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(57) Abstract: An ink jet paper as well as a method for its manufacture is disclosed comprising at least one image receiving coating layer and at least one pre-coat layer beneath said image receiving coating layer on a paper substrate, wherein the pre-coat layer comprises 100 parts in dry weight of a pigment part consisting of 20-75 parts in dry weight of a fine particulate calcium carbonate and/or kaolin; 10 - 70 parts in dry weight of at least one fine particulate silica and/or of a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong H<sub>3</sub>O<sup>+</sup> ion providers and optionally with additional treatment of gaseous carbon dioxide; and 0 - 30 parts of additional fine particulate pigments 4 - 20 parts in dry weight of a binder part 0-6 parts in dry weight of additives; and the image receiving coating layer comprises 100 parts in dry weight of a pigment part consisting of 50 - 100 parts in dry weight of at least one fine particulate silica; 0 - 50 parts in dry weight of a fine particulate polymer pigment; and 0 - 30 parts of additional fine particulate pigments 2 - 10 parts in dry weight of a binder 0-3 parts in dry weight of additives.



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## SPECIFICATION

## TITLE

## PAPER FOR INK JET PRINTING

## 5 TECHNICAL FIELD

The present document relates to the field of inkjet papers and methods for making them, and it in particular relates to inkjet papers with quick drying properties and high-gloss.

## BACKGROUND OF THE INVENTION

10 As outlined in WO 01/45956, ink-jet printers will produce an image on most papers, but the print quality varies heavily in dependence on the nature of the paper used. By "print quality" is meant factors such as the sharpness, intensity and uniformity of the image produced and its susceptibility to smudging immediately or shortly after the ink has been applied. In the case of colour printing, it is important also that the colours should  
15 not run into one another and that they should be vivid, with good brightness.

In order to achieve the highest quality colour images, with vivid bright colours which do not run into one another, it is necessary to e.g. apply a pigment coating to the paper. The pigment coating makes the paper highly absorptive to the aqueous ink vehicle, so that the vehicle drains away quickly into the body of the paper, leaving the coloured dye at  
20 the surface and thereby giving bright intense colours with minimal print bleed.

A wide variety of pigments has been proposed for such coatings, and WO 01/45956 states the use of gel-type silicas to be necessary to give the desired print quality. However, such silicas are expensive, and because of their rheological characteristics, they can only be used at relatively low solids content. This creates either a heavy drying  
25 load or a reduced machine speed at limited drying capacity.

The most widely used general-purpose paper coating pigments are kaolin and calcium carbonate, particularly precipitated calcium carbonate (PCC). They have been used or proposed for use in coated ink jet papers, but primarily as extenders or in low-cost

papers not designed to produce the highest quality colour images.

In view of the above problems, WO 01/45956 proposes to use a speciality cationic PCC product according to WO-A-96/29369A which is much cheaper than silica pigments, and is easier to use from a rheological standpoint in combination with a minor proportion of gel-type silica included in the formulation, and all this for an image receiving top coating layer. Remaining disadvantage is the relatively low solids content of the coating formulation.

## SUMMARY OF THE INVENTION

10 The object of the present invention is therefore to provide an improved inkjet paper eliminating at least one of the disadvantages mentioned above and/or providing an economically and technically viable alternative to the solutions according to the state-of-the-art.

The present invention solves the above problem by providing a method for making an ink jet paper as detailed further below as well as an inkjet paper comprising two layers, an image receiving coating layer for gloss and a pre-coat layer for printing ink vehicle absorption beneath this image receiving coating layer, wherein these two coating layers both have specific coating formulations and both having a clear positive effect upon the printing properties. It is to be noted that the specific choice as given below provides a solution to the difficult problem to provide a coating which on the one hand can be of high-gloss and quick ink-drying, can be printed with most commercial inkjet printers/colours leading to vivid colours without bleeding and similar effects, and additionally a coating that can be run on a normal coating machine such as a blade coater without problems. So the specific proposed choice of a specifically designed image receiving coating layer with a further specifically designed pre-coating layer has to be regarded not as a simple superposition of these two layers but as a synergetic system in as far as adherence and ink receiving properties concerned etc.

One of the key features of the invention is therefore the fact that the proposed inkjet paper comprises at least one image receiving coating layer and at least one pre-coat

layer beneath said image receiving coating layer on a paper substrate, wherein the pre-coat layer comprises a specific formulation as follows:

100 parts in dry weight of a pigment part consisting of

20-75 parts in dry weight of at least one type of fine particulate calcium carbonate and/or kaolin;

5 - 70 parts in dry weight of at least one type of fine particulate silica and/or of a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong  $\text{H}_3\text{O}^+$  ion providers and optionally with additional treatment of gaseous carbon dioxide; and

0 - 30 parts of additional fine particulate pigments

4 - 20 parts in dry weight of a binder part

0-6 parts in dry weight of additives.

At the same time the image receiving coating layer also comprises a specific formulation as follows:

100 parts in dry weight of a pigment part consisting of

50 - 100 parts in dry weight of at least one type of fine particulate silica; and

0 - 50 parts in dry weight of at least one type of fine particulate polymer, e.g. plastic or biopolymer pigment; and

0 - 30 parts of additional fine particulate pigments

2 - 10 parts in dry weight of a binder

0-3 parts in dry weight of additives.

The total coating recipe of the pre-coat layer and/or of the image receiving coating layer is chosen to be in an overall anionic state. This is in contrast to conventional inkjet coating formulations, in which normally in at least one of the coating layers, normally in the ink receptive coating layer, specifically a cationic total coating system is provided to fix the anionic inkjet dyes. One such conventional inkjet coating formulation based

on a purely cationic topcoat layer is for example described in EP 1114735, where for an ink receptive top coating fumed alumina particles with a cationic surface charge are used in order to fix the anionic inkjet dyes, this effect is even supplemented by adding a cationic fixative in a high amount. The cationic nature of the pigment of the ink receptive top coating layer is important according to this document EP 1114735 as if this pigment is partially replaced for example by colloidal silica, the colloidal silica has to be a cationic and therefore very specific type of colloidal silica.

