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(19) **United States**(12) **Patent Application Publication****Silenius et al.**(10) **Pub. No.: US 2004/0173329 A1**(43) **Pub. Date:****Sep. 9, 2004**(54) **COATED FIBROUS WEB AND PROCESS
FOR THE PRODUCTION THEREOF**(52) **U.S. Cl.** **162/135**; 162/181.1; 162/181.2;
427/212(76) Inventors: **Petri Silenius**, Lohja as (FI); **Jari
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Leskela**, Muijala (FI)(57) **ABSTRACT**Correspondence Address:
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The present invention relates to a coated fibrous web and a method for producing it. According to the present invention, a coated fibrous web comprises a filler-containing base web that has a pigment-containing coating layer on at least one surface. The filler of the base web consists at least partially of cellulose or lignocellulose fibrils, on the surface of which light scattering material particles have been deposited. The filler comprises cellulose or lignocellulose fibrils having an average thickness less than 5 μm produced from plant fibres by refining and screening. Considerable advantages are achieved with the present invention. With the help of the composite filler, the formation of the fibrous web can be improved significantly without impairing the retention, which makes it possible to achieve an extremely smooth substrate for the coating. The smoothness of the surface can also be improved. Furthermore, the fines-based carrier fraction of the filler compresses the surface of the base paper so that the coating does not penetrate too much into the fibre network. Due to these reasons even a small amount of coating produces good coverage and quality improving cost-efficiency.

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COATED FIBROUS WEB AND PROCESS FOR THE PRODUCTION THEREOF

[0001] The present invention relates to a coated fibrous web according to the preamble of claim 1.

[0002] This kind of a fibrous web generally comprises a base web with a filler, having a pigment-containing coating layer on at least one surface.

[0003] The present invention relates also to the method according to the preamble of claim 12 for producing a coated fibrous web.

[0004] The printability of paper and board—properties of the printing surface and the printing process—are improved by coating the paper with different mineral coatings. The purpose of the coating is to cover the fibres and the fibre flocks of the paper and board and, by these measures, to decrease the roughness of the surface and the size of the pores of the surface. The coatings usually consist of pigments and binders, as well as of various additives.

[0005] The coatability of paper, in other words the capability of the base paper to be covered with a coating, has become even more important with the increased demand for lightweight paper grades. Although the coverage can be affected by the properties of the coating mix and the coating manner, the qualities of the base paper are also important. Good formation and smoothness as well as suitable air resistance and porosity are properties of the base paper that are the most important factors affecting the coatability, especially when good quality is aspired with a small amount of coating. The fibre web to be coated usually contains filler. The filler improves the formation of the paper web by filling the spaces between the fibres. Also the opacity of the web can be improved with the help of the filler.

[0006] Finnish Patent Specification No. 100729 discloses a papermaking filler comprising porous aggregates formed by precipitated calcium carbonate particles on the surface of fines. What characterises this new kind of filler is that, according to the patent specification, the calcium carbonate is precipitated on fine fibrils produced by refining cellulose fibres and/or mechanical pulp fibres. The size distribution of the fines fraction corresponds mainly to the wire screen fraction P100.

[0007] Based on said patent specification it is possible to increase the content of calcium carbonate in paper, whereby the grammage of the paper can be lowered without changing “other important” properties of paper. The results of the publication are based on the data measured on laboratory sheets by the standards of SCAN-C 26:76 and SCAN-M 5:76, respectively. No mention about the coatability of the paper is made in the publication.

[0008] According to the present invention it has now been found, quite surprisingly, that by filling the paper or board web or a corresponding fibre web with the above-described filler, not only the other important properties of paper remain intact but also the coatability of fibre web is considerably improved.

[0009] Furthermore, within the scope of the present invention it has been found that also other fillers consisting at least partly of cellulose or lignocellulose fibrils, over which light scattering material particles has been precipitated, can be used as fillers. These particles are typically inorganic salts

precipitating in an aqueous phase, such as calcium carbonate, calcium sulphate, barium sulphate and calcium oxalate.

[0010] More specifically, the method according to the present invention is mainly characterised by what is stated in the characterising part of claim 1.

[0011] The method according to the present invention is characterised by what is stated in the characterising part of the claim 12.

