrates which are particularly suitable for high-speed inkjet printing and which are well printable with current high-speed inkjet printing devices.

## PRIOR ART

10 **[0002]** Inkjet printing has become one of the most popular and commonly used printing techniques. There is a wide range of substrates but also a wide range of different printing devices available on the market.

**[0003]** Printable substrates which are useful for ink-jet printing can be coated with a strong pigmented layer which then acts as an ink receiving layer.

15 **[0004]** On the other hand so-called uncoated inkjet papers are available, which normally on both sides are provided with a so-called sizing layer which is much thinner than the above-mentioned strong pigmented ink receiving layer and which may or may not comprise pigments.

**[0005]** EP 0 534 906 discloses a sizing process for the sizing of cellulosic fibre materials with polytertiary amine compounds. The corresponding sizing formulations are applied at a pH of 7.5 such as to make sure that the compounds are cationic.

20 **[0006]** WO 2009/096922 discloses an inkjet printable substrate with a porous ink receiving layer and a sobbing layer. The corresponding coating layer comprises a binder and a metal oxide particulate with an organosilane reagent.

**[0007]** WO 2006/067273 discloses a high-speed inkjet printing paper with a sizing layer containing of a single cationic fixing agent applied on the surface of the web. The cationic fixing agent can for example be polydadmac.

25 **[0008]** US 7704574 discloses a coated substrate suitable for ink-jet printing comprising several coating layers.

## SUMMARY OF THE INVENTION

**[0009]** It is therefore an object of the present invention to propose an improved uncoated inkjet printable substrate. The printable substrate comprises, on at least one side, an essentially unpigmented sizing layer, which forms the ink receiving layer, i.e. which is in direct contact with one surface of a raw cellulosic or lignocellulosic substrate layer, and which on the opposite side forms the surface of the printable substrate for receiving the ink. In accordance with the invention, sizing layer essentially consists of a combination of a cationic inorganic polyaluminium hydroxychloride compound with at least one organic cationic polydimethylammonium compound. This sizing formulation is applied as an aqueous formulation at a pH of less than 6 in which the cationic inorganic polyaluminium hydroxychloride is in solution and the cationic polydimethylammonium compound is in dispersion. Indeed using this particular way of application of the sizing formulation where the cationic inorganic aluminium hydroxychloride is present in solution as a cationic inorganic polyaluminium hydroxychloride in combination with the dispersion of cationic polydimethylammonium compound at this low pH leads to a final dried sizing layer with improved general properties and in particular printing properties. Indeed as will be shown further below a corresponding printable substrate showed high water fastness, exceptionally high optical densities for a large number of different printer devices and excellent colour gamut as well as sufficient drop spreading in 100% black areas.

35 **[0010]** As mentioned above, the sizing layer essentially consists of the above-mentioned constituents. In other words preferentially the sizing layer is completely free from additional compounds such as binders, pigments, brighteners. Certain processing aids such as rheology modifiers, defoamers etc. may be present, however only in very minor proportion, typically below 5 weight percent, preferably below 2 weight percent. In principle such processing aids can also be completely absent.

**[0011]** According to a further preferred embodiment, the cationic inorganic polyaluminium hydroxychloride is applied as a solution of polymeric  $(Al_2(OH)_5Cl \cdot 2.5H_2O)$ .

40 **[0012]** According to yet another preferred embodiment the organic cationic polydimethylammonium compound is selected from the group of polydadmac, N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin, or mixtures thereof. According to a preferred embodiment, the organic cationic polydimethylammonium is selected as a N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin, preferably with a molecular weight in the range of 50,000-80,000 g/mol.

45 **[0013]** Preferentially, the dry weight ratio of the cationic inorganic polyaluminium hydroxychloride to the organic cationic polydimethylammonium compound is in the range of 0.25 - 4. Preferably it is in the range of 0.5 - 2, or 0.75 - 1.5, most preferably this ratio is in the range of 1.

50 **[0014]** For increasing opacity and bulk but also for increasing printing properties, preferentially the raw cellulosic substrate comprises at least 5 weight percent of filler, preferably at least 10 or at least 15 weight percent of filler. Preferably up to 30% or up to 20% filler are present. The filler is preferably a fine particulate pigment filler, preferentially it is a

calcium carbonate filler, more preferably precipitated calcium carbonate filler. The corresponding cellulosic constituent of the raw substrate is preferentially softwood and/or Eucalyptus based pulp.