It is one of the surprising findings according to the present invention that it is possible to use coating layers of anionic overall nature for an inkjet paper and still to be able to fix the conventional inkjet dyes and to have the possibility of a glossy surface appearance. The fixing of the conventional inkjet dyes in these anionic coating layers can be supported by the presence of cationic systems like mordants which however are added to the coating in an amount small enough such that the overall coating is still anionic.

The additional fine particulate pigments can be selected from (preferably anionic) pigments such as carbonate, in particular calcium carbonate such as precipitated or ground calcium carbonate, clay, silica, in particular silica gel or colloidal silica, kaolin, talc, as well as combinations and mixtures thereof.

One of the important constituents of the image receiving coating layer and/or of the pre-coat layer is the fine particulate silica. In the pre-coat layer this can either be replaced or supplemented by a specific porous carbonate pigment, more specifically by a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong  $\text{H}_3\text{O}^+$  ion providers and optionally with additional treatment of gaseous carbon dioxide. Specifically it was found that using the proposed fine particulate ground calcium carbonate with (nano-sized) surface and internal (pore) structure modification, as e.g. disclosed in US 6,666,953 but without necessarily an involved treatment with gaseous carbon dioxide, and as for example available from Omya, CH under the trade name Hydrocarb V70, preferably of the type Hydrocarb V70 R240 ME, on the one hand provides for printing ink vehicle absorption and fast to very fast ink setting properties even if not being the

sole constituent of the pigment part. It was specifically found that it is possible to reach overall very fast ink setting properties similar to the ones which can be achieved if fine particulate silica is present in the pigment part, so the proposed specific pigment can be used to at least partially replace if not fully supplement or replace fine particulate silica in the coating while however maintaining similar if not equivalent overall very fast ink setting properties. This is a major achievement as a silica gel is not only difficult to handle in the coating process (e.g. problem of low solids of silica aqueous pigment slurries and prepared coatings and problem of dust formation) and leads to a number of side-effects of the prepared coatings which have to be corrected for e.g. by additional constituents of the coating formulation, but in addition to that the replacement provides a very attractive cost advantage as silica gel pigments usually are relatively expensive.

It should be noted that if the specific type of fine particulate ground calcium carbonate with surface and internal structure modification is used, in the pre-coat formulation the content of may go down to a minimum of one part in dry weight even, the other pigments complementing to 100 parts in dry weight.

A preferred embodiment of this aspect of the invention is characterised in that the fine particulate ground calcium carbonate with surface and internal structure modification and optionally an additional treatment with gaseous carbon dioxide has a median particle size in the range of approximately 1.5-2.5  $\mu\text{m}$ . It is also advantageous if the fine particulate ground calcium carbonate with surface and internal structure modification and optionally an additional treatment with gaseous carbon dioxide has an average internal pore size in the range of 0.01-0.1  $\mu\text{m}$ , preferably in the range of 0.03-0.08  $\mu\text{m}$ , most preferably around 0.05  $\mu\text{m}$ . Indeed this specific range of around 0.05  $\mu\text{m}$ , to provide high driving force for fast absorption rate and supplemented by a parallel system of interconnected intra-particulate pores or voids in the total pigment matrix with average pores or voids diameter of approximately 0.1 – 1  $\mu\text{m}$  for effective overall ink vehicles transport seems to be well matched to typical offset printing inks leading to very advantageous printing properties. Specifically, a pore system including the above Hydrocarb V70 and a corresponding matrix, optionally provided by a PCC pigment as detailed below, appears to be well matched, and 50 nm driving force pores seem to be

similarly powerful as in case of silicagel with typical size range of 10-30 nm pores. Without being bound to any theory, it seems that the parallel traffic system of relatively large pores in case of pigments of the type of Hydrocarb V70 plus (or combined with) a matrix, optionally based on such PCC, is even somewhat more effective.

- 5 Further the fine particulate ground calcium carbonate with surface and internal structure modification and optionally an additional treatment with gaseous carbon dioxide preferably has a surface area in the range of 30-80 m<sup>2</sup>/g, preferably in the range of 50-70 m<sup>2</sup>/g. Furthermore the fine particulate ground calcium carbonate with surface and internal structure modification and optionally an additional treatment with gaseous  
10 carbon dioxide can advantageously have a particle size distribution such that 73-83% of the particles is smaller than 2 µm, and that 35-44% of the particles is smaller than 1 µm.

- A very good porosity ideal for fast ink setting properties of the final high gloss paper can be achieved if the fine particulate ground calcium carbonate with surface and  
15 internal structure modification and optionally an additional treatment with gaseous carbon dioxide is preferably of the so-called roses type. This means that the individual particles of this pigment with a clustered nano-sized platelet structure and with internal nano-sized pores are of generally round and almost spherical shape, and they look similar to if not identical to the ones as disclosed in annex 4 of US 2006/0162884. Also  
20 other Hydrocarb V70 forms are possible, e.g. the so-called eggs, golf balls, brains and Beluga/Kaviar types as disclosed e.g. in the publications

*Achieving Rapid Absorption and Extensive Liquid Uptake Capacity in Porous Structures by Decoupling Capillarity and Permeability: Nanoporous Modified Calcium Carbonate, in Transport in Porous Media vol. 63, nr. 2, pp. 239-259, May 2006; or*

- 25 *Achieving Rapid Absorption and Extensive Liquid Uptake Capacity in Porous Structures by Decoupling Capillarity and Permeability: Nanoporous Modified Calcium Carbonate, in Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 236, Issues 1-3, pp. 91-102, April 1, 2004.*

According to a first preferred embodiment of the invention, the pre-coat layer uses one

or several standard fine particulate calcium carbonates, preferably a precipitated (PCC) or ground (GCC) calcium carbonate type. Preferred is a standard anionic PCC type with a surface area in the range of 2-40 m<sup>2</sup>/g. The carbonates can be intrinsically porous types, for example the above-mentioned fine particulate ground calcium carbonate type with surface and internal structure modification.

