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(54) Title: A COATING COMPOSITION, METHOD FOR PREPARING SUCH COMPOSITION, A METHOD OF COATING, A COATED SHEET AND USES OF THE COATING

(57) Abstract: The present invention relates to a coating composition for a sheet like cellulosic fibrous web comprising one or more enzyme hydrolysed water-soluble cellulose derivatives and to a method of preparing such a composition. The present invention further relates to a coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web substrate and also to a method of coating a sheet like cellulosic fibrous web. Still further the invention relates to use of the enzyme hydrolysed water-soluble cellulose derivatives as a coating composition for a sheet like cellulosic fibrous web.



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A COATING COMPOSITION, METHOD FOR PREPARING SUCH COMPOSITION, A METHOD OF COATING, A COATED SHEET AND USES OF THE COATING

5 FIELD OF THE INVENTION

The present invention relates to a coating comprising one or more enzymatically hydrolysed water-soluble cellulose derivatives and a method of degrading one or more water-soluble cellulose derivatives or preparing a coating. Furthermore, the present invention relates to a method of preparing a coating composition by enzymatically degrading one or more water-soluble cellulose derivatives. A coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web substrate is also within the scope of the present invention as well as a method of coating and use of the coating composition here described.

15 BACKGROUND OF THE INVENTION

Various coatings can be applied on the surface of fibrous material such as paper or board in order to improve their properties. Grease, water and/or moisture barrier properties are particularly important for paper and board that are used for products for packaging purposes. Coatings applied on the surface of paper or board should provide an effective barrier against leakage from the goods inside the package and/or protect the packaged goods from contamination and/or contact with the surroundings. The barrier requirements are especially stringent for packaging materials used for foodstuff and consumable liquids.

Coatings for packaging purposes should have good resistance for creasing and folding. The coating should not crack when the paper or board is folded into a box or wrapped around the product. Cracking may decrease or even completely destroy the barrier properties of the coating. They should not be tacky and have low blocking tendency but on the other hand heat sealability is desired.

For environmental reasons it would be desirable to use sustainable and renewable bio-based sources for coatings. Furthermore, the barrier coatings used for packages should preferably also satisfy the recyclability requirements, for example, they should not disturb the repulping process.

Conventional bio-based components used in coating compositions, such as starch, often do not perform well in barriers coatings. Furthermore, the bio-based component should preferably originate from non-food chain sources, which requirement is

not fulfilled e.g. by starch and starch derivatives. Cellulose or cellulose derivatives have been tested earlier in barrier applications. Drawbacks of the prior art include e.g. low solids content of the cellulose or cellulose derivatives coating products as dissolved in water and/or too high viscosity. Increased solids content and/or lower
5 viscosity of coating compositions/formulations are needed for more effective and profitable coatings as well as easier coating methods. Barrier coatings with improved performance are desired.

Indeed, there is a need for new coating formulations and methods related thereto
10 that would solve the problems presently encountered.

BRIEF DESCRIPTION OF THE INVENTION

The present invention provides sustainable and renewable bio-based sources for coating compositions, method for their preparation, coatings made therefrom and
15 coated product. Such coatings are easily biodegradable and/or repulpable e.g., together with paper or board.

Defects of the prior art including but not limited to undesired blocking properties of the paper or board products, low solids content of the cellulose or cellulose deriva-
20 tives when dissolved in water in coating compositions/ and/or too high viscosity of such compositions, can be overcome with the methods or products of the present invention. Surprisingly, also moisture and/or grease barrier properties of coatings can be improved with the present invention.

25 It has now been surprisingly found that a decreased weight average molecular weight MW or a specific weight average molecular weight MW range of the hydrolysed water-soluble cellulose derivatives can be used for obtaining very effective coating compositions for example for paper or board.

30 The first aspect of the invention is a coating composition for a sheet like cellulosic fibrous web. Characteristic features of said composition are depicted in claim 1.

The second aspect of the invention is method of preparing a coating composition by enzymatically degrading one or more water-soluble cellulose derivatives. Character-
35 istic steps of said method are depicted in claim 8.

The third aspect in the invention is a coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web substrate, Characteristic features of said fibrous web or a product comprising it are depicted in claim 13.

5

The fourth aspect of this invention is a method of coating a sheet like cellulosic fibrous web, wherein the method comprises applying the coating composition of any here described on said fibrous web.

10 Enzymatic degradation of water-soluble cellulose derivatives leads to decreased weight average molecular weight MW of said derivatives and thus viscosity of the composition can be decreased, and higher solids content of the composition can be achieved. This enables higher coat weights applied for the barrier coating. However, the coating of the present invention still withstands cracking when creased and/or
15 folded, e.g. on a substrate such as a paper or board. Terms 'hydrolysed cellulose derivatives' and 'degraded cellulose derivatives' as used here both refer to cellulose derivatives undergone an enzymatic treatment.

The fifth aspect of the invention is use of the coating composition of the present
20 invention for coating a sheet like cellulosic fibrous web for obtaining water, moisture and/or grease barrier properties.

Other objects, details and advantages of the present invention will become apparent from the following drawings, detailed description and examples.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows staining test images for samples coated with barrier formulates 1-3 in Table 2. Samples with coat weight ca. 8 g/m² are shown on the top row and samples with coat weight over 17 g/m² are shown on the bottom row.

30

Figure 2 shows olive oil grease barrier test images for samples coated with barrier formulates 1-3. The top row reveals samples with coat weight ca. 8 g/m² and the bottom row shows samples with coat weight over 17 g/m².

35 Figure 3 shows staining test results for all coating formulations with enzymatically hydrolysed HEC.

Figure 4 shows olive oil test results. On the top row there are samples with coating formulations 1-3 and on the bottom row with formulations 4- 6.

5 Figure 5 shows staining test images for coated samples using enzymatically hydrolysed cellulose derivatives.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a coating composition for a sheet like cellulosic fibrous web comprising one or more water-soluble cellulose derivatives selected from the group consisting of alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose, methyl cellulose (MC), and carboxymethyl cellulose hydrolyzed with an enzyme having cellulolytic activity, and having a final weight average molecular weight MW is 20 000 Da - 120 000 Da, such as, 30 000 - 100 000 Da. Here a final weight average molecular weight refers to molecular weight after enzyme hydrolysis. Weight average molecular weight MW's of the enzymatically hydrolysed celluloses of the present invention are clearly above the oligomer limit 1000 Da.