**[0015]** As mentioned above, it is important in order to have a combination of dissolved (and not dispersed) cationic inorganic polyaluminium hydroxychloride in combination with dispersed cationic polydimethylammonium in order to finally have a dried coating with optimum availability of the corresponding chemistry of these two constituents as concerns mordanting interaction with ink etc. In order to achieve this, the pH of the aqueous formulation should be lower than 6. According to a preferred embodiment, the aqueous formulation has an even lower pH, namely preferentially a pH of less than 5.5, more preferably of less than 5.3, typically in the range of 4.5-5.5.

**[0016]** According to one specific preferred embodiment, there is only one single organic cationic polydimethylammonium compound and this is selected to be N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin, for example as available under the trade name Cartafix DPR liquid from Clariant, and there is cationic inorganic polyaluminium hydroxychloride selected exclusively to be a solution of polymeric  $(Al_2(OH)_5C_2.5H_2O)$  (e.g. using the product Cartafix LA liquid from Clariant). In this case preferentially the dry weight ratio of the cationic inorganic polyaluminium hydroxychloride to the N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin is in the range of 0.5 - 2, preferably in the range of 1, and is applied at a pH in the range of 4.5-5.5, typically around 5.

**[0017]** Typically, the sizing layer is applied at a dry weight in the range of 1-4 g/m<sup>2</sup>, preferably in the range of 1-2 g/m<sup>2</sup>.

**[0018]** Typically the total weight of the inkjet printable substrate (inclusive of the sizing layer(s)) is in the range 40-150 g/m<sup>2</sup>, preferably 50 - 130 g/m<sup>2</sup>.

**[0019]** The sizing layer can be applied on one single side of the raw cellulosic substrates, preferably it is however applied on both sides of the raw cellulosic substrate. Preferentially the sizing is applied online, so within the paper machine and subsequent to the actual formation of the web. Prior to the sizing step, the web can be only partially dried, preferably to a residual humidity in the range of 1 - 10%, preferably 2-5%, more preferably 3-4%. Preferentially the sizing layer is applied on both sides using a size press, in which the web is, in an online process, passed through a pair of rolls which deliver the sizing formulation in the desired amount.

**[0020]** Furthermore the present invention relates to a method for making an inkjet printable substrate as described above. According to this process, preferentially an essentially untreated raw cellulosic substrate web is coated or impregnated with a sizing formulation essentially consisting of a combination of a cationic inorganic polyaluminium hydroxychloride compound with at least one organic cationic polydimethylammonium compound, preferably with one single organic cationic polydimethylammonium compound and this under conditions such that the sizing formulation is present as an aqueous formulation at a pH of less than 6 in which the cationic inorganic polyaluminium hydroxychloride is in solution and the cationic polydimethylammonium compound is in dispersion.

**[0021]** According to a preferred embodiment of the method, the total solids content in the sizing formulation is in the range of 5-30%, preferably in the range of 10 - 20 % or 12-15%.

**[0022]** As mentioned above, it is preferred to apply the sizing formulation on-line and essentially immediately subsequent to the process of the making of the raw cellulosic substrate web (optionally after partial drying) and for the sizing the web is passed through a size press. Further embodiments of the invention are laid down in the dependent claims.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0023]** Preferred embodiments of the invention are described in the following with reference to the drawings, which are for the purpose of illustrating the present preferred embodiments of the invention and not for the purpose of limiting the same. In the drawings,

Fig. 1 shows a schematic cut through a substrate according to the invention.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

**[0024]** In the following experimental section the production of uncoated inkjet papers with sizing formulations according to the present invention shall be described and their printing properties shall be illustrated. The following description shall not be used for limiting the scope of the general invention as outlined above and as defined in the appended claims.

**[0025]** In the laboratory uncoated printable substrates were produced using the sizing formulations as given in table 1 below. Sizing treatment was applied on one side.

**[0026]** C1 and C3 are comparative examples while C7, C10 and C11 are examples according to the invention.

## EP 2 392 467 A1

Table 1: Sizing formulations, wherein the following definitions are applicable: SC: solids content (as actually analysed in the starting material); contents are given as parts in dry weight in the final coating formulation which had a total solids content adjusted in the range of 12-15 % w/w.

|              | SC (%) | Formulation C1 | Formulation C3 | Formulation C7 | Formulation C10 | Formulation C11 |
|--------------|--------|----------------|----------------|----------------|-----------------|-----------------|
| Cartafix DPR | 23,8   |                | 100            | 50             | 25              | 75              |
| Cartafix LA  | 42,3   | 100            |                | 50             | 75              | 25              |

**[0027]** Cartafix DPR is an aqueous dispersion (> 23% w/w) of a high charge density polyamine/epichlorohydrin-based cationic; main ingredient 1,3-Propanediamine, N,N-dimethyl-, polymer with (chloromethyl)oxirane; Density (20°C) 1.06 kg/l; pH (as supplied) 4.5.