According to a further preferred embodiment, the pre-coat layer comprises 100 parts in dry weight of a pigment part consisting of 40-75 parts in dry weight, preferably 50-60 parts in dry weight, of a fine particulate ground or precipitated calcium carbonate; 25-70 parts in dry weight, preferably 40-60 parts in dry weight of at least one fine particulate silica pigment and/or of a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong H<sub>3</sub>O<sup>+</sup> ion providers and optionally with additional treatment of gaseous carbon dioxide.

For cost reasons but also for managing bleeding problems which might exist if the silica part in the pre-coat consists of colloidal silica only, it can be advantageous to combine within the silica part of colloidal silica and a silica gel. A certain minimum amount of silica gel is necessary for achieving this reduced bleeding behaviour, however for rheological reasons the silica gel contents should not be too high. Correspondingly therefore it is advantageous if the fine particulate silica pigment in the pre-coat layer is composed of 5-50, preferably 10-50 parts in dry weight of a colloidal silica and 10-40 parts in dry weight of a silica gel. Even more beneficial effects can be achieved if the fine particulate silica pigment in the pre-coat layer is composed of 10-30, preferably 15-30, parts in dry weight of a colloidal silica and of 20-35, preferably 25-35 parts in dry weight of a silica gel. The silica gel in the pre-coat layer can have a particle size distribution such that the average particle size is in the range of 0.1-10 µm, preferably below 7 µm and most preferably below 4.0 µm. Preferably the pore volume of the silica gel is above 1.0 cm<sup>3</sup>/g, more preferably more than 1.5cm<sup>3</sup>/g. The colloidal silica in the pre-coat layer can have a particle size distribution such that the average particle size is in the range of 10 – 120 nm, preferentially 40 – 100 nm.

A further preferred embodiment of the present invention is characterised in that the

binder part in the pre-coat layer comprises a latex binder and a second binder selected from the group of polyvinyl pyrrolidone binder, PVA, gelatine and mixtures thereof. Specifically it is advantageous if the binder part comprises 2-20, preferably 2-14 (or even 2 – 6) parts in dry weight of a latex binder, preferably a styrene butadiene-binder and 2-8, preferably 4-8 parts in dry weight of a polyvinyl pyrrolidone binder, preferably of polyvinyl pyrrolidone with a molecular weight of more than 20'000 Da, even more preferably of more than 30'000 Da, most preferably in the range of 40'000 Da – 80'000 Da.

A still further preferred embodiment of the present invention is characterised in that the pre-coat layer comprises 100 parts in dry weight of a pigment part consisting of 50-75 parts in dry weight, preferably 40-60 parts in dry weight, of a particulate ground or precipitated calcium carbonate, wherein the particulate calcium carbonate has a particle size distribution such that 60% of the particles are smaller than 2  $\mu\text{m}$ , preferably such that 50 % of the particles are smaller than 1  $\mu\text{m}$ , even more preferably smaller than 0.7  $\mu\text{m}$ ; further it preferably comprises 25-50 parts in dry weight, preferably 40-60 parts in dry weight of a fine particulate silica pigment, e.g. consisting of the two silica types as mentioned above.

In as far as the image receiving coating layer is concerned, according to a further embodiment of the present invention this layer comprises

100 parts in dry weight of a pigment part consisting of

60 – 100, preferably 60 - 90 parts in dry weight of a fine particulate colloidal silica pigment; and

0 – 40, preferably 10 - 40 parts in dry weight of a fine particulate polymer pigment;

3 - 6 parts in dry weight of a binder;

0-2 parts in dry weight of additives.

According to a further embodiment of this image receiving coating layer the particulate, preferably solid or vacuolated polymer pigment in the image receiving coating layer has a particle size distribution such that more than 90 % of the particles are smaller than

0.5µm, preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3 µm, in particular between 0.1 and 0.2 µm, or in the case of a vacuolated polymer pigment also with a mean particle size range of about 0.6 – 1 µm. Indeed it is found that the polymer pigment (biopolymer and/or plastic pigment) can have a stabilising effect on the rheology of the coating formulation and it can reduce the shock effect when a cationic additive, e.g. a cationic, preferably polymeric mordant, is added to the coating formulation.

A further embodiment of the present invention is characterised in that the binder part in the image receiving coating layer consists of a PVA-binder, a PVP-binder, a gelatine binder or mixtures thereof.

Preferably the image receiving coating layer comprises a mordant for the dyes. In order not to disturb the anionic (silica) surroundings in this coating the (cationic, preferably polymeric) mordant content should be as low as possible while still allowing fixation of the dye. This can be achieved if the mordant is present in 0.1 – 1.5, preferably 0.5-1.5 parts in dry weight thereof.

As mentioned above, normally the image receiving coating is directly adjacent to the pre-coat layer.

Typically the pre-coat layer has a coating thickness in the range of 5-30 gsm, preferably in the range of 10-20 gsm, and/or the topcoat layer has a coating thickness in the range of 2-20 gsm, preferably of 5-10 gsm.

It is preferred among other reasons for allowing production of the coating layer is without problems to have a pre-coat formulation essentially free of cationic (e.g. mordant) components. It is furthermore preferred if the image receiving coating is transparent.

As usual, the present coatings can be supplemented with additives, and the additives in the pre-coat and/or the image receiving coating can be selected from the group of defoamers, colorants, brighteners, dispersants, thickeners, water retention agents, preservatives, crosslinkers, lubricants and pH control agents, mordants and mixtures thereof.

As mentioned above, the image receiving coating layer (but preferably not at the pre-coat) may comprise a cationic mordant for the dye as an additive. Beneficially, this in an amount of 0.1-1.5 parts per dry weight, preferably 0.5-1 parts per dry weight.

As mentioned above it is one beneficial element of the proposed coating formulations that colloidal silica pigment in the image receiving coating layer and/or in the pre-coat can be an unmodified anionic colloidal silica.

As also mentioned above, the fine particulate calcium carbonate pigment in the pre-coat can be a precipitated calcium carbonate pigment, preferably a needle-shaped type and/or an anionic type. It may also be of the above-mentioned fine particulate ground calcium carbonate type with surface and internal structure modification.

