

(19)



(11)

EP 1 921 207 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

14.05.2008 Bulletin 2008/20

(51) Int Cl.:

D21H 21/52 (2006.01)

(21) Application number: **06025073.5**

(22) Date of filing: **10.11.2006**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

Designated Extension States:

AL BA HR MK RS

(72) Inventors:

- **Goldhalm, Gisela
1120 Wien (AT)**
- **Drexler, Gerhard
3361 Aschbach (AT)**

(71) Applicant: **Mondi Business Paper Services AG
3363 Ulmerfeld-Hausmening (AT)**

(74) Representative: **Landgraf, Elvira
Schulfeld 26
4210 Gallneukirchen (AT)**

(54) **Method for application of nano-particles during a papermaking process**

(57) The invention deals with a method of making a paper with improved surface properties, characterized in that that nano-hybrid particles containing 1-99% organic nano particles of polystyrene or a styrene copolymer and 99-1% inorganic particles are applied in the wet end of

the paper making process or as a solution or dry onto the wet or dried paper fiber web as well as the paper produced by said process.

EP 1 921 207 A1

Description

[0001] The invention deals with a method for inline application of nano-hybrid particles during a papermaking process.

[0002] EP-A 1 422 248 discloses an aqueous dispersion containing nano-particles which is used as a paper sizing composition to improve the surface characteristics of the paper or the like.

Application of this composition on porous substrates such as paper is not very effective, because the nano-particles tend to disappear in the pores of the substrate during application, especially when applied with a blade or roll.

[0003] It is desirable to further improve the surface characteristic of porous substrates such as paper, by using all beneficial properties of a coating solution and to simplify the method of producing said paper.

[0004] It is an object of the invention to provide a method for producing a paper especially a printing paper with improved surface properties, especially enhanced optical appearance and improved print quality.

[0005] Object of the invention is therefore a method of making a paper with improved properties, characterized in that nano-hybrid particles containing 1-99% organic nano particles of polystyrene or a styrene copolymer and 99-1% inorganic particles is applied in the wet end of the paper making process or onto the wet or dried paper fiber web.

[0006] The nano-hybrid particles consist of an organic and an inorganic part. Preferably the organic part is nano sized having a particle size of about 2 - 100 nm. The organic part preferably is of spherical shape.

The inorganic part may be nano sized too or micro sized (50 nm - 20 μ m) and may have different shapes.

[0007] The organic nano-particles are adhered to the surface of the inorganic particles, thus when applied in an aqueous solution on the surface of a porous substrate the nano-particles cannot disappear in the pores but are kept close to the surface.

[0008] Organic part of the nano-hybrid particles may be a polymer or a copolymer preferably polystyrene or styrene copolymers. Especially preferred are styrene maleimid copolymers or other styrene containing copolymers e.g. with butadiene, acrylic acid and the like. The styrene part may also have functional groups such as sulfonic acid groups, carboxylic groups or pyridine groups.

[0009] The nano-hybrid particles may be prepared for example by dissolving the polymer or a copolymer of maleic anhydride with a vinyl monomer in water, adding a RNH₂ compound, R being H, alkyl with 1 - 18 carbon atoms or aryl and heating the resultant mixture in the presence of larger particles to make the imides. The polymeric particles will settle down on the larger particles.

[0010] Inorganic part can be CaCO₃ (ground or precipitated), TiO₂, clay, aluminium oxide, aluminium hydroxide, talkum, zincoxide, zeolithe and the like.

[0011] The hybrid particles contain 1-99 wt% organic and 99-1 wt% inorganic material. Preferably the hybrid particles contain 3-45% of organic material and 97-55 wt% of inorganic material.

5 **[0012]** The nano-hybrid particles are preferably applied dry or preferably in an aqueous suspension with a solid content of 1-99%, preferably 10 - 80wt%, more preferably 35 - 70 wt% .

10 **[0013]** For application at the wet end the composition preferably contains 1- 20% of organic material and 99 - 80 wt% of inorganic material, for application on the dry or wet fiber web, the composition preferably contains 3 - 45 wt% of organic material and 97 - 55 wt% of inorganic material.

15 **[0014]** The nano-hybrid particles can be applied in the wet end by addition to the fiber suspension or applied onto the wet or dried fiber web.