**[0028]** Cartafix LA is an aqueous solution (> 40% w/w) of polymeric highly basic aluminium hydroxyl chloride, chemically indicated as  $Al_2(OH)_5Cl \cdot 2 \cdot 3H_2O$ ; its cationic charge density is about 4-5 times higher than that of aluminium sulphate; Density (20°C) 1,33 kg/l; pH (1% solution) 4.5.

**[0029]** As a substrate an uncoated raw base paper (83 g/m<sup>2</sup>) which was based on standard softwood kraft pulp (45-50%) and standard Eucalyptus kraft pulp (50-45%). The pulp mixture as such was additionally provided with 18.5 % w/w of a commercially available PCC, with scalenohedral particle size, a mean particle diameter  $1.8 \pm 0.2 \mu m$ ,  $57 \pm 5\%$  particles < 2  $\mu m$ , a BET specific surface area  $5.5 \pm 1 m^2/g$  and a Tappi (R 457, ISO 2469) brightness  $94.5 \pm 1\%$ .

**[0030]** The raw base substrate was surface sized on one side by means of a hand sheet rod coater device wherein approximately 1.5 g/m<sup>2</sup> sizing material was applied as to all papers C1, C3, C10 and C11. As to paper C7 the amount of sizing material was also varied to respectively 0.7 g/m<sup>2</sup>, 1.4 g/m<sup>2</sup>, 1.6 g/m<sup>2</sup>, 2.8 g/m<sup>2</sup> and 3.6 g/m<sup>2</sup>. In practice varying application amounts were provided for via appropriate aqueous dilution of the mixture of Cartafix DPR and Cartafix LA. The sizing layer was dried using conventional infrared drying techniques.

**[0031]** The final moisture was in the range of 4.5-5.5%. The final grammage (area weight) of the uncoated paper was in the range of 85 g/m<sup>2</sup>. No calendaring was being applied.

**[0032]** The resulting uncoated paper products and (as referent) a commercial available top-brand uncoated ink-jet paper were printed in black (at varying coverage % of 20%, 40%, 60%, 80% and 100%) on a deskjet printer Epson C88. The 100% black images have been used to visually evaluate whether the drop spreading is sufficient to obtain a fully covered full tone. Results are collected in table 2 given below.

Table 2: Visual evaluation of the drop spreading in 100% black area (Epson C88). Rating: 1 = very low spreading; 2= insufficient spreading; 3= sufficient spreading

|                      | Top-brand uncoated ink-jet paper | C1 | C3 | C7 | C10 | C11 |
|----------------------|----------------------------------|----|----|----|-----|-----|
| Spreading capability | 3                                | 2  | 1  | 3  | 3   | 2   |

**[0033]** All papers, inclusive of the referent paper did perform very good in the water fastness test, executed according ISO standard 18935.

**[0034]** Concomitant results as to the resulting (black) optical densities (the higher the better) on the printer Epson C88 have been collected in table 3 given below.

Table 3: Black optical density gradient in relation to % coverage (Epson C88). Unless specified otherwise the sizing layer is applied in 1.5 gsm on one side. Generally gsm stands for g/m<sup>2</sup>.

|   | 100% black | 80% black | 60% black | 40% black | 20% black |
|---|------------|-----------|-----------|-----------|-----------|
| Commercial top-brand uncoated ink-jet paper | 1,65       | 1,07      | 0,65      | 0,38      | 0,16      |
| C1  | 1,66       | 1,07      | 0,61      | 0,35      | 0,14      |
| C3  | 1,63       | 0,86      | 0,46      | 0,25      | 0,10      |