[0012] The present invention provides considerable advantages. Thus, a composite filler consisting of fibrils and mineral pigments has been found to provide the base paper with properties that are, as far as coatability is concerned, better than what can be achieved with fillers that are at the present commercially available. Since the composite filler used in the present invention surprisingly can improve considerably the formation of the fibre web without impairing retention, a very smooth coating substrate can be obtained by means of the present invention. The smoothness of the surface can also be improved. Furthermore, the fines-based carrier fraction makes the surface of the base paper denser so that the coating does not penetrate too much into the fibre network. Due to these reasons, even a small amount of coating provides good coverage and a high quality of the coating, improving the cost efficiency.

[0013] In the following, the present invention will be examined more closely with the help of a detailed description and some working examples.

[0014] In the examples below, the filler used in the present invention is based on fibrils obtained from chemical pulp. In this context, chemical pulp refers to a pulp, which has been treated with cooking chemicals for delignification of the cellulose fibres. According to a preferred embodiment, fibrils have been obtained by refining a pulp produced by the sulphate process or by another alkaline pulping process. The present invention can also be applied to modification of fibrils obtained from chemimechanical and mechanical pulp, in addition to chemical pulps.

[0015] Typically, the average thickness of cellulose or lignocellulose fibrils is smaller than 5 μm , conventionally smaller than 1 μm . The fibrils are characterized by at least one of the following criteria:

[0016] a. they correspond to a fraction which passes a 50-mesh (or preferably a 100-mesh) screen; and

[0017] b. their average thickness is 0.01-10 μm (preferably at maximum 5 μm and in particular at maximum 1 μm) and their average length is 10-1500 μm .

[0018] The source material for the fibrils, i.e. the fines based on cellulose or other fibers, is fibrillated by beating it in a pulp refiner. The desired fraction may, when necessary, be separated by using a screen, but fines need not always be screened. Suitable fibril fractions include wire screen fractions P50-P400. Preferably refiners with grooved blades are used.

[0019] The light-scattering material particles in the filler are inorganic or organic salts that can be formed from their source materials by precipitation in an aqueous medium. Such compounds include calcium carbonate, calcium oxalate, calcium sulphate, barium sulphate, and mixtures thereof. The material particles are deposited on the fibrils.

The amount of an inorganic salt compound in proportion to the fibril amount is approx. 0.0001-95% by weight, preferably approx. 0.1-90% by weight, most suitably approx. 60-80% by weight, calculated from the amount of filler, and approx. 0.1-80% by weight, preferably approx. 0.5-50% by weight, of the paper.

[0020] In the following, the present invention is examined with particular reference to a product according to FI Patent Specification No. 100729, but it is clear that the present invention can be adapted for other products mentioned hereinbefore by changing appropriately the source materials of the light scattering pigment.

[0021] The filler is produced by precipitating a mineral pigment on the surface of fine fibrils prepared from cellulose fibres and/or mechanical pulp fibres. For example, the precipitation of calcium carbonate can be carried out by feeding into an aqueous slush of fibrils an aqueous calcium hydroxide solution which possibly contains a solid calcium hydroxide, and a compound which contains carbonate ions and is at least partly dissolved in water (e.g. sodium carbonate or ammonium carbonate). It is also possible to introduce into the aqueous phase carbon dioxide gas that, in the presence of calcium hydroxide, produces calcium carbonate. There are formed string-of-pearls-like calcium carbonate crystal aggregates, which are held together by fibrils, i.e. fine strands, and in which the calcium carbonate particles are deposited onto the fine fibrils and attached to them. The fine fibrils together with calcium carbonate form string-of-pearls-like strands, and the calcium carbonate aggregates primarily resemble strings of pearls in a pile. In water (slush) the ratio of the effective volume of the aggregates to the pulp is very high compared with the corresponding ratio of conventional calcium carbonate used as filler. By "effective volume" is meant, in this case, the volume required by the pigment.

[0022] The diameter of the calcium carbonate particles in the aggregates is about 0.1 to 5 μm , typically about 0.2 to 3 μm . In particular, the fibrils correspond to wire screen fractions P50 (or P100) to P400. In the filler at least 80%, preferably up to 90%, of the light scattering pigments are attached to the fibrils.