[0015] For application in the wet end of the paper making process up to 20 - 35 wt% of the nano hybrids may be added.

Usually the fiber content of the paper fiber suspension will be 0,6 to 1,5 wt%.

[0016] In the second case (application to the dry or wet fiber web) the nano-hybrid particles suspension may be applied pure or mixed with different types of binders, eg. starch and starch derivates, PVOH, branched polymers, styrene acrylate latex, styrene butadiene latex, casein and/or several additives for brightness, shading and adjustment of the dielectrical properties, as NaCl, KCl, CaCl₂, and the like.

25 **[0017]** Starch and starch derivatives may be added in an amount up to 10 wt%, preferably 1 - 2 wt%, PVOH may be added up to 10 wt%, preferably 0- 5 wt%, branched polymers up to 20 wt%, preferably 2-10 wt%, styrene acrylate latex, and styrene butadiene latex up to 20 wt%, preferably 5- 12 wt%. Additives for brightness may be present in an amount of 0 - 5 wt%, preferably 1- 2 wt%, shading additives may be present in an amount of 0 - 2 wt% preferably 0 - 1 wt%, additives for the adjustment of dielectric properties may be added 0 - 7 wt % , preferably 0 - 2 wt % .

40 **[0018]** The nano particles may be applied inline or offline on the fiberweb.

Inline application of the dry nano-hybrid particles or the suspension of the nano-hybrid particles may be carried out by conventional surface coating methods e.g. size press, film press, blade, roller bar, curtain coating, spray coating and the like.

45 **[0019]** Offline application may be carried out by conventional surface coating methods e.g. size press, film press, blade, roller bar, curtain coating, spray coating and the like or by conventional printing techniques such as intaglio or gravure printing or flexographic printing or the like.

55 **[0020]** Further, if applied in the wet end of the paper making process addition of the aqueous solution of nano-hybrid particles results in improved process parameters, such as improved de-watering performance. Thus the

process or method for preparing the paper becomes more economical and thus cheaper.

[0021] The paper produced shows improved surface appearance, as well as improved printing quality, especially in laser and digital printing processes.

[0022] Product will be an uncoated, pigmented or coated office and communication paper. Depending on process parameters the resulting paper may be glossy or have a matt glaze.

Example1:

[0023] Production of a multipurpose grade:

Hybrid pigment:

10 wt % organic nanoparticle

90 wt% precipitated calcium carbonate (PCC)

pH=10

50 % slurry

added to a 4 wt% fiber suspension in the mixing vat + additives (defoamers, starch, retention aids, optical brighteners, shading colors, sizing agent ...)

Content of this suspension is

50 wt% hybrid pigment

46 wt% fibers

4 wt % additives

This suspension is diluted down to 0,8 % and processed on the paper machine as conventional or laser grade paper.

Example2:

[0024] Production of a pigmented laser or digital printing grade paper

Coating contents:

100 parts	Hybrid pigment Consisting of 30 parts talcum 30 parts clay 40 parts Styrenemaleimid-Copolymer
10 parts	Styrene butadiene latex
0,5parts	Highly branched polymer (Hybrane)
0,7 parts	Rheology modifier (PVOH)
1 part	Optical brightener
0,1 part	Shading color
0,1 part	defoamer
0,1 part	biocide

Solid content: 50 % +/- 2 %

pH=7-10

Application on film press with rod no.4 or different rod.

Application of 15 g/m² per side

Machine calendering or offline calendering for enhanced smoothness

Product:

[0025]