**EP 2 392 467 A1**

(continued)

|                              | <b>100% black</b> | <b>80% black</b> | <b>60% black</b> | <b>40% black</b> | <b>20% black</b> |
|------------------------------|-------------------|------------------|------------------|------------------|------------------|
| 5 C7 (0.7gsm sizing layer)   | 1,65              | 1,10             | 0,62             | 0,35             | 0,15             |
| C7 (1.4 gsm sizing layer)    | 1,85              | 1,16             | 0,64             | 0,35             | 0,15             |
| 10 C7 (1.6 gsm sizing layer) | 2,10              | 1,20             | 0,63             | 0,32             | 0,14             |
| C7 (2.8 gsm sizing layer)    | 1,83              | 1,14             | 0,61             | 0,33             | 0,13             |
| 15 C7 (3.6 gsm sizing layer) | 2,30              | 1,16             | 0,58             | 0,31             | 0,13             |
| C10                          | 1,79              | 1,12             | 0,62             | 0,34             | 0,14             |
| C11                          | 2,00              | 1,11             | 0,57             | 0,31             | 0,13             |

20 **[0035]** The resulting uncoated paper products C3, C7, C 10 and (as referent) (same) commercial available top-brand uncoated ink-jet paper were additionally printed in full color on a deskjet printer Canon IP4500. Results as to resulting C,Y,M,K optical densities have been collected in table 4 below.

25 Table 4: Optical densities C,Y,M, K (Canon IP4500). Unless specified otherwise the sizing layer is applied in 1.5 gsm on one side.

|  | <b>C</b> | <b>M</b> | <b>Y</b> | <b>K</b> |
|--|----------|----------|----------|----------|
| 30 Commercial top-brand uncoated ink-jet paper | 0,93     | 1,17     | 0,92     | 1,95     |
| C3   | 0,86     | 1,26     | 0,87     | 1,50     |
| C7 (0.7gsm sizing layer)                       | 0,94     | 0,94     | 0,84     | 1,27     |
| 35 C7 (1.4 gsm sizing layer)                   | 0,98     | 1,00     | 0,86     | 1,37     |
| C7 (1.6 gsm sizing layer)                      | 1,03     | 1,11     | 0,94     | 1,61     |
| 40 C7 (2.8 gsm sizing layer)                   | 1,00     | 1,17     | 0,90     | 1,68     |
| C7 (3.6 gsm sizing layer)                      | 1,04     | 1,30     | 0,93     | 1,81     |
| 45 C10   | 1,00     | 0,97     | 0,87     | 1,50     |

50 **[0036]** Concomitant results as to the resulting color gamut data ((L)ab-color space) on the printer Canon IP4500 have been collected in table 5 given below. Next to the same top-brand uncoated ink-jet paper also a top-brand coated pigmented ink-jet paper and a premium-brand coated pigmented ink-jet paper have been included as referents.

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**EP 2 392 467 A1**

Table 5: (L)ab color space data (color gamut) on printer Canon IP4500. Unless specified otherwise the sizing layer is applied in 1.5 gsm on one side.

|     | (L)ab   | Yellow | Green | Cyan   | Blue   | Magenta | Red   |       |
|-----|---|--------|-------|--------|--------|---------|-------|-------|
| 5   | Commercial premium-brand coated pigmented ink-jet paper | a      | -2,25 | -58,21 | -24,08 | 3,99    | 67,98 | 58,32 |
| 10  |   | b      | 70,32 | 20,32  | -44,84 | -51,66  | 1,49  | 32,18 |
| 15  | Commercial top- brand coated pigmented ink-jet paper    | a      | 0,5   | -47,54 | -22,48 | 2,31    | 58,24 | 50,36 |
| 20  |   | b      | 67,92 | 20,33  | -44,39 | -44,8   | -2,14 | 24,25 |
| 25  | Commercial top-brand uncoated ink-jet paper             | a      | 1,08  | -42,68 | -19,44 | -0,09   | 52,47 | 44,43 |
| 30  |   | b      | 60,87 | 14,46  | -42,76 | -41,19  | -2,39 | 20,96 |
| 35  | C3  | a      | 1,87  | -42,92 | -18,23 | 3,29    | 57,18 | 49,2  |
| 40  |   | b      | 63,33 | 14,48  | -39,98 | -43,81  | -2,49 | 22,93 |
| 45  | C7 (0.7 gsm sizing layer)                               | a      | 1,73  | -41,91 | -20,6  | -3,24   | 48,3  | 41,5  |
| 50  |   | b      | 60,81 | 12,43  | -40,65 | -37,7   | -3,67 | 19    |
| 55  | C7 (1.4 gsm sizing layer)                               | a      | 1,64  | -43,13 | -21,09 | -3,36   | 50,74 | 44,06 |
| 60  |   | b      | 61,26 | 10,41  | -41,38 | -39,48  | -2,58 | 21,19 |
| 65  | C7 (1.6 gsm sizing layer)                               | a      | 2,59  | -43,02 | -22,23 | -1,24   | 53,87 | 47,28 |
| 70  |   | b      | 65,25 | 12,93  | -42,36 | -41,25  | -0,98 | 24,71 |
| 75  | C7 (2.8 gsm sizing layer)                               | a      | 1,1   | -45,64 | -22,66 | 0,45    | 57,42 | 50,51 |
| 80  |   | b      | 65,15 | 13,56  | -42,91 | -43,42  | -0,59 | 25,42 |
| 85  | C7 (3.6 gsm sizing layer)                               | a      | 1,07  | -47,81 | -23,1  | 3,02    | 60,91 | 53,98 |
| 90  |   | b      | 67,62 | 14,81  | -44,82 | -45,74  | 0,54  | 28,45 |
| 95  | C10   | a      | 1,9   | -42,66 | -21,31 | -3,81   | 49,78 | 42,85 |
| 100 |   | b      | 62,72 | 10,68  | -41,75 | -39,06  | -3,12 | 20,51 |