[0023] The paper pulp is slushed by a process known per se (typically to solids content of about 0.1 to 1%) and it is spread on the wire. The above-mentioned filler is added to the fibre slush most suitably in the headbox of a paper or board machine, usually in an amount of about 1 to 100% by weight of fibres of pulp. In other words, the amount of the filler can be up to equal to—or greater than—the amount of the actual pulp. In principle, it is also possible to produce a base web, the fibre material of which consists totally of fibrils of the filler, which implies that the present filler can form from 1 to 100% by weight of the fibre material of the base web.

[0024] The pulp is webbed in a paper or board machine to form a paper or board web. The fibre web is dried and coated and possibly processed further, for example, by calendering.

[0025] Coating can be carried out as single-coating or double-coating, whereupon the coating colour can be used as single-coat mixes and as so called precoating and surface-coat mixes. Also triple coatings are possible. In general, the coating colour according to the present invention contains

from 10 to 100 parts by weight of at least one pigment or mixture of pigments, from 0.1 to 30 parts by weight of at least one binder and from 1 to 10 parts by weight of other additives known per se.

[0026] The typical composition of a precoating mixture is as follows:

Coating pigment (for example, coarse calcium carbonate)	100 parts by weight
Binder	1–20% of the weight of the pigments
Additives and auxiliary agents	0.1–10% of the weight of the pigments
Water	the rest

[0027] Water is added to the precoating mix so that the solids content is generally from 40 to 70%.

[0028] According to the present invention, the composition of the surface-coat mixture or single-coat mixture is as follows:

Coating pigment I (for example, fine carbonate)	10–90 parts by weight
Coating pigment II (for example fine kaolin)	10–90 parts by weight
Pigment total	100 parts by weight
Binder	1–20 parts by weight
Additives and auxiliary agents	0.1–10 parts by weight
Water	the rest

[0029] Water is added to this kind of a coating colour so that the dry solids content is typically from 50 to 75%.

[0030] According to the present invention, in the coating colours presented above it is possible to use pigments that have a steep particle size distribution, so that the case at maximum 35% of the pigment particles are smaller than 0.5 μm , preferably at maximum 15% are smaller than 0.2 μm .

[0031] The present invention is applicable to any pigment. Precipitated calcium carbonate, ground calcium carbonate, calcium sulphate, calcium oxalate, aluminium silicate, kaolin (hydrous aluminium silicate), aluminium hydroxide, magnesium silicate, talc (hydrous magnesium silicate), titanium dioxide and barium sulphate, and mixtures thereof can be mentioned as examples of the pigments. Synthetic pigments can also be used. Of the pigments mentioned above, the main pigments are kaolin, calcium carbonate, precipitated calcium carbonate and gypsum, which in general constitute over 50% of the dry solids in the coating mix. Calcined kaolin, titanium dioxide, satin white, aluminium hydroxide, sodium silicoaluminate and plastics pigments are additional pigments, and their amounts are in general less than 25% of the dry solids in the mix. Of the special pigments, special-quality kaolins and calcium carbonates, as well as barium sulphate and zinc oxide, should be mentioned.

[0032] The present invention is applied especially preferably to calcium carbonate, calcium sulphate, aluminium silicate and aluminium hydroxide, magnesium silicate, titanium dioxide and/or barium sulphate, as well as mixtures thereof, in which case, especially preferably, the principal

pigment in the pre-coat mixes is calcium carbonate or gypsum and in surface-coat mixes and single-coat mixes the principal pigment consists of mixtures of calcium carbonate or gypsum and kaolin.

[0033] It is possible to use any known binders generally employed in paper production as binders in the coating colours. Besides the individual binders, it is also possible to use mixtures of binders. Examples of typical binders include synthetic latexes made up of polymers or copolymers of ethylenically unsaturated compounds, e.g. copolymers of the butadiene-styrene type, which possibly also have a comonomer containing a carboxyl group, such as acrylic acid, itaconic acid or maleic acid, and polyvinyl acetate having comonomers that contain carboxyl groups. Together with the materials cited above, it is also possible to use, for example, the water-soluble polymers, starch, CMC, hydroxyethyl cellulose and polyvinyl alcohol as binders.