Enzymatic degradation (hydrolysis) of water-soluble cellulose derivatives leads to decreased weight average molecular weight MW of said derivatives and thus viscosity of the composition can be decreased, and higher solids content of the composition can be achieved. This enables higher coat weights applied for the barrier coating. However, the coating of the present invention still withstands cracking when creased and/or folded, e.g. on a substrate such as a paper or board.

25 The cellulase hydrolysis provides the above advantages. With endoglucanase hydrolysis (endoglucanase or endoglucanase enriched enzyme product) more uniform average MW is achieved resulting in better performance and application, e.g., low tendency to stack to the roller.

30 In one embodiment at least 20 weight-% of the water-soluble cellulose derivatives of the coating are hydrolysed water-soluble cellulose derivatives. In this connection an expression "water soluble cellulose derivatives" means that the cellulose derivatives are individually dispersed throughout the water solution and they do not settle out or separate from the water solvent.

35 In one embodiment said coating composition comprises water-soluble cellulose derivatives in amount 20-100 weight-%, preferably 30-90 weight-%, more preferably

40-70 weight-% of the total solids content of the coating composition or the coating. For example, the coating composition may comprise water-soluble cellulose derivatives in amount of 20 – 99 weight-%, 30 – 99 weight-%, 40 – 99 weight-%, 50 – 99 weight-%, or 60 – 97 weight-%, calculated from total solids content of the coating composition, respectively.

In one embodiment the coating composition further comprises one or more constituent(s) selected from the group comprising a plasticizer, pigment particle, starch, binder, thickener, cross-linker, lubricant, and dispersing agent; or the method of any of the previous claims, wherein one or more agents are selected from the group comprising a plasticizer, inorganic pigment, starch, binder, thickener, cross-linker, lubricant, and dispersing agent.

In one embodiment one or more constituents to the composition comprising hydrolysed water-soluble cellulose derivatives enables obtaining an optimal coating. In one embodiment one or more constituents are selected from the group comprising a plasticizer, inorganic pigment, starch, binder, thickener, cross-linker, lubricant, and dispersing agent. Indeed, the composition of the present invention can comprise one or more constituents selected from the group comprising a plasticizer, pigment particle, starch, binder, thickener, cross-linker, lubricant, and dispersing agent. Respective agents may be contained in a coating composition discussed above.

The plasticizer may be selected from a group comprising polyol, such as sorbitol, mannitol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol or polyethylene glycol; fatty acids; monosaccharides, ethanolamine; triethanolamine; urea; lecithin and glycerol. According to one embodiment the plasticizer may be selected from sorbitol, polyethylene glycol or glycerol. Often the incorporation of a plasticizer into a barrier coating makes the barrier coating layer too tacky which may easily lead to blocking problems. Now it has been unexpectedly found that the tackiness of the barrier coating layer comprising plasticizer is significantly decreased when the barrier coating layer comprises the enzymatically hydrolysed water-soluble cellulose derivatives. This means that it is possible to obtain a coating layer where the cracking and blocking resistance properties can be balanced with the flexibility in order to obtain a coating with optimal properties for the desired purpose.

In one embodiment the composition may comprise plasticizer in amount of 1 – 50 weight-%, 3 – 40 weight-%, 5 – 30 weight-%, 10 – 20 weight-%, weight-% calculated from total solids content of the composition, respectively.

- 5 The pigment particle can be e.g. an inorganic mineral pigment which may optionally be selected from kaolin, talc, calcium carbonate (e.g. ground calcium carbonate or precipitated calcium carbonate) or any mixture thereof. Calcium carbonate is one preferred embodiment. The particle size D50 of the pigment particles or inorganic pigment particles may be <5 µm. According to one embodiment the composition
- 10 may comprise inorganic mineral particles, wherein at least 45% of the inorganic mineral particles has particle size <2 µm. Addition of inorganic mineral pigment may further improve the obtained barrier properties. It has been unexpectedly found that the enzymatically hydrolysed water-soluble cellulose derivatives increase the flexibility of the coating in a manner that allows incorporation of high amounts of inorganic pigment particles to the coating. This may not only improve the barrier properties,
- 15 but also makes the coating more economic to produce.

According to one embodiment the coating composition may comprise pigment particles or inorganic pigment particles in an amount of 5 – 40 weight-%, 10 – 35 weight-%, or 15 – 30 weight-% from the total dry solids content of the composition, respectively.

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For example, the coating composition (ready for use) may comprise 40 – 90 weight-%, 50 – 90 weight-% or 60 – 90 weight-% of water-soluble cellulose derivatives, 5 – 40 weight-%, 10 – 35 weight-%, or 15 – 30 weight-% of pigment particles or inorganic pigment particles, and 1 – 50 weight-%, 3 – 40 weight-%, 5 – 30 weight-%, 5 – 20 weight-%, or 5 – 10 weight-% of plasticizer, 0 – 30 weight-% binder, such as polyvinyl alcohol (PVA), and up-to 1 weight-% buffering agent and residues of an enzyme composition calculated from the total dry solids content of the coating composition, respectively, the total amount of the components adding up to 100%.

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Starch may increase the brittleness of the coating and reduce the resistance for cracking. Therefore, starch is not needed in the composition of the present invention or the amount of starch can be minimised. In one embodiment the composition is free of starch.

35

In one embodiment of the invention the coating composition may further comprise an additional coating binder, e.g. polyvinyl alcohol. The weight average molecular weight of the polyvinyl alcohol may be $< 100\,000$ g/mol, such as $< 90\,000$ g/mol. Polyvinyl alcohol that is especially suitable for use as an additional coating binder may have a weight average molecular weight of $\leq 70\,000$ g/mol, such as $13\,000 - 70\,000$ g/mol. Polyvinyl alcohol may be at least partially hydrolysed. Polyvinyl alcohol, when used as an additional coating binder, may improve the film formation and both water vapour and mineral oil barrier properties of the coating. Polyvinyl alcohol may also reduce blocking tendency of the obtained coating structure. In one embodiment the composition or coating is free of an additional coating binder such as polyvinyl alcohol.

According to a further embodiment the coating composition layer may comprise one or more of the following additive agents: thickener(s), cross-linker(s), lubricant(s), alkyl ketene dimer(s), alkenyl succinic anhydride(s), and dispersing agent(s).