**[0037]** In a pilot trial uncoated printable substrates were produced using the sizing formulations and sizing amounts as given in table 6 below. As to sizing formulations B,C and D, based on optimum sizing formulation C7 in table 1, sizing coat weights were varied in three trial points Sizing treatment was applied on both sides.

Table 6: Sizing formulations, wherein the following definitions are applicable: SC: solids content (as actually analysed in the starting material); contents are given as parts in dry weight in the final coating formulation which had a total solids content adjusted in the range of 12-15 % w/w.

|    | SC (%)                                    | Formulation A | Formulation B | Formulation C | Formulation D |    |
|----|---|---------------|---------------|---------------|---------------|----|
| 50 | Cartafix DPR                              | 27,4          | 100           | 50            | 50            | 50 |
| 55 | Cartafix LA                               | 46,4          |               | 50            | 50            | 50 |
|    | Applied sizing coat weight per side (gsm) | 1.2           | 1.3           | 2             | 3.5           |    |

## EP 2 392 467 A1

**[0038]** As a substrate an uncoated raw base paper (83 g/m<sup>2</sup>) which was based on standard softwood kraft pulp (45-50%) and standard Eucalyptus kraft pulp (50-45%). The pulp mixture as such was additionally provided with 18.5 % w/w of a commercially available PCC, with scalenohedral particle size, a mean particle diameter  $1.8 \pm 0.2 \mu\text{m}$ ,  $57 \pm 5\%$  particles  $< 2 \mu\text{m}$ , a BET specific surface area  $5.5 \pm 1 \text{ m}^2/\text{g}$  and a Tappi (R 457, ISO 2469) brightness  $94.5 \pm 1 \%$ . The raw base substrate was surface sized on both sides by means of a metered size press and varying amounts sizing material (1.2 - 3.6 g/m<sup>2</sup>/side) were applied to the raw base paper. In practice varying application amounts were provided for via appropriate aqueous dilution of the mixture of Cartafix DPR and Cartafix LA. The sizing layer was dried using conventional infrared drying techniques.

**[0039]** The final moisture was in the range of 3.6-4.5%. The final grammage (area weight) of the uncoated paper was in the range of approximately 85 - 90 gm<sup>2</sup>. No calendaring was being applied.

**[0040]** The resulting uncoated paper products were full-color printed on high-speed ink-jet press Oce Jetstream 2200.

**[0041]** The printed 100% black images have been used to visually evaluate drop spreading behaviour: As to sizing formulations B, C and D a rating 3 = sufficient spreading was given and as to sizing formulation A only a rating 1= very low spreading resulted. This is completely in line with similar results in the above laboratory trial.

**[0042]** Water fastness test results (according ISO standard 18935) were very good as to all sizing formulations A, B, C and D. This is completely in line with similar results in the above laboratory trial.