The end paper can have a gloss above or equal to 45% according 75°DIN, preferably above or equal to 50%, even more preferably above or equal to 55%, so very high-gloss levels can be achieved especially after calendering.

Furthermore, as stated above, the present invention relates to a method for producing an inkjet paper as given above. Preferentially, this method is characterised in that in a first step the pre-coat formulation is applied to the paper substrate with a solids content above 40%, preferably in the range of 50-60%, most preferably in the range of 50-55%, and wherein subsequently in a second step the image receiving coating layer formulation is applied with a solids content above or equal to 40%, preferably between 40 and 55%, most preferably between 40 and 50%. Indeed it is one of the unexpected but highly beneficial advantages of the proposed coating formulation that in contrast to the coating formulations according to the state-of-the-art for such types of inkjet papers, the coating formulations can be applied with a relatively high solids content allowing high production speed and low drying efforts. Preferentially, the formulations are applied using blade coating, rod coating, air knife coating, curtain coating, preferably blade coating with a speed of more than 600 m/min, preferably with a speed of more than 800 m/min, even more preferably with a speed of at least 900 m/min.

For a glossy paper, after application of the two coating layers the paper can be calendered.

Further embodiments of the present invention are outlined in the dependent claims.

To summarize, the following main aspects of the invention emerge:

The concept of the new ink jet paper is containing at least two coating layers: one pre-coating layer which is the absorptive layer and one top coating layer which is providing gloss and both layers synergistically enhancing printing properties.

The obtained coated paper will dry quickly after printing on common ink jet printers and have a high gloss level (up to or even above 55% according DIN75). The coating will be porous contrary to a large part of glossy inkjet papers.

In the pre-coating layer a typical recipe is as given in Table 1:

|                                                                   | Parts |
|-------------------------------------------------------------------|-------|
| PCC (e.g. Opacarb A60)                                            | 50    |
| Colloidal silica (e.g. Ludox PW50)                                | 20    |
| Silica gel (e.g. Syloid 803)                                      | 30    |
| Non-latex-binder, preferably PVP-binder (e.g. PVP or Luvitec K30) | 6     |
| Latex binder (e.g. Eurolatex L0607)                               | 4     |
| Additives, e.g. optical brightener                                | 0.5   |

Table 1, Precoat layer

The Opacarb pigment is a fine PCC is available from SMI (Specialty Minerals Inc., USA). It can be replaced with GCC, other PCC types.

The Ludox PW50 is a colloidal silica available from Grace Davison, USA. In this recipe any colloidal silica can be used.

Syloid C803 is a porous silica gel pigment available from Grace Davison, USA . It can be replaced by other anionic porous pigments such as other silica gel types, the above-mentioned fine particulate ground calcium carbonate type with surface and internal structure modification, alumino silicates, PCC, calcined clay. This pigment provides the main porosity of the coating layer. It can be used from 10 to 50 parts in the coating.

PVP or Luvitec K30 is a polyvinyl pyrrolidone binder e.g. available from ISP or BASF (DE). In this recipe it is a binder and dye mordant. It can be replaced by other binder types such as polyvinyl alcohol or other PVP grades and copolymers, gelatines.

Eurolatex L0607 is a SB latex of supplier EOC. It can be replaced with other latexes (SB or acrylate type).

The solids content of the pre coating recipe is maximized. Solids levels are typically between 50 and 55%, preferably between 50 and 60%.

- 5 Note that preferably there is no cationic aid used in the pre-coating layer as opposed to other inkjet receiving layers. The coating layer hereby stays essentially completely anionic.

Colour density in the coating layer is obtained by using a combination of colloidal silica and PVP with the PCC.

- 10 The coating composition can be applied by any number of well known techniques such as blade coating, rod coating, air knife coating, curtain coating. Specific for this coating is that due to the high solids content it can be coated at high speeds typically 900m/min or higher e.g. with the blade coater.

- 15 The coating thickness can be from 5 till 30 gsm per side but is preferably from 10-20 gsm.

For a top coating recipe a typical recipe is as given in Table 2:

|                                                      | Parts |
|------------------------------------------------------|-------|
| Colloidal silica (e.g. Ludox PW50)                   | 80    |
| Plastic pigment (e.g. DPP 3710)                      | 20    |
| Binder (e.g. Mowiol 4-88)                            | 4     |
| Dye mordant (e.g. Induquat ECR 35 L or Cartafix VXU) | 1     |

Table 2: Image receiving coating layer

The top coating layer is highly porous to obtain a fast flow of the inkjet fluids to the absorptive pre-coating.

- 20 The Ludox PW50 is colloidal silica. In this recipe any anionic colloidal silica can be used.

DPP 3710 is a plastic pigment particle available from Dow Chemicals. It provides high gloss levels and can be replaced with other plastic pigment types.

Mowiol 4-88 is a PVOH based binder available from Kuraray. It can be replaced with

other hydrophilic binders such as PVP, gelatine. It can be used from 0 to 20 parts.

Optionally Induquat ECR35L available from Indulor Chemie or Cartafix VXU from Clariant is used as a cationic mordant (poly-DADMAC). It can be used from 0.1 to 1.5 parts. It can be replaced/supplemented with other mordant types.

- 5 The amount of mordant in the coating recipe can be kept low to keep the total coating recipe in an overall anionic state.

The solids content of the top coating recipe is maximized. Solids levels are typically between 40 and 50%, preferably between 40 and 55%.

- 10 The top coating composition can be applied by any number of well known techniques such as blade coating, rod coating, air knife coating, curtain coating. Specific for this coating is that due to the high solids content it can be coated at high speeds typically 900m/min or higher, preferably with a blade coater.

The coating yield for the top coating can be from 2 till 20 gsm per side but is preferably from 5-10 gsm.