The molecular weight can be determined by size-exclusion chromatography (SEC) using Viscotek GPCmax TDA 302 SEC equipment. Eluent was 0.1 M NaNO_3 . Column set consisted of three columns (Waters Ultrahydrogel 2000, 500 and 120) and a guard column. Pullulan standards (Polymer Standards Service) with molecular weights between $342 - 708\,000$ Da were used for conventional calibration with refractive index detection.

In one embodiment of the coating composition has viscosity of the coating is $50 - 3000$ mPas or cP measured at 23 °C using 100 rpm and Brookfield DV-E viscometer.

The coating composition may be in form of a dispersion, suspension or semi-solid or solid composition comprising enzymatically hydrolysed water-soluble cellulose derivatives and optionally further constituents up to 50 wt.-% calculated from total dry matter. The final coating may be in solid form.

As used herein “a dispersion” refers to a system in which distributed particles of one material are dispersed in a continuous phase of another material. The two phases may be in the same or different states of matter.

As used herein “a suspension” refers to a dispersion of particles sufficiently large for sedimentation. In one embodiment a suspension is a heterogeneous mixture of a fluid that contains solid particles sufficiently large for sedimentation.

5 In one embodiment the coating composition may be a coating composition ready to be applied on a cellulosic fibrous web. A composition comprising one or more enzyme hydrolysed water-soluble cellulose derivatives having a weight average molecular weight MW 20 000 Da- 120 000 Da, such as 30 000 Da- 100 000 Da or 30 000 Da and 95 000 Da may be in form of dispersion, suspension, semi-solid or
10 solid powder like form. Preferred range depends e.g. on the application. It may be supplemented with a diluent (such as water) before application on a substrate, or a coating layer.

In one embodiment said one or more water-soluble cellulose derivatives is/are selected from the group comprising or consisting of an alkyl cellulose, hydroxyalkyl
15 cellulose, hydroxyalkyl alkyl cellulose; and any combination thereof.

In one embodiment said one or more water-soluble cellulose derivatives is/are selected from the group comprising or consisting of methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxymethyl cellulose (HMC), hydroxyethyl cellulose
20 (HEC), methyl hydroxyethyl cellulose (MHEC), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), and any combination thereof.

In one embodiment one of said water-soluble cellulose derivatives is HEC or CMC, especially HEC. CMC is readily degradable by cellulase degrading enzymes. HEC
25 provides a durable coating.

The present invention also concerns method of preparing a coating composition by enzymatically degrading one or more water-soluble cellulose derivatives, wherein
30 the method comprises

- (a) providing an aqueous suspension of one or more water-soluble cellulose derivatives selected from alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose, methyl cellulose (MC), and carboxymethyl cellulose; and
- (b) contacting said suspension with an enzyme having cellulolytic activity;
- 35 (c) allowing to react at conditions conducive for activity of said enzyme;
- (d) optionally removing excess of water; and

(e) optionally adding one or more agents to the composition comprising degraded water-soluble cellulose derivatives.

The reaction of step (c) may be continued until said water-soluble cellulose derivatives have having a weight average molecular weight MW is 20 000 Da - 120 000 Da, such as, 30 000 -100 000 Da.

In one embodiment the reaction time of item (c) is continued until a desired viscosity in view of dry matter is obtained. Thus, in one embodiment the enzymatic reaction is followed by viscosity measurements.

In one embodiment the enzyme activity is killed by heating the water-soluble cellulose derivative composition, optionally up to at least 85°C, 90°C, 95°C or 100°C, optionally after obtaining suitable viscosity. The coating or the coating composition may comprise inactivated enzymes or residues of enzyme composition.

The incubation time (contact time with enzymes), activity of the enzyme preparation and reaction conditions are adapted to allow degradation until a desired viscosity is achieved. A person skilled in the art is able to select conditions, such as temperature, consistency and pH, conducive for activity of the enzyme preparation(s).

It is to be noted that the enzymatic reaction may be performed in lower consistency (dry matter content) than dry matter of the final coating composition. The dry matter content may be increased by removal of water and/or by adding further constituent to the composition after the enzymatic treatment. The hydrolysed water-soluble cellulosic derivatives may be subjected for removal of water for obtaining a higher solid content of even drying the hydrolysed water-soluble cellulosic derivatives in order to modify the consistency of the coating or enhancing the transportation.

As used herein “a water-soluble cellulose derivative” refers to any water-soluble cellulose derivative which is optionally selected from the group comprising or consisting of an alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose and any of their mixture. In one embodiment the water-soluble cellulose derivative is selected from the group comprising or consisting of methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxymethyl cellulose (HMC), hydroxyethyl cellulose (HEC), methyl hydroxyethyl cellulose (MHEC; (hydroxyethyl)methyl cellulose), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC; (hydroxypropyl)-

methyl cellulose), and any combination or mixture thereof. CLM 10 In one embodiment said derivate is selected from methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxymethyl cellulose (HMC), hydroxyethyl cellulose (HEC), methyl hydroxyethyl cellulose (MHEC), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC). In one embodiment said derivate is selected from HEC and CMC.

Enzymatically hydrolysed water-soluble cellulose derivatives are able to effectively function as a grease and/or moisture barrier, especially against liquid grease or oil, and sometimes even as a mineral oil barrier. It has been found that when at least one of the hydrolysed water-soluble cellulose derivatives is present in the coating, the coating is more flexible and does not crack so easily at creasing or folding. Moreover, the hydrolysed water-soluble cellulose derivatives provide increased dry solid content for the composition formulation, thus making it easier to apply on the surface of the substrate to be coated and providing for a better film forming properties.

With the present invention it is possible to produce coatings where the content of bio-based components is high while maintaining the essential barrier and crack resistance properties on an excellent, good or at least acceptable level. The shares of the coating composition to be prepared are discussed in connection of the coating composition and evidently applicable to the process also. The method makes it possible to produce coating compositions with high solid content and a viscosity allowing easy application of the coating composition.

In the method of the present invention when the enzyme(s) are allowed to contact with the water-soluble cellulose derivatives viscosity of the composition decreases. In one embodiment water-soluble cellulose derivatives are further added to the composition during or after allowing the enzyme(s) to contact with the water-soluble cellulose derivatives in order to increase the solids content and viscosity of the composition.