**[0043]** Results as to resulting C,Y,M,K optical densities have been collected in table 7 below.

Table 7: Optical densities C,Y,M, K (Oce Jetstream 2200).

|                | Formulation A |      | Formulation B |      | Formulation C |      | Formulation D |      |
|----------------|---------------|------|---------------|------|---------------|------|---------------|------|
| drop size (pL) | 7             | 12   | 7             | 9    | 7             | 9    | 7             | 9    |
| Cyan           | 0,80          | 1,03 | 1,01          | 1,09 | 1,00          | 1,09 | 1,00          | 1,06 |
| Magenta        | 0,70          | 0,72 | 0,77          | 0,85 | 0,75          | 0,83 | 0,73          | 0,81 |
| Yellow         | 0,73          | 0,73 | 0,87          | 0,96 | 0,86          | 0,95 | 0,84          | 0,91 |
| Black          | 0,73          | 0,85 | 1,17          | 1,29 | 1,19          | 1,31 | 1,20          | 1,22 |

**[0044]** Concomitant results as to the resulting color gamut data [(L)ab-color space) on the printer Oce jetstream 2200 have been collected in table 8 given below.

Table 8: (L)ab color space data (color gamut) on printer Oce Jetstream 2200.

|               | drop size (pL) |   | Yellow | Green | Cyan  | Blue  | Magenta | Red  |
|---------------|----------------|---|--------|-------|-------|-------|---------|------|
| Formulation A | 7              | a | -2,5   | -40,2 | -23,7 | 9,5   | 51,4    | 46,2 |
|               |                | b | 55,1   | 15,2  | -38,2 | -37,5 | -12,4   | 28,1 |
| Formulation A | 12             | a | -2,6   | -40,9 | -24,7 | 4,3   | 52,4    | 47,0 |
|               |                | b | 55,6   | 7,1   | -42,3 | -40,5 | -12,6   | 29,8 |
| Formulation B | 7              | a | -3,8   | -46,0 | -29,3 | 7,8   | 55,6    | 45,1 |
|               |                | b | 63,9   | 14,3  | -43,9 | -40,5 | -13,4   | 28,9 |
| Formulation B | 9              | a | -2,8   | -45,8 | -28,8 | 7,6   | 57,9    | 46,0 |
|               |                | b | 67,6   | 13,7  | -44,6 | -39,6 | -11,6   | 29,0 |
| Formulation C | 7              | a | -4,1   | -47,1 | -29,8 | 7,5   | 54,6    | 43,8 |
|               |                | b | 63,7   | 14,5  | -43,5 | -40,2 | -13,5   | 29,1 |
| Formulation C | 9              | a | -3,0   | -46,3 | -29,5 | 7,5   | 56,8    | 45,4 |
|               |                | b | 67,6   | 13,1  | -45,0 | -39,6 | -11,7   | 28,8 |
| Formulation D | 7              | a | -4,1   | -46,8 | -30,8 | 6,2   | 53,7    | 42,3 |
|               |                | b | 63,4   | 11,3  | -43,7 | -40,1 | -13,6   | 26,0 |
| Formulation D | 9              | a | -3,1   | -46,5 | -29,6 | 5,3   | 55,9    | 44,6 |
|               |                | b | 66,6   | 12,6  | -43,9 | -39,7 | -11,4   | 27,9 |

**EP 2 392 467 A1**

**[0045]** The resulting uncoated paper products were full-color printed on high-speed ink jet press Kodak VL2000.

**[0046]** The printed 100% black images have been used to visually evaluate drop spreading behaviour: As to sizing formulations B, C and D a rating 3 = sufficient spreading was given and as to sizing formulation A only a rating 1= very low spreading resulted. This is completely in line with similar results in the above laboratory trial.

**[0047]** Water fastness test results (according ISO standard 18935) were very good as to all sizing formulations A, B, C and D. This is completely in line with similar results in the above laboratory trial.

**[0048]** Results as to resulting C,Y,M,K optical densities have been collected in table 9 below.

Table 9: Optical densities C,Y,M, K (Kodak VL2000).

|                | <b>Commercial top-brand uncoated ink-jet paper</b> | <b>Formulation A</b> | <b>Formulation B</b> | <b>Formulation C</b> | <b>Formulation D</b> |
|----------------|--|----------------------|----------------------|----------------------|----------------------|
| drop size (pL) | 11   | 11                   | 11                   | 11                   | 11                   |
| Cyan           | 0,99   | 0,98                 | 1,10                 | 1,09                 | 1,06                 |
| Magenta        | 0,95   | 1,05                 | 1,04                 | 0,98                 | 0,93                 |
| Yellow         | 0,85   | 0,87                 | 0,97                 | 0,94                 | 0,89                 |
| Black          | 1,12   | 1,02                 | 1,23                 | 1,20                 | 1,16                 |

**[0049]** Concomitant results as to the resulting color gamut data [(L)ab-color space) on the printer Kodak VL2000 have been collected in table 10 given below.