15

## SHORT DESCRIPTION OF THE FIGURES

In the accompanying drawings preferred embodiments of the invention are shown in which:

- 20 Figure 1 shows the colour density of end paper on three different printer types; and

Figure 2 shows the colour gamut of end paper on three different printer types.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- 25 A new coating development has lead to a coating recipe that shows good inkjet printability, quick ink drying and high gloss. This coating can be applied with blade at high speeds and is overall anionic of nature. The development is consisting of a special pre-coating layer in combination with a highly porous top coating layer. After

calendering the coating can be printed on a variety of commercial ink-jet printers with different settings to become photo quality prints with lifelike colours. High gloss levels can be obtained while maintaining enough porosity for the inkjet printability of the medium. Colour gamut and optical density are on the accepted high level of commercial papers.

In the inkjet industry it is common knowledge that the best way to have high optical densities is to use a mordant for the dyes. These mordants are cationic polymers which are also used for water fastness of the prints. It is easy to use this kind of polymers when all the other pigments in the coating bear the same charge, thus are being cationic (e.g. as detailed in WO 01/45956). In regular pigmented inkjet papers this is not an issue since alumina is a cationic pigment by nature and silicas are available in cationic grades as well.

In our concept however we are using standard PCC's or the above-mentioned fine particulate ground calcium carbonate type with surface and internal structure modification and unmodified colloidal and other silica particles. These are all anionic by charge and therefore the mixing process with cationic polymers is very difficult. When only as little as 1 part of cationic polymer is added to a PCC slurry a heavy agglomeration caused by a shock effect is very often observed. This shock effect is due to the zero charge of the mixture at that moment. Overdosing of cationic polymers leads to a cationic coating which is not an option since this might cause shock effects with regular produced anionic coatings commonly run for offset purposes when changing the coating formulations on the machine.

Therefore the proposal here is to add low amounts of cationic polymers to the coating, resulting in a unique overall anionic ink jet coating concept. Upon wetting with the inkjet fluids these polymers will still be able to bind the anionic dyes and provide further improved colours of the prints.

The results from laboratory trials led to a preferred formulation with just one pre-coating and one top coating recipe as given in Table 3.

|  |    |    |
|--|----|----|
|  |    |    |
|  | P5 | T5 |

| Pigments                    |       |       |
|-----------------------------|-------|-------|
| Opacarb A 60                | 50,00 |       |
| Ludox PW 50                 | 20,00 | 80,00 |
| Syloid C 803                | 30,00 |       |
| DPP 3710                    |       | 20,00 |
| PVP K 30                    | 6,00  |       |
| Mowiol 4-88                 |       | 4,00  |
| Litex 7110                  | 4,00  |       |
| Induquat ECR 35 L           |       | 1,00  |
| Final solids of coating (%) | 55    | 48    |

Table 3: coating formulation, P=Pre-coat, T=Topcoating

The pre-coat layer was applied at 17 gsm and the top coating layer at 8 gsm. In this way coating machine speed of up to 900 m/min were possible. The paper was calendered to a gloss level of 55% or 55.6% according 75°DIN.

The optical density and the colour gamut of such papers is given in Figure 1 and 2, respectively, for three different ink jet printer types (a: Epson R200, b: Canon 4200, c: HP 5150), respectively. As comparative example commercial paper HP Everyday was used.

This paper does show the right optical density levels and has vivid colours. It shows no bleed at Epson, HP and the Canon.

Overall the colours are vivid and bright, optical density levels are high, especially in CMY the optical density of this paper is higher than the HP Everyday paper. As it shows from the graphs the colour gamut in total is larger compared to the colour gamut of the HP Everyday paper.

The paper could produce photo quality prints on various pre-installed settings for photo paper on various printers, also photo printing software packages delivered with the printer can be used for good quality prints.

The paper was also tested on a commercial large format printer The prints produced were clear and sharp.

So the current invention preferably contains two coating layers: a pre-coating and a top

coating as follows:

Pre-coating:

Main pre-coat components: colloidal silica and PVP are supposed to actually fix the dyes;

- 5 Colloidal silica such as Ludox PW50 equal/above 10 pph; inter-particle porosity provides (additional) absorptivity ; can be fully or partially replaced by the above-mentioned fine particulate ground calcium carbonate type with surface and internal structure modification;

- Carbonate such as PCC Opacarb A60 can be replaced by e.g. GCC like Covercarb 75;  
10 possible range of these carbonates 20-75, preferred 40-60 pph;

Silica gel such as Syloid C803 gives additional porosity; can be fully or partially be replaced by the above-mentioned fine particulate ground calcium carbonate type with surface and internal structure modification;

- Binder such as Litex 7110 and/or Eurolatex L0607 essentially needed for improved  
15 adhesion of coating layers to substrate;

PVP role as dye mordant (and binder) and its seemingly limited cationogenity related to mesomeric/resonance mechanism;

Solids content of new pre-coat 50-55% versus about 10-30% for regular ink jet coating;

The pre-coating is thus preferentially consisting out of:

- 20 Opacarb A60: Fine PCC needle-shaped: provides porosity;  
Ludox PW50: fine colloidal silica: provides absorptivity and improved colour density of the prints;  
Syloid C 803: porous silica: provides improved liquid absorption and buffer volume;  
25 PVP K 30: binder against colour fading, improved colour density;  
Litex 7110: SB-latex: provides improved fixation of the coating layer ;

Top coating:

Top coating layer is preferably transparent.

The top coating is thus preferably consisting out of:

Ludox PW50: fine colloidal silica: gloss and porosity, transparent;

5 DPP3710: fine solid sphere plastic pigment: reduce shock effects, provides (additional) gloss;

Mowiol 4-88: binder: protective colloid for cationic mordant;

Induquat ECR35L: mordant: improved colour density, dye fixative;

Common issues for both coatings:

10 Solids content of new pre-coat (practically) 50-55% and topcoat 48-50%, normally 50% max. versus about only 10-30% for regular ink jet coating; allows high coating application speeds up to 900 - 1100 m/min.

15 Quick dry behaviour of new ink jet paper: faster than regular 'swellable type' ink jet papers and about equally fast as porous (cationic and expensive alumina based) ink jet papers in market. No actual drying speed data according specific test available. Based on perception/observations: the printed paper can be touched immediately after removing it from the print tray.