The coating composition of the coating may be obtained by enzymatically degrading water-soluble cellulose derivatives with one or more cellulases (e.g. cellulases of two or more different types), one or more endoglucanases (such as endo-1,4- β -D-glucanase), or a combination comprising one or more cellulases and one or more endoglucanases. In one embodiment the combination comprising one or more cellulases and one or more endoglucanases comprises at least 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90 or 95% cellulases or endoglucanases (% based on

the number or activity of enzymes). In one embodiment the combination comprising one or more cellulases and one or more endoglucanases comprises at least 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90 or 95% endoglucanases (% based on the number or activity of enzymes). A cellulase is an enzyme produced e.g. by fungi, bacteria, and protozoans that catalyzes cellulolysis i.e. the decomposition of cellulose and optionally some related polysaccharides. Cellulases degrade cellulose and consequently produce glucose as the end product. The group of cellulases comprises β -1,4-endoglucanases, β -1,4-exoglucanases, and β -1,4-glucosidases. Endoglucanases act randomly to hydrolyze interior β -1,4-glucan linkages of the cellulose chain thereby breaking the cellulose chain into smaller units, thus producing either oligosaccharides or smaller polysaccharide units. In one embodiment one or more endoglucanases (such as a combination of endoglucanases of two or more different types) give higher weight average molecular weight MW degradation products of cellulose derivatives than one or more cellulases. Indeed, in one embodiment degradation of cellulose derivative chains by one or more endoglucanases is preferred. An expression "endoglucanase enriched cellulase" as used here means that the amount of endocellulase activity is increased compared to a cellulase activity produced by a host in which the cellulase profile has not been modified. This can be a cause by regulating activity of genes encoding cellulolytic enzymes or by expressing endocellulases in a recombinant production host. In one embodiment endoglucanase activity is the main activity of the cellulase preparation.

The activity of a cellulase and/or an endoglucanase to degrade water-soluble cellulose derivatives can be determined by an enzyme assay wherein said enzyme(s) is(are) allowed to contact with water-soluble cellulose derivatives. The activity of an enzyme to degrade water-soluble cellulose derivatives can be determined e.g. by detecting the weight average molecular weight MW or the amount of hydrolysed water-soluble cellulose derivatives (e.g. as shown in examples of the present disclosure). The presence, absence or level of hydrolysed water-soluble cellulose derivatives can be detected or measured by any suitable method known in the art after allowing the enzymes(s) to contact with a composition comprising water-soluble cellulose derivatives. Non-limiting examples of suitable detection and/or measuring methods include but are not limited to filtration, solvent extraction, centrifugation, electrophoresis, liquid chromatography, gas chromatography, affinity chromatography, ion exchange chromatography, mass spectrometry or any combination thereof. The degradation process may also be followed by viscosity measurements.

In one embodiment the incubation is continued until the desired viscosity or average molecular weight distribution for the water-soluble cellulose derivative composition to be contacted with the enzyme(s) for 10 seconds - 20 minutes (such as 15, 20, 25, 30, 35, 40, 45, 50, or 55 seconds, or one, two, three, four, five, six, seven, eight, 5 nine, ten, 11, 12, 13, 14, 15, 16, 17, 18, or 19 minutes) or even longer at a temperature below 90°C such as 30 – 80°C, 40 - 65°C or 50 – 60°C.

In the water-soluble cellulose derivative composition water-soluble cellulose derivatives may be present 2 – 15 weight-% (such as 5 – 10% or 7%), e.g. the composition 10 water-soluble cellulose derivatives are present 2 – 15% (such as 5 – 10% or 7%).

In one embodiment, the solids content of the composition comprising one or more water soluble cellulose derivatives to be treated with the enzyme having cellulolytic activity derivatives is 1 – 5% (weight-%, e.g. 2, 3 or 4%).

15 In one embodiment, viscosity of the composition treated with the enzyme is less than 5000, 4500, 4000, 3500, 3000, 2500, 2000, 1900, 1800, 1700, 1600, 1500, 1400, 1300, 1200, 1100 or 1000 mPas or cps (e.g. at room temperature, about 23 °C), and/or more than 60, 100, 200, 300, 400, 500, 600, 700, 800, 900 or 1000 20 mPas or cps (e.g. at room temperature).

The viscosity of the coating treated with the enzyme and ready to be applied on a surface is less than 5000, 4500, 4000, 3500, 3000, 2500, 2000, 1900, 1800, 1700, 1600, 1500, 1400, 1300, 1200, 1100 or 1000 mPas or cps (e.g. at room temperature, about 23 °C), and/or more than 60, 100, 200, 300, 400, 500, 600, 700, 800, 900 or 1000 mPas or cps (e.g. at room temperature about 23 °C). Viscosity of the coating or composition can be measured e.g., with a viscometer such as s 25 Brookfield DV-E (Brookfield GmbH, Lorch, Germany) viscometer, e.g. at 100 rpm.

30 The composition of hydrolysed water-soluble cellulose derivatives may be concentrated by removing water by e.g. evaporation until desired consistency or even to dryness for the coating composition is achieved. At this stage, it may be necessary to dissolve powder like composition with water, or dilute a composition to desired consistency. Also further agents discussed above in connection of the coating composition, may be added to obtain a ready to be applied coating composition. The final 35 constituents of the coating composition ready to be applied and thus also the coating, have been discussed above.

In one embodiment of the coating or method of the present invention, the coating or composition is in a suspension, dispersion, semi-solid or solid form; or in a powder or paste form. As discussed, the consistency may be modified before application by adding water and/or additives. The coating composition may be delivered as a hydrolysed water soluble derivatives, or a premix or a ready to be applied coating composition.

In one embodiment the cellulose derivatives suitable for the present invention are water-soluble at least at room temperature (+ 21 °C). For example methyl cellulose and hydroxypropylmethyl cellulose become water insoluble in hot water (about + 75 °C), but they are still suitable for use for the present invention, and may even provide limited water barrier properties, especially against hot liquids, for the coating layer in addition the grease barrier properties.

The present invention also concerns a coated cellulosic sheet like fibrous web or a product comprising a coated fibrous web, wherein the fibrous web has been coated with the coating composition disclosed here. In one embodiment the web comprises cellulosic or lignocellulosic fibres, or the substrate is a fibrous web, such as a paper, board, tissue or the like. In one embodiment the substrate is a paper or board. The cellulosic or lignocellulosic fibres may have been obtained by any conventional pulping process, including chemical, mechanical, chemi-mechanical pulping processes. The cellulosic fibrous web (the substrate) may also comprise or consist of recycled fibres. In one embodiment the substrate has a grammage of 25 – 800 g/m², 30 – 700 g/m², or 40 – 500 g/m².