[0034] Furthermore, it is possible to use conventional additives and auxiliary agents, such as dispersants (e. g. sodium salt of polyacrylic acid), agents affecting the viscosity and water retention of the mix (e. g. CMC, hydroxyethyl cellulose, polyacrylates, alginates, benzoate), so-called lubricants, hardeners used for improving water-resistance, optical auxiliary agents, anti-foaming agents, pH control agents, and preservatives in the coating composition. Examples of lubricants include sulfonate oils, esters, amines, calcium or ammonium stearates; of agents improving water resistance, glyoxal; of optical auxiliary agents, diaminostilbene disulfonic acid derivatives; of anti-foaming agents, phosphate esters, silicones, alcohols, ethers, vegetable oils; of pH control agents, sodium hydroxide, ammonia; and finally of preservatives, formaldehyde, phenol, quaternary ammonium salts.

[0035] The coating mix can be applied to the material web in a manner known per se. The method according to the present invention for coating paper and/or board can be carried out with a conventional coating apparatus, i.e. by blade coating, or by film coating or JET application.

[0036] During coating, a coating layer having a grammage of 5-30 g/m² is formed at least on one surface, preferably on both surfaces. An uncoated side can be treated, for example, by web sizing.

[0037] With the aid of the present invention, coated and optionally calendered cellulose-containing material webs having excellent printing properties, good smoothness and high opacity and brightness, can be produced. By "cellulose-containing material" we refer to the paper or board or a corresponding cellulosic material derived from a lignocellulose-containing raw material, in particular from wood or from annual or perennial plants. The said material can be wood-containing or wood-free, and it can be produced from mechanical, semi-mechanical (chemimechanical) or chemical pulp. Chemical pulp or mechanical pulp may be bleached or unbleached. The material may also contain recycled fibers, in particular recycled paper or recycled board. The material may also contain recycled fibers, in particular recycled paper or recycled board. The grammage of the material web ranges typically from 35 to 500 g/m², typically it is about 50 to 450 g/m².

[0038] In general the grammage of the base paper is 20-250 g/m², preferably 30-80 g/m². By coating a base

paper of this type, the grammage of which is approx. 50-70 g/m², with 10-20 g of coating/m²/side and by calendering the paper a product that has a grammage of 70-110 g/m², a brightness of at least 90%, an opacity of at least 90% is obtained. An especially preferred product is a coated offset paper in which high gloss and high opacity and bulk are combined. The present invention is suitable also for production of coated fine paper, possibly also for those that contain mechanical pulp.

[0039] The following non-limiting examples illustrate the present invention. The measurement results indicated for the paper properties in the examples have been determined by the following standard methods:

[0040] Surface roughness: SCAN-P76:95

[0041] Porosity: SCAN-P60

[0042] Resistance of air permeability: SCAN-M8,P19

EXAMPLE 1

[0043] Production of Filler

[0044] Refining of Chemical Pulp

[0045] Birch sulphate pulp was refined with a Valmet JC-01 refiner to produce pulp that is suitable for production of the filler. The consistency of refining was about 4% and the total energy consumption was 343 kWh/t and the specific edge load was 0.5 J/m.

[0046] Properties of the product are presented in Table 1.

TABLE 1

Fibre properties before and after refining		
	Before refining	After refining
Fibre length (length), mm	0.86	0.58
Fibre length (weight), mm	1.00	0.77
SR°	16	86

[0047] Carbonating of Pulp

[0048] Carbonating was performed in tap water according to the FI Patent Specification No. 100729. The water slurry was obtained, the dry matter content of which was 2.22% and total amount 248 m³. The final product had CaCO₃ content of 69.7% and a specific surface area 10.6 m²/kg.