Table 10: (L)ab color space data (color gamut) on printer Kodak VL2000.

|   | drop size (pL) |   | <b>Yellow</b> | <b>Green</b> | <b>Cyan</b> | <b>Blue</b> | <b>Magenta</b> | <b>Red</b> |
|---|----------------|---|---------------|--------------|-------------|-------------|----------------|------------|
| Commercial top-brand uncoated ink-jet paper | 11             | a | -1,2          | -40,4        | -27,0       | 13,0        | 53,3           | 42,7       |
|   |                | b | 60,7          | 14,3         | -43,7       | -29,0       | -6,5           | 19,1       |
| Formulation A                               | 11             | a | -0,8          |              | -28,0       |             | 57,7           |            |
|   |                | b | 64,5          |              | -40,5       |             | -3,8           |            |
| Formulation B                               | 11             | a | 0,3           | -42,7        | -28,2       | 16,5        | 57,7           | 48,8       |
|   |                | b | 70,4          | 18,4         | -46,6       | -29,3       | -4,0           | 27,3       |
| Formulation C                               | 11             | a | 0,0           | -44,5        | -28,7       | 14,8        | 55,9           | 48,5       |
|   |                | b | 69,7          | 17,1         | -46,4       | -30,4       | -4,5           | 27,4       |
| Formulation D                               | 11             | a | -0,4          | -45,3        | -29,5       | 10,2        | 53,6           | 46,2       |
|   |                | b | 68,5          | 14,9         | -45,7       | -31,2       | -4,9           | 25,6       |

LIST OF REFERENCE SIGNS

**[0050]**

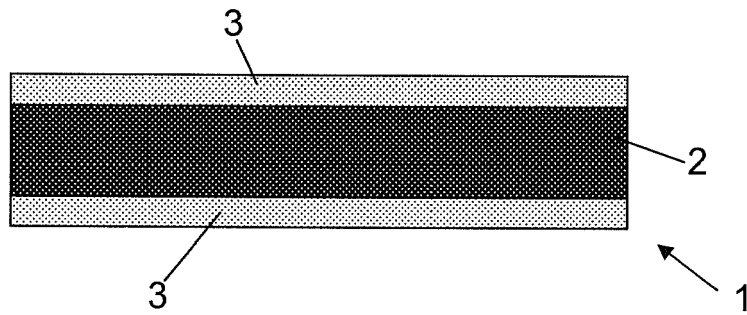
- 1 ink-jet substrate
- 2 raw cellulosic substrate
- 3 sizing layer

**Claims**

**1.** Inkjet printable substrate (1) with an essentially unpigmented sizing layer (3) on at least one surface of a raw cellulosic or lignocellulosic substrate (2), wherein the sizing layer (3) essentially consists of a combination of a cationic inorganic polyaluminium hydroxychloride compound with at least one organic cationic polydimethylammonium compound, applied as an aqueous formulation at a pH of less than 6 in which the polyaluminium hydroxychloride is in solution and the cationic polydimethylammonium compound is in dispersion.