In one embodiment the coated substrate or the product has KIT test value of at least 7, water vapor transmission rate (WVTR) less than 110 g/m²/d (e.g. at 23 °C and 50 % relative humidity); and/or increased grease barrier properties compared to a substrate or product with a coating obtained without enzymatic degradation.

The KIT test value measures the repellency of the coating to oil and grease. The measurements can be performed according to standard TAPPI method T-559 pm-96.

In one embodiment the coated substrate or the product has decreased blocking tendency compared to a coated sheet like cellulosic fibrous web or a product

comprising said coated sheet like cellulosic fibrous web with a coating obtained without enzymatic degradation.

5 Grease barrier properties can be measured e.g. after oil treatment (such as olive oil treatment) followed by ASTM F119-82 test method. For example, oil can be dropped on cotton fabric placed on the coated side of the substrate and 50 grams weight can be placed on top of the substrate. Then said coated substrates can be placed at 40 °C oven for 120 minutes and photographed for evaluation of grease penetration.

10 WVTR value can be obtained e.g. by using Systech Permeation Analyzers M7002 instrument. WVTR value can be measured by using any standard method such as ASTM F-1249, ISO 15105-2, ISO 15106-3, and/or DIN 53122-2.

15 Water resistance can be tested e.g. by using Cobb60 test (standard test method ISO 535).

20 Hexane vapor transmission rate (HVTR) was determined by using a cup method. In the method, 20 grams of hexane was placed in a metal cup. Barrier sample was placed on top of the cup between two gaskets, coated side down. Metal frame was used to tighten the sample to the cup. Weight loss of hexane was recorded for 24 hours and calculated per area $\text{g}/(\text{m}^2 \cdot \text{d})$.

Method correlates with migration of mineral oil from recycled fiber based packaging to foodstuff.

25 For a blocking test a coated substrate can be placed against a top side coating and treated e.g. at 40 °C temperature and 150 bar pressure for four hours.

30 The coat weight of one coating layer or all coating layers together can be freely chosen depending on the desired end use and desired barrier properties of the substrate or product. In one embodiment the coating (e.g. consisting of one or two or more coating layers) has a coat weight 0.5 – 25 g/m^2 , 3 – 25 g/m^2 , or at least 3, 4, 5, 6, 7, 10, 15, or 17 g/m^2 . If there is more than one coating layer on a substrate in one embodiment the first coating layer may have a higher coat weight than the second coating layer, or vice versa. The coat weights of different coating layers may vary.

Indeed, the substrate may comprise one, two or more coating layers. In one embodiment, the substrate comprises a plurality of first coating layers and/or plurality of second coating layers, wherein the first coating layers are preferably chemically identical with each other, and the second coating layers are preferably chemically identical with each other. Chemically identical means that the coating layers are made from same components in identical amounts, i.e. coating layers are made by using identical coating formulation. A coating may be applied in one or both sides of the substrate.

10 The present invention further concerns a method of coating a sheet like cellulosic fibrous web, wherein the method comprises applying the coating of the present invention on a substrate. The coating may be applied on the surface of the substrate by using any conventional coating techniques, such as rod coating, blade coating, spray coating or curtain coating. The coating of the present invention can be applied directly on the surface of a substrate, such as a sheet-like substrate. In some embodiments the surface of the substrate may be surface sized, e.g. with a layer of hydrophobic surface size, before application of the coating layer, but preferably the coating layer is applied directly on the surface of a substrate which is free from any pre-existing treatment layers, such as surface sizing layers. The sheet-like substrate may comprise an internal size.

The sheet like cellulosic web formed substrate coated with the coating of the present invention can be used e.g. for making a foodservice package or for liquid packaging. Typical examples of foodservice packages are packages for fast food, ready-to-eat meals, sandwiches, bakery products, such as cookies, doughnuts, or the like. The coating of the present invention can be used for coating a substrate for obtaining e.g. water, moisture and/or grease barrier properties, and/or better creasing or blocking results.

30 Thus, the present invention concerns use of the enzyme hydrolysed water-soluble cellulose derivatives having a weight average molecular weight MW 20 000 Da-120 000 Da, preferably 30 000 Da - 100 000 Da or 30 000 Da - 95 000 Da as a coating composition for a sheet like cellulosic fibrous web.

35 In the present context, if not otherwise stated, all weight-% values given for the various components are calculated from the total dry solids content of the composition.

It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described below but may vary within the scope of the claims.

5

EXAMPLES

Materials and methods

10 Several hydroxyethyl cellulose grades have been tested

Hydroxyethylcellulose 1 (HEC 1) having Mw 220000 Da

Hydroxyethylcellulose 2 (HEC 2) having Mw 232000 Da

Hydroxyethylcellulose 3 (HEC 3), modified HEC having Mw 160000 Da

Enzymes used in the tests were Cellulase from *Trichoderma reesei* and endo-1,4-
15 β -D-glucanase from *Acidothermus cellulolyticus* from Sigma Aldrich and commercial enzymes from Novozymes; Fibercare R and U, which have endoglucanase as main activity.

HEC products were dissolved in water by mixing with magnetic stirrer and heated
20 up to 60°C. Enzymatic degradation was tested for HEC 1 (Hydroxyethylcellulose 1) by dissolving it at 7% solids content and keeping the HEC solution at temperature 50-60°C. 0.2 grams of the enzymes were added per 100 grams of HEC solution. As viscosity decreased dry HEC was added in order to increase the solids content. Target solids content was 20% and target viscosity was around 1000 cPas. Enzyme
25 activity was killed by heating the sample up to 90°C when suitable viscosity was obtained.

Enzymatic degradation was also tested for other cellulose derivatives. Used
products are listed in table 1. Fibercare R was used for degradation.

30

Table 1. Tested cellulose derivatives in the second part of enzymatic degradation studies.

Sample		Viscosity
HEC4	MHEC	(2%) 6000-8000 mPas
HEC5	HPC	(1%) 1275-3500 cps
HEC 2	HEC	(5%) 110-150 cps
HEC6	HPMC	(4%) 2700-5040 mPas

HEC 3	modified HEC	(1%) 500-750
MC	MC	(2%) 300-560 cps
EC	EC	not soluble in water

Barrier coating tests were carried out for the enzymatically hydrolysed HEC samples. Used coating formulations are summarized in table 2.

- 5 **Table 2.** Coating formulations used for enzymatically hydrolysed hydroxyethyl cellulose.