EXAMPLE 2

[0049] Production of Base Paper

[0050] The product produced in Example 1 was used as a filler in coated fine papers. The following table presents the results that were obtained in the test where fine paper was produced on the pilot machine (FEX) of STFI in Stockholm:

TABLE 2

<u>Properties of the surface of fine paper</u>					
Filler	Filler content, %	Formation, %	Porosity Ml/min (Bendtsen)	Resistance of air permeability, s (Gurley)	Roughness ml/min (Bendtsen)
PCC	18.0	10.6	761	17.6	814
PCC	21.0	11.1	799	16.1	862
SuperFill	17.8	10.4	543	26.5	771
Superfill	22.4	9.5	439	32.3	611

[0051] It appears from the results of the table that a fines-based filler described in this invention improves formation and smoothness of the base paper in comparison to a commercial PCC filler to the degree that the effect on the coatability of paper is surprisingly good. The effect grows in direct relation to the amount of the filler. Moreover, the impermeability or density of the surface is greater with the filler in question (SuperFill), a property, which can be taken advantage of, especially in the context of the lightweight papers, as the coatability of the mix is better.

EXAMPLE 3

[0052] Mill Trial

[0053] A1. Production of Filler-Containing Paper

[0054] A base paper that has a grammage of 56 g/m², was produced in factory conditions for coating. The slush consisted of a mixture of birch pulp (74%) and pine pulp (24%). After refining, the SR value of the pine was 32 to 34° and that of birch was 22 to 25°. The SR value of the pulp in the headbox was 35 to 40°.

[0055] The wire compartment of the paper machine had a hybride wire of Valmet (Sym-former), and the wet pressing compartment consisted of a Valmet Sym-Press II that has a triple compressor and a conventional drying section.

[0056] Three different fillers were used in the base paper, namely products Finntalc F 15 SL (talc of Mondo Minerals), Albacor HO (PCC of Specialty Minerals) and a composite filler described in the Example 1, referred to hereinafter as "SuperFill". Talc was used as filler in amounts of 10% and 15% and SuperFill in amount of 10%, 15% and 20%.

[0057] Nanoparticles and cationic starch (Compozil Plus; EKA NP 780 nanoparticle and EKA PL 1510 C-PAM, supplier: EKA Chemicals) were used as retention chemicals. The dosage amounts in the case of talc and PCC were as follows: nanoparticle 280 g/t, polymer 70 g/t, and with SuperFill: nanoparticle 280 g/t, polymer 50 g/t. The amounts of cationic starch and resin adhesive used were 8 kg/t and 5.2 g/t. The alum was administered for talc at 13 kg/t and with PCC and SuperFill at 19 kg/t.

[0058] A2. Results

[0059] The coulter-oil porosity was measured from the base paper samples. No significant differences were observed in the pore size distribution with low filler contents. 75% of all pores were in the range of 1.2 to 1.8 μ m (around the maximum point). When the filler content was increased to 20%, significant differences were observed. In the case of PCC, the median of the pore size increased as the

amount of filler was increased. The median decreased and the distribution narrowed with the SuperFill filler, whereupon 75% of the values were around 0.8 μ m. The same effect can be seen with talc but in a smaller scale. When the filler content is 20% with Superfill as the filler, the median of the pore size was only 60% of the corresponding value of the PCC, and the width of the pore size distribution (75% of values) was only 34% of values obtained with the PCC.

[0060] Thus, it can be concluded from the data that the SuperFill provides paper, the surface of which is more enclosed than the surface of the paper filled with PCC, which facilitates the coating and improves the quality of paper due to the better coverage. In other words, better glossier and smoother surface is obtained as the coating pigments cannot penetrate into the base paper as easily.

[0061] B1 Online-Coating

[0062] The base paper described hereinbefore was coated one-side and the other side was surface-sized. The ABC single-blade coater of BTG was used for coating. The surface sizing was performed in the same unit by film transferring on the backing-roll of the coater. The machine velocity was 750 m/min and length of the reeler of the web was 252 cm. Online-coating was carried out after the fourth drying group and the coating was dried with drying cylinders (the 5th drying group).

[0063] Online-coating was made on base papers that had fillers containing 15% of talc or SuperFill, respectively. Only the wire side was coated (13 g/m²), the surface side was surface-sized (0.5 g/m²).

[0064] Runnability of the online-coater was good with the SuperFill. The coating conditions were kept constant and they are presented in the Table 3. The composition of the coating mix or solids content did not change during the test.