Other apparent advantages of new concept: a) extra feature = can on paper be regularly coated and printed at two sides (uncommon in case of regular ink jet papers).

## CLAIMS

1. Method for producing an inkjet paper comprising at least one image receiving coating layer and at least one pre-coat layer beneath said image receiving coating layer on a paper substrate, wherein

5 the pre-coat layer comprises

100 parts in dry weight of a pigment part consisting of

20-75 parts in dry weight of a fine particulate calcium carbonate and/or kaolin;

10 10 - 70 parts in dry weight of a fine particulate silica and/or of a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong  $\text{H}_3\text{O}^+$  ion providers and optionally with additional treatment of gaseous carbon dioxide; and

0 - 30 parts of additional fine particulate pigments

15 4 - 20 parts in dry weight of a binder part

0-6 parts in dry weight of additives;

and the image receiving coating layer comprises

100 parts in dry weight of a pigment part consisting of

50 - 100 parts in dry weight of a fine particulate silica; and

20 0 - 50 parts in dry weight of a fine particulate polymer pigment; and

0 - 30 parts of additional fine particulate pigments

2 - 10 parts in dry weight of a binder

0-3 parts in dry weight of additives.,

25 wherein in a first step the pre-coat formulation is applied to the paper substrate with a solids content above 40% and wherein subsequently in a second step the

image receiving coating layer formulation is applied with a solids content above or equal to 40%.

2. Method according to claim 1, wherein the pre-coat formulation is applied to the paper substrate with a solids content in the range of 50-60%, preferably in the range of 50-55%

3. Method according to any of the preceding claims, wherein the image receiving coating layer formulation is applied with a solids content between 40-55%, preferably between 40 and 50%.

4. Method according to any of the preceding claims, wherein the formulations are applied using blade coating, rod coating, air knife coating, curtain coating.

5. Method according to any of the preceding claims, wherein at least one of the formulations is applied using blade coating with a speed of more than 600 m/min, preferably with a speed of more than 800 m/min, even more preferably with a speed of at least 900 m/min.

6. Method according to any of the claims 1 - 5, wherein after application of the two coating layers the paper is calendered.

7. Method according to any of the preceding claims, wherein the pre-coat and/or the receiving coating formulations are in an overall anionic state.

8. Ink jet paper, preferably made using a method according to any of the preceding claims, comprising at least one image receiving coating layer and at least one pre-coat layer beneath said image receiving coating layer on a paper substrate, wherein

the pre-coat layer comprises

100 parts in dry weight of a pigment part consisting of

20-75 parts in dry weight of a fine particulate calcium carbonate and/or kaolin;

5 - 70 parts in dry weight of a fine particulate silica and/or of a fine particulate ground calcium carbonate with surface and

internal structure modification as a result of treatment with one or more medium to strong  $\text{H}_3\text{O}^+$  ion providers and optionally with additional treatment of gaseous carbon dioxide and

0 - 30 parts of additional fine particulate pigments

5                   4 - 20 parts in dry weight of a binder part

0-6 parts in dry weight of additives;

and the image receiving coating layer comprises

100 parts in dry weight of a pigment part consisting of

50 - 100 parts in dry weight of a fine particulate silica; and

10                   0 - 50 parts in dry weight of a fine particulate polymer, such as plastic and/or biopolymer, pigment; and

0 - 30 parts of additional fine particulate pigments

2 - 10 parts in dry weight of a binder

0-3 parts in dry weight of additives.

15    9.    Ink jet paper according to claim 8, wherein the pre-coat layer comprises 100 parts in dry weight of a pigment part consisting of

40-75 parts in dry weight, preferably 50-60 parts in dry weight, of a fine particulate ground or precipitated calcium carbonate;

20                   25-70 parts in dry weight, preferably 40-60 parts in dry weight of a fine particulate silica pigment and/or of a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong  $\text{H}_3\text{O}^+$  ion providers and optionally with additional treatment of gaseous carbon dioxide.

25    10.    Inkjet paper according to one of the claims 8 or 9, wherein the fine particulate silica pigment in the pre-coat layer is composed of 5 – 50, preferably 10-50 parts in dry weight of a colloidal silica and 10-40 parts in dry weight of a silica gel.