	1	2	3	4	5	6
HEC	60			60		
HEC + cellulase		60				
HEC + endoglucanase			60			
HEC + Fibercare R				60		
HEC + Fibercare U						60
HydroCarb 60	30	30	30	30	30	30
PEG-300	10	10	10	10	10	10

- A Brookfield DV-E (Brookfield GmbH, Lorch, Germany) viscometer was used for measurement of the coating colors' bulk viscosity immediately after preparation. Different spindles were used in accordance with the respective samples' viscosity range. The measurements were performed at 100 rpm.

- Laboratory coating tests were carried out by using draw down coater K control coater (RK Print Coat Instruments, Litlington, UK) with different wound rods and coating speeds. Samples were dried using InfraRR IR dryers for 60 seconds directly after coating. Single and double coated samples were prepared. The used substrate in coating tests was virgin fiber based cartonboard (Avanta Prima) with basis weight of 265 g/m². Barrier coating was applied on the uncoated bottom side.

- Coat weight was determined by weighting the coated samples and uncoated base papers and coat weight was obtained by the weight difference. Simple converting test was done for the samples including sample creasing using Cyklos CPM 450 creasing and perforation unit. Creasing and folding was done in machine and cross directions. Staining test was done for the creased samples by using methyl red dissolved in ethanol. For folding Cobb roller was used to give uniform folding pressure.

Water resistance was tested using Cobb60 test. Water vapor barrier properties were measured using Systech Permeation Analyzers M7002 instrument. Grease barrier properties were tested using olive oil following ASTM F119-82 test method. Oil was dropped on cotton fabric placed on the barrier coated side of the folded sample and 50 gram weight was placed on top of the sample. Samples were placed at 40 °C oven for 120 minutes and photographed for evaluation of grease penetration. Blocking tests were carried out at 40 °C temperature and 150 bar pressure for four hours. The barrier coated sample was placed against the top side coating. Used scale for blocking test results is following; 1: Samples did not adhere together, 2: Noise can be heard when pulling the sample strips apart, 3: Coating defect <50 % of the surface area, 4: Coating defect >50 % of the surface area, 5: Base paper delamination.

Results and discussion

Enzymatic degradation

Obtained molecular weights for HEC 1 by using different enzymes are summarized in table 3.

Table 3. Molecular weight results for enzymatically hydrolysed hydroxyethyl cellulose samples. Cellulase mixture is a cellulase from *Trichoderma reesei* (Sigma Aldrich). An enzyme preparation has been added to HEC.

Sample	Solids content (%)	Mw (Da)
HEC 1	7	220450
+ endoglucanase	7	62400
+ endoglucanase	18	66900
+ Fibercare R	7	83000
+ Fibercare R	16	84900
+ Fibercare U	14	89800
Cellulase	7	34350
Cellulase mixture	20	33300

Cellulase degradation gave lower weight average molecular weight MW for HEC than endoglucanase. Pure endoglucanase treatment showed lower average molecular weight than the commercial Fibercare enzymes. It can be seen that weight average molecular weight MW is very similar at lower solids content in the beginning of the degradation test and at high solids content in the end of the degradation. All samples showed average molecular weight clearly above oligomer limit (1000 Da).

Coating results

Hydroxyethyl cellulose

In the first set of samples coating formulations 1-3 were tested and the results are shown in table 4. Sample 1 was reference without enzymatic degradation, sample 2 was hydrolysed using cellulase and sample 3 with endoglucanase. Staining test images are summarized in figure 1 and olive oil test results in figure 2.

Table 4. Coat weight and barrier data for coated samples using coating formulations 1-3.

	1	2	2	2	3	3	3
Average Coat weight (g/m ²)	7.9	7.8	19.2	19.7	8.0	17.0	18.2
WVTR (g/(m ² *d))	142	-	82	88	-	103	94
KIT flat	6	3	8	9	4	12	12
KIT creased MD	6	3	7	9	4	10	12
KIT creased CD	6	3	6	8	3	12	12

At low coat weight enzymatically hydrolysed samples with higher solids content did not improve barrier properties, KIT values are as matter of fact poorer for the enzymatically hydrolysed samples. Higher coat weight samples were achieved for enzymatically hydrolysed HEC samples and for those samples it can be seen that endoglucanase gives better KIT values.

Lower weight average molecular weight samples show better creasing properties compared to the original HEC grade at coat weight around 8 g/m². Sample with endoglucanase used for degradation showed best folding properties. Minor cracking can still be seen on the samples with coat weight up to 20 g/m².

In the second test series commercial Fibercare enzymes were used. Coat weight and barrier results are summarized in table 5.

25

Table 5. Coat weigh and barrier data for coated samples using formulations 1-6.

Coating formulation	1	2	3	4	5	6
Coat weight (g/m ²)	7.9	7.8	8.0	3.6	8.4	9.1

WVTR (g/(m ² *d))	142	-	-	140	98.8	101.2
KIT flat	6	3	4	1	9	5
KIT creased MD	6	3	4	1	7	5
KIT creased CD	6	3	3	1	7	5
Blocking	1	-	-	0	0.5	1

Sample 5 with Fibercare R as enzyme showed best water vapor barrier properties, KIT values and good blocking resistance. Staining test results are shown in figure 3 and olive oil test results in figure 4.

5

In the staining test images coating formulations 5 and 6 using Fibercare enzymes for degradation showed coating layers without pinholes and no cracking at crease.

In the olive oil test reference samples P1 and P4 showed clearly more oil penetration than the enzymatically hydrolysed samples.

10

Other cellulose derivatives

Obtained solids contents, maximum coat weights for double coated samples and KIT values for the samples with good film formation are summarized in table 6 and staining test results for the different enzymatically hydrolysed cellulose derivatives are shown in figure 5.

15

Table 6. Solids contents before and after enzymatical degradation, maximum coat weights and KIT values for best samples.

<i>Cellulose derivatives</i>		Start solids (%)	End Solids %	Br100	Max coat weight (g/m ²)	KIT flat/ creased
HEC 4 methyl cellulose derivates	MHEC	2	5	68	5.2	7/7
HEC 5 Hydroxypropylcellulose	HPC	1	3	1004	3.4	
HEC 2, hydroxyethylcellulose	HEC	5	13.5	217	9.2	12/9
HEC 6 HYPROMELLOSE	HPMC	4	4.4	565	4.1	11/7
HEC3Modified HEC	HEC	1	2	297	3.2	
MC	MC	2	5.4	77	4.8	

Highest solids contents were obtained for HEC, MHEC, methyl cellulose and HPMC. The higher the solids content the higher the obtained coat weight. Only with HEC, MHEC and HPMC good enough film formation was obtained in order to measure
 5 KIT values. HEC and HPMS showed as flat surface good KIT values but creasing caused some cracking and lowered KIT value and showed stain penetration in figure 5.