## EP 2 392 467 A1

2. Inkjet printable substrate (1) according to claim 1, wherein the sizing layer (3) is completely free from additional compounds such as binders, pigments, brighteners.
- 5 3. Inkjet printable substrate (1) according to any of the preceding claims, wherein the cationic inorganic polyaluminium hydroxychloride is applied as a solution of polymeric  $(Al_2(OH)_5Cl \cdot 2.5H_2O)$ .
- 10 4. Inkjet printable substrate (1) according to any of the preceding claims, wherein the organic cationic polydimethylammonium compound is selected from the group of polydadmac, N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin, or mixtures thereof, wherein preferably N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin is used with a molecular weight in the range of 40,000-80,000 g/mol.
- 15 5. Inkjet printable substrate (1) according to any of the preceding claims, wherein the dry weight ratio of the polyaluminium hydroxychloride to the organic cationic polydimethylammonium compound is in the range of 0.25 - 4, preferably in the range of 0.5 - 2, or 0.75 - 1.5, most preferably in the range of 1.
- 20 6. Inkjet printable substrate (1) according to any of the preceding claims, wherein the raw cellulosic substrate (2) comprises at least 5 weight percent of filler, preferably at least 10 or at least 15 weight percent of filler, wherein the filler is a calcium carbonate filler, preferably precipitated calcium carbonate filler.
- 25 7. Inkjet printable substrate (1) according to any of the preceding claims, wherein the aqueous formulation has a pH of less than 5.5, preferably of less than 5.3, more preferably in the range of 4.5-5.3.
- 30 8. Inkjet printable substrate (1) according to any of the preceding claims, wherein there is one single organic cationic polydimethylammonium compound and this is selected to be N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin, wherein the cationic inorganic polyaluminium hydroxychloride is applied as a solution of polymeric  $(Al_2(OH)_5Cl \cdot 2.5H_2O)$ , and wherein the dry weight ratio of the polyaluminium hydroxychloride to the N,N-Dimethyl-1,3-Propanediamine polymer with epichlorhydrin is in the range of 0.5 - 2 and is applied as a pH in the range of 4.5-5.5.
- 35 9. Inkjet printable substrate (1) according to any of the preceding claims, wherein the sizing layer (3) is applied at a dry weight in the range of 1-4 g/m<sup>2</sup>, preferably in the range of 1-2 g/m<sup>2</sup>, wherein preferably the sizing layer is applied on both sides of the raw cellulosic substrate (2).
- 40 10. Inkjet printable substrate (1) according to any of the preceding claims, wherein the total weight of the inkjet printable substrate, inclusive of the sizing layer(s), is in the range 40 - 150 g/m<sup>2</sup>, preferably 50 - 130 g/m<sup>2</sup>.
- 45 11. Method for making in inkjet printable substrate (1) according to any of the preceding claims, wherein an essentially untreated raw cellulosic substrate web (2) is coated with a sizing formulation essentially consisting of a combination of a polyaluminium hydroxychloride compound with at least one organic cationic polydimethylammonium compound, as an aqueous formulation at a pH of less than 7 in which the polyaluminium hydroxychloride is in solution and the cationic polydimethylammonium compound is in dispersion.
- 50 12. Method according to claim 11, wherein the total solids content in the sizing formulation is in the range of 5-30%, preferably in the range of 10-20%.
- 55 13. Method according to any of the preceding claims 11-12, wherein on-line and subsequent to the process of the making of the raw cellulosic substrate web for the sizing the web is passed through a size press.



**FIG. 1**



EUROPEAN SEARCH REPORT

Application Number  
EP 10 16 5096

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |  |  |
|---|--|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (IPC)  |
| X   | US 2004/033377 A1 (KOENIG MICHAEL F [US])<br>19 February 2004 (2004-02-19)<br>* paragraphs [0002], [0009], [0010],<br>[0019], [0020], [0022], [0026],<br>[0027], [0035], [0036], [0044],<br>[0058], [0069], [0070] * | 1-13   | INV.<br>B41M5/00<br>B41M5/52<br>B41M5/50 |
| A   | US 2007/092666 A1 (HOOD DAVID K [US] ET AL)<br>26 April 2007 (2007-04-26)<br>* the whole document *  | 1-13   |  |
| A   | EP 1 571 000 A2 (OJI PAPER CO [JP]; SEIKO EPSON CORP [JP])<br>7 September 2005 (2005-09-07)<br>* the whole document *  | 1-13   |  |
|   |  |  | TECHNICAL FIELDS SEARCHED (IPC)          |
|   |  |  | B41M<br>D21H                             |
| The present search report has been drawn up for all claims  |  |  |  |
| Place of search<br>Munich   |  | Date of completion of the search<br>22 October 2010  | Examiner<br>Pulver, Michael              |
| CATEGORY OF CITED DOCUMENTS   |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |  |
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EPO FORM 1503 03.82 (P/4C01)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 10 16 5096

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-10-2010

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|-------------------------|------------------|
| US 2004033377 A1                       | 19-02-2004       | US 2009053431 A1        | 26-02-2009       |
| US 2007092666 A1                       | 26-04-2007       | NONE                    |                  |
| EP 1571000 A2                          | 07-09-2005       | DE 602005000415 T2      | 16-05-2007       |
|  |                  | JP 2005280338 A         | 13-10-2005       |
|  |                  | KR 20060043306 A        | 15-05-2006       |
|  |                  | US 2005202187 A1        | 15-09-2005       |

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- EP 0534906 A [0005]
- WO 2009096922 A [0006]
- WO 2006067273 A [0007]
- US 7704574 B [0008]