10

Laser and digital printing paper

80 - 300 g/m²

15 Claims

1. Method of making a paper with improved surface properties, **characterized in that** that nano-hybrid particles containing 1-99% organic nano particles of polystyrene or a styrene copolymer and 99-1% inorganic particles are applied in the wet end of the paper making process or as a solution or dry onto the wet or dried paper fiber web.
2. Method according to claim 1, **characterized in that** nano-hybrid particles contain 3-45% of organic material and 97-55 % of inorganic material. For application onto the wet or dried fiber web.
3. Method according to claim 1, **characterized in that** nano-hybrid particles contain 1- 20% of organic material and 99 - 80% of inorganic material for application in the wet end of the paper making process.
4. Method according to one of claims 1-3, **characterized in that** the organic part of the nano-hybrid particles consist of styrene copolymers with maleic imide, butadiene or acrylic acid.
5. Method according to one of claims 1 to 4 **characterized in that** the inorganic particles are CaCO₃ (ground or precipitated), TiO₂, clay, aluminium oxide, aluminium hydroxide, talkum, zincoxide or zeolithe.
6. Method according to one of claims 1 to 5 **characterized in that**, the organic particles are formed from an copolymer of styrene with maleic imide or butadiene or acrylic acid.
7. Method according to one of claims 1 to 6 **characterized in that** the solution applied contains binders, eg. starch and starch derivatives, PVOH, branched polymers, styrene acrylate latex, styrene butadiene latex, casein and/or several additives for brightness, shading and adjustment of the dielectrical properties, as NaCl, KCl, CaCl₂, and the like.

8. Method according to claims 1 to 7, **characterized in that** the nano hybrid particles are applied inline by conventional surface coating methods e.g. size press, film press, blade, roller bar, curtain coating or spray coating. 5
9. Method according to claims 1 to 7, **characterized in that** the nano hybrid particles are applied offline by conventional surface coating methods e.g. size press, film press, blade, roller bar, curtain coating, spray coating or by conventional printing techniques such as intaglio or gravure printing or flexographic printing. 10
10. Use of the paper produced according to one of claims 1 to 9 as uncoated, pigmented or coated office and communication paper. 15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 02 5073

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 2001/036990 A1 (BOBSEIN BARRETT RICHARD [US] ET AL) 1 November 2001 (2001-11-01) * paragraphs [0016], [0029], [0030]; claims 1,2 *	1,5,10	INV. D21H21/52
X	DE 39 24 846 A1 (BASF AG [DE]) 14 February 1991 (1991-02-14) * claims 1-3; example 1 *	1,5,10	
X	US 4 567 099 A (VAN GILDER RON L [US] ET AL) 28 January 1986 (1986-01-28) * claims 1-3; example 1 *	1,5,10	
X	US 2002/136871 A1 (LOCKETT NICOLE ALISA RENEE [US]) 26 September 2002 (2002-09-26) * paragraphs [0041], [0042]; claims 1-14 *	1,10	
A	WO 03/031719 A (FLETCHER BUILDING HOLDINGS LTD [NZ]; GUY BRADLEY MARK [AU]; SCEATS KEV) 17 April 2003 (2003-04-17) * the whole document *	1-10	
A	US 2004/161594 A1 (JOYCE MARGARET K [US] ET AL) 19 August 2004 (2004-08-19) * the whole document *	1-10	
A	WO 2004/030917 A (SAPPI NETHERLANDS SERVICES B V [NL]; HAENEN JEAN-PIERRE [NL]; DE JONG) 15 April 2004 (2004-04-15) * the whole document *	1-10	TECHNICAL FIELDS SEARCHED (IPC)
			D21H
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 22 May 2007	Examiner Karlsson, Lennart
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

1
EPO FORM 1503 03.82 (P04C01)

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

EP 06 02 5073

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.

22-05-2007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2001036990 A1	01-11-2001	ZA 200102213 A	18-09-2001
DE 3924846 A1	14-02-1991	NONE	
US 4567099 A	28-01-1986	AU 573887 B2	23-06-1988
		AU 4658085 A	26-06-1986
		CA 1244569 A1	08-11-1988
		JP 61152897 A	11-07-1986
US 2002136871 A1	26-09-2002	AU 2002235415 A1	06-08-2002
		CA 2430976 A1	01-08-2002
		EP 1354098 A2	22-10-2003
		JP 2004518039 T	17-06-2004
		WO 02059422 A2	01-08-2002
WO 03031719 A	17-04-2003	AU 2002343275 A1	22-04-2003
US 2004161594 A1	19-08-2004	WO 2004074574 A2	02-09-2004
WO 2004030917 A	15-04-2004	AU 2003271659 A1	23-04-2004
		BR 0306602 A	07-12-2004
		CA 2497751 A1	15-04-2004
		JP 2006501382 T	12-01-2006
		KR 20050060087 A	21-06-2005
		US 2006257593 A1	16-11-2006

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1422248 A [0002]