Enzymatic degradation, Hydroxyethyl cellulose

10 Hydroxyethyl cellulose 1, having a molecular weight of Mw = 220000 Da was selected for enzymatic degradation studies. Highest solids content applicable for it in paper coating application is about 7%.

First way (Method 1) to carry out the enzymatic degradation was to add enzyme
 15 into 7% HEC solution and the solution was heated to 60 °C and 0.2 grams enzyme is added per 100 ml of cellulose derivative solution. Dry HEC powder is added when viscosity decreases. When similar viscosity level to original HEC solution is obtained for enzymatically hydrolysed HEC, the solution was heated to ca 90 °C in order to kill the enzyme, to get stable sample. Molecular weights and solids con-
 20 tents of the hydrolysed HEC prepared using different enzymes according to Method 1 are presented in Table 7:

Table 7

Used enzyme	Obtained Mw (kDa)	Solids content after enzymatic treatment (%)
Endo-1,4- β -D-glucanase from <i>Acidothermus cellulolyticus</i>	65	20
Cellulase from <i>Trichoderma</i>	33	20
Fibercare R	85	18
Fibercare U	90	18

25 Second way (Method 2) to carry out the enzymatic treatment was to add dry HEC powder in cold water (solids content ca. 50%) and adding 0.2 grams of enzyme was added per 100 ml of cellulose derivative solution. Sample was heated to 60°C and diluted if viscosity increased too high. After completing the enzymatic degradation,

sample is heated to ca 90°C in order to kill the enzyme. The obtained molecular weight and solids content according to Method 2 are presented in Table 8.

Table 8

5

Enzyme	Obtained Mw (kDa)	Solids content after enzymatic treatment (%)
Fibercare R	113	18

In bench scale reactor (Method 3) enzymatic degradation was carried as follows: Cold water and enzyme was placed in reactor and heated to 60°C. Dry HEC powder was added in 4 batches. Calculated solids content was 17%. After completing the enzymatic degradation, the sample was heated to ca 90°C in order to kill the enzyme. The obtained molecular weight and solids according to Method 3 are presented in Table 9.

15 **Table 9**

Enzyme	Obtained Mw (kDa)	Solids content after enzymatic treatment (%)
Fibercare R	96	18

Enzymatic degradation, Carboxymethyl cellulose

Enzymatic degradation was carried out for two CMC grades; CMC 1 and CMC 2, having molecular weights Mw 261 and 338 kDa, respectively. The enzymatic degradation was carried out by adding enzyme into 10% or 7% CMC solution for CMC 1 and CMC 2, respectively. Samples were heated to 60°C. 0.2 grams of enzyme was added per 100 ml of CMC solution. Solids content was increased as more dry CMC powder was added when viscosity decreases. When similar viscosity level to original CMC solution was obtained for enzymatically hydrolysed product, the sample was heated to ca 90°C in order to kill the enzyme, in order to get stable sample. Obtained molecular weights and solids contents by using different enzymes are presented in Table 10.

Table 10

CMC grade/Enzyme	Obtained Mw (kDa)	Solids content after enzymatic treatment (%)
CMC1/Fibercare R	33	18
CMC1/Fibercare U	33	18
CMC2/Fibercare R	37	13
CMC2 /Fibercare U	37	13

Enzymatic degradation, Test methods

Enzymatic degradation was carried out in laboratory scale in a glass beaker and magnetic stirrer + heating. In bench scale reaction was carried out in glass reactor with heating and anchor stirrer.

A Brookfield DV-E viscometer was used for measurement of the coating colors' bulk viscosity immediately after preparation at room temperature (23°C). Different spindles were used in accordance with the respective samples' viscosity range. The measurements were performed at 100 rpm.

Laboratory coating tests were carried out by using draw down coater K control coater (RK Print Coat Instruments, Litlington, UK) with different wound rods and coating speeds. Samples were dried using InfraRR IR dryers for 60 seconds directly after coating. Double coated samples were prepared. The used substrate was virgin fiber based cartonboard with basis weight of 265 or 247(mentioned separately when used) g/m². Barrier coating was applied on the uncoated bottom side.

Coat weight was determined by weighting the coated samples and uncoated base papers and coat weight was obtained by the weight difference. Simple converting test was done for the samples including sample creasing using Cyklos CPM 450 creasing and perforation unit. Creasing and folding was done in machine and cross directions. Staining test was done for the creased samples by using methyl red dissolved in ethanol. For folding Cobb roller was used to give uniform folding pressure.

Water resistance was tested using Cobb60 test. Water vapor barrier properties were measured using Systech Permeation Analyzers M7002 instrument. Grease barrier

- properties were tested using olive oil following ASTM F119-82 test method. Oil was dropped on cotton fabric placed on the barrier coated side of the folded sample and 50 gram weight was placed on top of the sample. Samples were placed at 40 °C oven for 120 minutes and photographed for evaluation of grease penetration. Blocking tests were carried out at 40 °C temperature and 150 bar pressure for four hours. The barrier coated sample was placed against the top side coating. Used scale for blocking test results is following; 1: Samples did not adhere together, 2: Noise can be heard when pulling the sample strips apart, 3: Coating defect <50 % of the surface area, 4: Coating defect >50 % of the surface area, 5: Base paper delamination.
- 10 The molecular weight was determined by size-exclusion chromatography (SEC) using Viscotek GPCmax TDA 302 SEC equipment. Eluent was 0.1 M NaNO₃. Column set consisted of three columns (Waters Ultrahydrogel 2000, 500 and 120) and a guard column. Pullulan standards (Polymer Standards Service) with molecular weights between 342 - 708 000 Da were used for conventional calibration with refractive index detection.

COATING/BARRIER TESTS

With calcium carbonate as coating pigment

- Using pure enzymes was tested first. Barrier coating was prepared by mixing the different HEC samples with calcium carbonate pigment and polyethylene glycol as plasticizer as presented in Table 11.