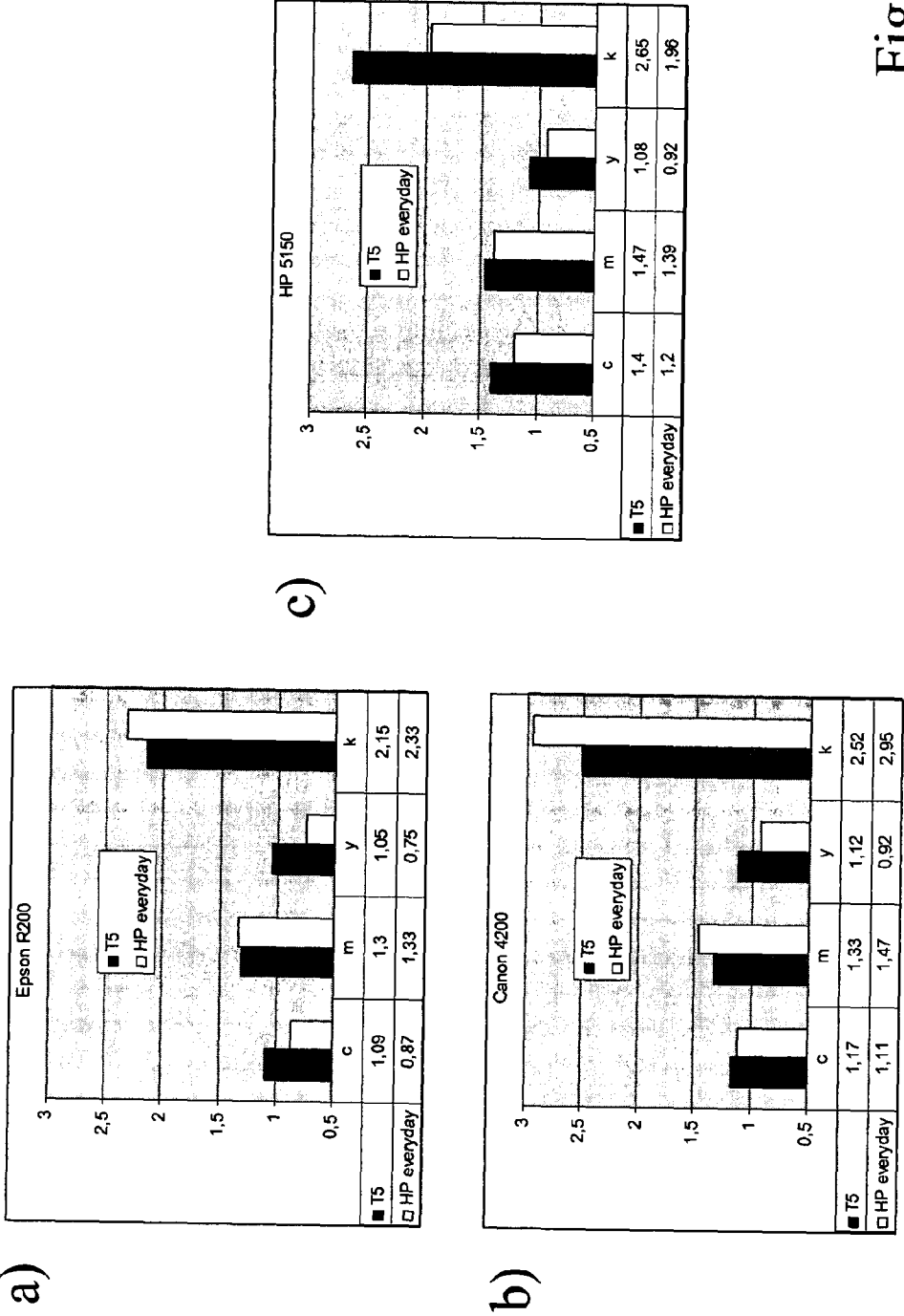
11.    Inkjet paper according to claim 10, wherein the fine particulate silica pigment in

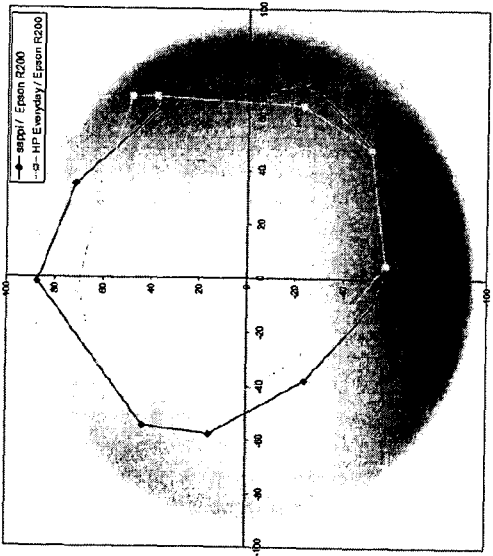
the pre-coat layer is composed of 10 – 30, preferably 15-30 parts in dry weight of a colloidal silica and of 20 – 35, preferably 25-35 parts in dry weight of a silica gel.

12. Inkjet paper according to any of claims 10 or 11, wherein the silica gel in the pre-coat layer has a particle size distribution such that the average particle size is in the range of 0.1-10  $\mu\text{m}$ , preferably below 7  $\mu\text{m}$  and most preferably below 4.0  $\mu\text{m}$  and/or the colloidal silica in the pre-coat layer has a particle size distribution such that the average particle size is in the range of 10 – 120 nm, preferably 40 – 100 nm.
13. Inkjet paper according to any of the claims 8 - 12, wherein the binder part in the pre-coat layer comprises a latex binder and a second binder selected from the group of polyvinyl pyrrolidone binder, PVA, gelatine and mixtures thereof.
14. Inkjet paper according to claim 13, wherein the binder part comprises 2-20, preferably 2-14 parts in dry weight of a latex binder, preferably a styrene butadiene-binder and 2-8, preferably 4-8 parts in dry weight of a polyvinyl pyrrolidone binder, preferably of polyvinyl pyrrolidone with a molecular weight of more than 20'000 Da, even more preferably of more than 30'000 Da, most preferably in the range of 40'000 Da – 80'000 Da.
15. Inkjet paper according to any of the claims 8-14, wherein the pre-coat layer comprises 100 parts in dry weight of a pigment part consisting of 50-75 parts in dry weight, preferably 40-60 parts in dry weight, of a fine particulate ground or precipitated calcium carbonate, wherein the fine particulate calcium carbonate has a particle size distribution such that 50 % of the particles are smaller than 1  $\mu\text{m}$ , preferably smaller than 0.7  $\mu\text{m}$ ;
- 25-50 parts in dry weight, preferably 40-60 parts in dry weight of a fine particulate silica pigment and/or of a fine particulate ground calcium carbonate with surface and internal structure modification as a result of treatment with one or more medium to strong  $\text{H}_3\text{O}^+$  ion providers and optionally with additional treatment of gaseous carbon dioxide.

