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

Auftragsverfahren von Nanopartikeln für Papierherstellung

Procédé d'application des nanoparticules dans une procédé de fabrication de papier

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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.

[0003] 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.

[0004] 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.

[0005] 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.

[0006] Object of the invention is therefore a method of making a paper with improved surface properties, characterized in that that nano-hybrid particles consisting of organic nano particles and inorganic particles, the organic nano-particles being adhered to the surface of the inorganic particles wherein the nanohybrid particles contain 1-99% organic nano particles of polystyrene or a styrene copolymer having a size of 2 - 100 nm and 99-1% inorganic particles having a size of 50 nm - 20 μm are applied in the wet end of the paper making process by addition to the fiber suspension or applied onto the wet or dried paper fiber web.

[0007] 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.

[0008] 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.

[0009] 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.

[0010] 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 RNH_2 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.

[0011] Inorganic part can be $CaCO_3$ (ground or precipitated), TiO_2, clay, aluminium oxide, aluminium hydroxide, talkum, zincoxide, zeolithe and the like.

[0012] 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.

[0013] 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% .

[0014] 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.

[0015] 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.

[0016] 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%.

[0017] 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, $CaCl_2$, and the like.

[0018] 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 %.

[0019] 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.

[0020] 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.

[0021] 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.

[0022] The paper produced shows improved surface appearance, as well as improved printing quality, especially in laser and digital printing processes.

[0023] Product will be an uncoated, pigmented or coated office and communication paper. Depending on process parameters the resulting paper may be glossy ot have a matt glaze.

Example1:

[0024] 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:

[0025] 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/m^2 per side
Machine calendering or offline calendering for enhanced smoothness

Product:

[0026]

Laser and digital printing paper
80 - 300 g/m^2

Claims

1. Method of making a paper with improved surface properties, **characterized in that** that nano-hybrid particles consisting of organic nano particles and inorganic particles, the organic nano-particles being adhered to the surface of the inorganic particles wherein the nanohybrid particles contain 1-99% organic nano particles of polystyrene or a styrene copolymer having a size of 2 - 100 nm and 99-1% inorganic particles having a size of 50 nm - 20 μm are applied in the wet end of the paper making process by addition to the fiber suspension or applied 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 to 3 **characterized in that** the inorganic particles are $CaCO_3$ (ground or precipitated), TiO_2, clay, aluminium oxide, aluminium hydroxide, talkum, zincoxide or zeolithe.

5. Method according to one of claims 1 to 4 **characterized in that**, the organic paricles are formed from an copolymer of styrene with maleic imide or butadiene or acrylic acid.

6. Method according to one of claims 1 to 5 **characterized in that** the solution applied contains 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, $CaCl_2$, and the like.

7. Method according to claims 1 to 6, **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.

8. Method according to claims 1 to 6, **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.

9. Use of the paper produced according to one of claims 1 to 9 as uncoated, pigmented or coated paper.

Patentansprüche

1. Verfahren zur Herstellung von Papier mit verbesserten Oberflächeneigenschaften, **dadurch gekennzeichnet, dass** Nano-Hybridpartikel, die aus organischen Nanopartikel und anorganischen Partikeln bestehen, wobei die organischen Nanopartikel haftend auf die Oberfläche der anorganischen Partikel aufgebracht werden, wobei die Nano-Hybridpartikel 1 bis 99 % organische Nanopartikeln aus Polystyrol oder einem Styrolcopolymer mit einer Größe von 2 bis 100 nm und 99 bis 1% anorganische Partikel mit einer Größe von 50 nm bis 20 μm enthalten, in der Nasspartie des Papierherstellungsvorgangs zur Anwendung kommen, indem sie der Fasersuspension zugesetzt werden, oder auf das nasse oder getrocknete Papierfaservlies aufgebracht werden.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Nano-Hybridpartikel 3 bis 45 % an organischem Material und 97 bis 55 % an anorganischem Material zum Aufbringen auf das nasse oder getrocknete Faservlies einbringen.