TABLE 3

<u>Coating conditions</u>		
	Talc	SuperFill
Basis weight of base paper, g/m ²	53.8	53.0
Basis weight of roller, g/m ²	70.1	68.5
Basis weight of coating, g/m ²	13.1	12.6
Moisture of base paper, %	1.5	1.7
Moisture of roller, %	5.9	5.4
Blade pressure, kPa	188.7	182.9
Thickness, μ m	86.0	94.0

[0065] Properties of coated and calendered papers were determined.

[0066] The coated and calendered paper that contains SuperFill has about 5% units better gloss and 0.1 pps units better smoothness than a corresponding paper filled with talc. This is a very good result, taking into account that the coater amounts of the SuperFill papers were even slightly smaller. The light scattering factor and brightness of the SuperFill papers were also considerably better than the corresponding papers filled with talc.

[0067] On the basis of these results, it can be concluded that with composite pigments the penetration of the coating colour into the base paper can be effectively decreased and a better coverage and gloss of the coating obtained. This is

probably due to the fact that the pores of the paper are small, their size distribution is narrow and the smoothness of the base paper is extremely good.

1. A coated fibrous web comprising

a filler-containing base web, which has a pigment-containing coating layer at least on one of the surfaces,

characterised in that

the filler of the base web consists at least partially of cellulose or lignocellulose fibrils, on which light scattering material particles have been precipitated.

2. A fibrous web according to claim 1, characterised in that the filler comprises cellulose or lignocellulose fibrils that have an average thickness of less than 5 μm , produced by refining and screening of plant fibres.

3. A fibrous web according to claim 2, characterised in that the light scattering material particles are precipitated on fibrils, which correspond to a fraction passing through a 50-mesh screen and/or having an average thickness of 0.01 to 5 μm and an average length of 10 to 1500 μm .

4. A fibrous web according to any of claims 1 to 3, characterised in that the light scattering material particles are inorganic salts that can be formed from their source materials by precipitating in an aqueous medium.

5. A fibrous web according to claim 4, characterised in that the light scattering material particles are calcium carbonate, calcium oxalate, calcium sulphate, barium sulphate or mixtures thereof.

6. A fibrous web according to any of claims 1 to 5, characterised in that the material particles are precipitated on the fibrils.

7. A fibrous web according to claim 6, characterised in that the amount of the light scattering material particle in proportion to the amount of fibrils is 0.0001 to 95% by weight, preferably about 0.1 to 90% by weight, most suitably about 60 to 80% by weight, based on the amount of filler, and about 0.1 to 60% by weight, preferably 0.5 to 50% by weight of paper.

8. A fibrous web according to any of the preceding claims, characterised in that it is coated with calcium carbonate,

gypsum, aluminium silicate, kaolin, aluminium hydroxide, magnesium silicate, talc, titanium oxide, barium sulphate, zinc oxide, synthetic pigment or mixtures thereof.

9. A fibrous web according to any of the preceding claims, characterised in that the filler, which comprises cellulose or lignocellulose fibrils, over which the light scattering material particles have been precipitated, forms from 10 to 100% by weight of the filler of the base web.

10. A fibrous web according to any of the preceding claims, characterised in that the filler, which comprises cellulose or lignocellulose fibrils, on which the light scattering material particles have been precipitated, forms from 10 to 100% by weight of the fibre material of the base web.

11. A fibrous web according to any of the preceding claims, characterised in that it comprises coated, wood-containing or wood-free paper.

12. A method of producing a fibrous web, according to which method a pigment-containing coating layer is applied at least on one surface of a base web containing fibre material, characterised by forming the base web from a slush of the fibre material, to which a product comprising cellulose or lignocellulose fibrils, on which light scattering material particles have been deposited, is added as a filler.

13. A method according to claim 12, characterised by using a filler that comprises cellulose or lignocellulose fibrils having an average thickness of less than 5 μm produced by refining and screening plant fibres.

14. A method according to claim 12, characterised by using a filler, the light scattering material particles of which have been deposited on fibrils, which correspond to a fraction, which passes through a 50-mesh screen and/or have an average thickness of 0.1 to 10 μm and an average length of 10 to 1500 μm .

15. A method according to any of claims 12 to 14, characterised by using a filler in which at least 80% of the light scattering pigment particles are attached to the fibrils.

16. A method according to claim 12, characterised by coating the base web in a paper machine with a pigment containing coating mixture.

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