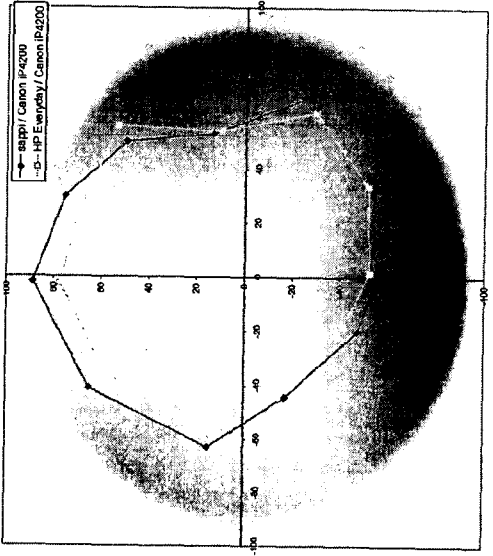
16. Inkjet paper according to any of the claims 8 - 15, wherein the image receiving coating layer comprises
- 100 parts in dry weight of a pigment part consisting of
- 60 – 100, preferably 60 - 90 parts in dry weight of a fine particulate colloidal silica pigment; and
- 0 – 40, preferably 10 - 40 parts in dry weight, preferably 10-30 parts in dry weight, of a fine particulate polymer pigment;
- 3 - 6 parts in dry weight of a binder
- 0-2 parts in dry weight of additives.
17. Inkjet paper according to claim 16, wherein the particulate, preferably solid or vacuolated polymer pigment in the image receiving coating layer has a particle size distribution such that more than 90 % of the particles are smaller than 0.5µm, preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3 µm, in particular between 0.1 and 0.2 µm, or in the case of a vacuolated polymer pigment also with a mean particle size of about 0.6 – 1 µm.
18. Inkjet paper according to any of the claims 8 - 17, wherein the binder part in the image receiving coating layer consists of a PVA-binder, a PVP-binder, a gelatine binder or mixtures thereof.
19. Inkjet paper according to any of the claims 8 - 18, wherein the image receiving coating layer comprises a mordant for the dyes, preferably 0.1-1.5, preferably 0.5 – 1.5 parts in dry weight thereof .
20. Inkjet paper according to any of the claims 8 - 19, wherein the image receiving coating is directly adjacent to the pre-coat layer.
21. Inkjet paper according to any of the claims 8-20, wherein the pre-coat layer has a coating thickness in the range of 5-30 gsm, preferably in the range of 10-20 gsm, and wherein the topcoat layer has a coating thickness in the range of 2-20 gsm, preferably of 5-10 gsm.

22. Inkjet paper according to any of the claims 7 - 20, wherein the pre-coat formulation is essentially free of cationic components and/or wherein the overall coating charge is anionic.
23. Inkjet paper according to any of the claims 8 - 22, wherein the image receiving coating is transparent.
24. Inkjet paper according to any of the claims 8 - 23, wherein the additives in the pre-coat and/or the image receiving coating are selected from the group of defoamers, colorants, brighteners, dispersants, thickeners, water retention agents, preservatives, crosslinkers, lubricants and pH control agents and mixtures thereof.
25. Inkjet paper according to any of the claims 8-24, wherein the image receiving coating layer comprises a cationic mordant for the dye as an additive in an amount of 0.1-1.5 parts per dry weight, preferably 0.5-1 parts per dry weight.
26. Inkjet paper according to any of the claims 8-25, wherein the pre-coat layer is essentially free of cationic mordant additives.
27. Inkjet paper according to any of the claims 8-26, wherein the colloidal silica pigment in the image receiving coating layer is a unmodified anionic colloidal silica.
28. Inkjet paper according to any of the claims 8-27, wherein the fine particulate calcium carbonate pigment in the pre-coat is a precipitated calcium carbonate pigment, preferably a needle-shaped type and/or an anionic type.
29. Inkjet paper according to any of the claims 8 - 28, wherein the end paper has a gloss above or equal to 45% according 75°DIN, preferably above or equal to 50%, even more preferably above or equal to 55%.
30. Inkjet paper according to any of the claims 8 – 29, wherein the pre-coat and/or the receiving coating layer(s) are overall anionic.

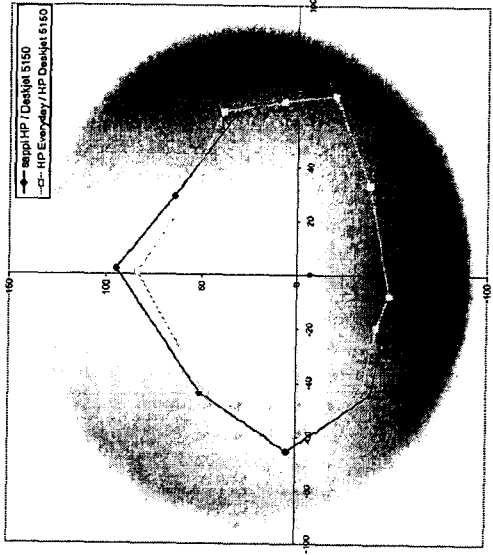




a)



b)



c)

Fig. 2

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2008/005763

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B41M5/52

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)  
B41M

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 practical, 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. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 5 985 424 A (DEMATTE MICHAEL L [US] ET AL) 16 November 1999 (1999-11-16)<br>column 3, lines 9-64<br>claims                                                | 1-30                  |
| A         | WO 2006/003391 A (EASTMAN KODAK CO [US]; BAKER JULIE [GB])<br>12 January 2006 (2006-01-12)<br>paragraph [0015]<br>claims 1,9-12<br>paragraphs [0047], [0048] | 1-30                  |
| X         | EP 1 114 735 A (WESTVACO CORP [US])<br>11 July 2001 (2001-07-11)<br>paragraphs [0005], [0006]<br>paragraphs [0009] - [0014]<br>paragraph [0023]              | 8-30                  |

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                    |
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| <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> |                                                    |
| Date of the actual completion of the international search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Date of mailing of the international search report |
| 17 October 2008                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 31/10/2008                                         |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Authorized officer<br><br>Martins Lopes, Luis      |

# INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/005763

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                         | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | <p>US 6 632 488 B2 (OKUMURA YOSHITAKA [JP] ET AL) 14 October 2003 (2003-10-14)<br/> examples I-2<br/> examples III-1<br/> claims<br/> column 3, lines 45-67<br/> -----</p> | 1-30                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/005763

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s)                                            | Publication<br>date                                  |
|-------------------------------------------|----|---------------------|-----------------------------------------------------------------------|------------------------------------------------------|
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| WO 2006003391                             | A  | 12-01-2006          | EP 1773598 A1<br>JP 2008505780 T<br>US 2008062234 A1                  | 18-04-2007<br>28-02-2008<br>13-03-2008               |
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| US 6632488                                | B2 | 14-10-2003          | DE 69907993 D1<br>DE 69907993 T2<br>EP 0938980 A2<br>US 2003068473 A1 | 26-06-2003<br>19-05-2004<br>01-09-1999<br>10-04-2003 |