3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Nano-Hybridpartikel 1 bis 20 % an organischem Material und 99 bis 80 % an anorganischem Material für das Aufbringen in der Nasspartie des Papierherstellungsvorgangs enthalten.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** es sich bei den anorganischen Partikeln um $CaCO_3$ (gemahlen oder gefällt), TiO_2, Ton, Aluminiumoxid, Aluminiumhydroxid, Talkum, Zinkoxid oder Zeolith handelt.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die organischen Partikel aus einem Copolymer von Styrol mit Maleinsäureimid oder Butadien oder Acrylsäure gebildet sind.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die aufgebrachte Lösung Bindemittel enthält, z.B. Stärke und Stärkederivate, PVOH, verzweigte Polymere, Styrol-Acrylat-Latex, Styrol-Butadien-Latex, Kasein und/oder mehrere Hilfsstoffe zur Aufhellung, zur Tönung und zur Einstellung dielektrischer Eigenschaften, wie etwa NaCl, KC1, $CaCl_2$ und Ähnliches.

7. Verfahren nach den Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die Nano-Hybridpartikel prozessintegriert mittels herkömmlicher Oberflächenbeschichtungsverfahren aufgebracht werden, z.B. mittels einer Leimpresse, einer Filmpresse, einer Rakel, eines Drehstabs, durch Vorhangstreichen oder durch Sprühstreichen.

8. Verfahren nach den Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die Nano-Hybridpartikel separat mittels herkömmlicher Oberflächenbeschichtungsverfahren aufgebracht werden, z.B. mittels einer Leimpresse, einer Filmpresse, einer Rakel, eines Drehstabs, durch Vorhangstreichen, durch Sprühstreichen oder mittels herkömmlicher Drucktechniken wie etwa im Stichtiefdruck- oder Rotationstiefdruckverfahren oder im Flexodruckverfahren.

9. Verwendung des Papiers, das nach einem der Ansprüche 1 bis 9 hergestellt wurde, als unbeschichtetes, pigmentiertes oder beschichtetes Papier.

Revendications

1. Procédé de préparation d'un papier ayant des propriétés de surface améliorées, **caractérisé en ce que** des particules nanohybrides se composant de particules nanométriques organiques et de particules inorganiques, les particules nanométriques organiques adhérant à la surface des particules inorganiques, les particules nanohybrides contenant de 1 à 99 % de particules nanométriques organiques de polystyrène ou d'un copolymère de styrène ayant une taille de 2 à 100 nm et de 99 à 1 % de particules inorganiques ayant une taille de 50 nm à 20 μm, sont appliquées dans la partie humide du procédé de préparation de papier par ajout à la suspension de fibres ou appliquées sur le réseau des fibres de papier humide ou sec.

2. Procédé selon la revendication 1, **caractérisé en ce que** les particules nanohybrides comprennent de 3 à 45 % de matière organique et de 97 à 55 % de matière inorganique, pour une application sur le réseau de fibres humide ou sec.

3. Procédé selon la revendication 1, **caractérisé en ce que** les particules nanohybrides comprennent de 1

à 20 % de matière organique et de 99 à 80 % de matière inorganique, pour une application dans la partie humide du procédé de préparation de papier.

4. Procédé selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** les particules inorganiques sont $CaCO_3$ (broyé ou précipité), TiO_2, l'argile, l'oxyde d'aluminium, l'hydroxyde d'aluminium, le talc, l'oxyde de zinc ou une zéolithe.

5. Procédé selon l'une quelconque des revendications 1 à 4, **caractérisé en ce que** les particules organiques sont formées à partir d'un copolymère de styrène avec un imide maléique ou un butadiène ou un acide acrylique.

6. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** la solution appliquée comprend des liants, par exemple de l'amidon et des dérivés d'amidon, un PVOH, des polymères ramifiés, un latex de styrène-acrylate, un latex de styrène-butadiène, de la caséine et/ou plusieurs additifs pour la brillance, la nuance et l'ajustement des propriétés diélectriques, tels que NaCl, KCl, $CaCl_2$ et analogues.

7. Procédé selon l'une quelconque des revendications 1 à 6, **caractérisé en ce que** les particules nanohybrides sont appliquées en continu par des procédés de revêtement de surface conventionnels, par exemple par revêtement par presse colleuse, presse à film, lame, barre de compression rotative, encollage en rideau ou atomisation.

8. Procédé selon l'une quelconque des revendications 1 à 6, **caractérisé en ce que** les particules nanohybrides sont appliquées de manière discontinue par des procédés de revêtement de surface conventionnels, par exemple par revêtement par presse colleuse, presse à film, lame, barre de compression rotative, encollage en rideau, atomisation ou par des techniques d'impression conventionnelles telles que l'impression en relief ou par héliogravure ou l'impression flexographique.

9. Utilisation du papier produit selon l'une quelconque des revendications 1 à 8, en tant que papier non couché, pigmenté ou couché.

REFERENCES CITED IN THE DESCRIPTION

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