Table 11

Coating formulation	1	2	3
HEC Mw 220000	60		
HEC hydrolysed with cellulase		60	
HEC hydrolysed with endoglucanase			60
HydroCarb 60	30	30	30
PEG-300	10	10	10

Table 12

	No enzyme	Cellulase			Endoglucanase		
Coating formulation	1	2	2	2	3	3	3
Coat weight (g/m ²) (average)	7.9	7.8	19.2	19.7	8.0	17.1	18.2
WVTR	142	-	82	88	-	103	94
KIT (flat)	6	3	8	9	4	12	12
KIT (creased)	MD 6 CD 6	MD 3 CD 3	MD 7 CD 6	MD 9 CD 8	MD 4 CD 3	MD 10 CD 12	MD12 CD12
Blocking	1	-	4.5	5	-	3.75	3.75

If comparing samples 1, 2 and 3 at same coat weight (ca. 8 g/m²), it can be seen that grease barrier properties for creased samples improved due to less cracking.

- 5 Higher coat weights can be obtained as the solids content is higher for the enzymatically hydrolysed HEC. For the higher coat weight samples better KIT values and blocking properties were obtained by using endoglucanase for enzymatic degradation. Also water vapor barrier properties were improved by the enzymatic degradation.
- 10 Commercial enzymes with endoglucanase as main activity (Fibercare R and U) were tested next. Similar coating formulations, Table 13, were prepared as in the first part.

Table 13

	1	2	3
HEC Mw 220000	60		
HEC hydrolysed with Fibercare R		60	
HEC hydrolysed with Fibercare U			60

HydroCarb 60	30	30	30
PEG-300	10	10	10

Table 14

	Ref./ No enzyme	FiberCare R	FiberCare U
Coating formulation	1	2	3
Coat weight (g/m ²) (average)	3.7	8.4	9.1
WVTR	140	99	101
KIT (flat)	1	9	5
KIT (creased)	MD 1 CD 1	MD 7 CD 7	MD 5 CD 5
Blocking	0	0.5	1

5 Similar improvement in WVTR was seen by using Fibercare enzymes that was observed with pure enzymes, Table 14. With Fibercare R best KIT values were obtained for coat weight of 8 g/m². Only minor olive oil penetration was detected for Fibercare samples.

10 Comparison of different degradation protocols using Fibercare R was carried out using a reference coating formulation containing 30% calcium carbonate and 20% PEG 300, in Table 15. HEC-FCR was prepared by method 1, HEC- high solids degrading by method 2 and HEC – pilot test by method 3.

Table 15

	HEC-FCR 3	HEC-High solids degrading	HEC - pilot test
HEC, enzymatically hydrolysed	50	50	50
Hydrocarb 60	30	30	30
PEG-300	20	20	20
Solids (%)	29.8	25.5	27.5

Coat weight (g/m ²)	14.8	14.8	13.2
KIT flat/creased/folded	12/10/3	12/11/7	12/8/2
HVTR (g/m ² *d)	1	2	9

5 Hexane vapor transmission rate (HVTR) was determined by using a cup method. In the method, 20 grams of hexane was placed in a metal cup. Barrier sample was placed on top of the cup between two gaskets, coated side down. Metal frame was used to tighten the sample to the cup. Weight loss of hexane was recorded for 24 hours and calculated per area g/(m²*d).

Method correlates with migration of mineral oil from recycled fiber based packaging to foodstuff

10 Similar barrier results were obtained with all enzymatic degradation methods. All samples showed good folding properties and good grease, and mineral oil barrier properties (HVTR).

Calcium carbonate as coating pigment + amount of plasticizer
Table 16; 20% plasticizer

	HEC-FCR 1	HEC-FCR 2	HEC-FCR 3	HEC-FCR 4	HEC-FCR 5
HEC L, enzymatically hydrolysed	70	60	50	40	30
Hydrocarb 60	10	20	30	40	50
PEG-300	20	20	20	20	20
Solids (%)	23.7	26.4	29.8	34.2	40
Coat weight (g/m ²)	12.7	13.4	14.8	12	12
KIT flat/creased/folded	12/10/5	12/12/8	12/10/3	8/7/4	7/6/3
HVTR (g/m ² *d)	1	0	1	10	15

The coating formulations with calcium carbonate and 20% of PEG 300 showed no cracking at crease up to 30% pigment content. The same samples showed also good mineral oil barrier properties, Table 16.

Table 17; 10% plasticizer

	HEC-FCR 6	HEC-FCR 7	HEC-FCR 8	HEC-FCR 9	HEC-FCR 10
HEC, enzymatically hydro- lysed	80	70	60	50	40
Hydrocarb 60	10	20	30	40	50
PEG-300	10	10	10	10	10
Solids (%)	21.4	23.6	26.2	29.0	33.3
Coat weight (g/m ²)	12.0	13.2	14.4	11.2	12.4
KIT flat/creased/fol- ded	12/11/7	12/11/7	12/10/3	12/7/2	7/5/3
HVTR (g/m ² *d)	0	0	0	6	5

5

The coating formulations with calcium carbonate and 10% of PEG 300 showed only very minor cracking at crease up to 30% pigment content. The same samples showed also good mineral oil barrier properties. The best KIT values for the folded samples were obtained when the pigment content was 20% or lower. Table 17.

10 COATING/BARRIER TESTS; Kaolin and talc as coating pigment

Enzymatic degradation of HEC was done by using Fibercare R enzyme. Base substrate used was folding boxboard, grammage 247 g/m². Double coating was applied for all samples.

Table 18; Talc

	HEC-FCR 1	HEC-FCR 2	HEC-FCR 3	HEC-FCR 4	HEC-FCR 5
HEC, Enzymatic degrada- tion	80	70	60	50	40
Finntalc C15 B	10	20	30	40	50

PEG-300	10	10	10	10	10
Coating rod/speed	2x3/10	2x3/10	2x2/10	2x1/10	2x0/10
	HEC-FCR 1	HEC-FCR 2	HEC-FCR 3	HEC-FCR 4	HEC-FCR 5
Coat weight (g/m ²) average	7.9	8.4	7.7	8.0	8.7
KIT flat	12	9	7	4	7
KIT creased	12	8	6	4	5
KIT folded	1	2	0	0	0
HVTR (g/m ² *d)	3	7	21	37	44
Blocking	1.3	1	1	1	1

Talc containing coating formulations, Table 18, showed more cracking at fold in staining test but the olive oil test results were still good up to 40% pigment content. HVTR results were at good level for samples containing 10 and 20% talc.

5 Table 19; Kaolin

	HEC-FCR 6	HEC-FCR 7	HEC-FCR 8	HEC-FCR 9	HEC-FCR 10
Enzymatically hydrolysed HEC	80	70	60	50	40
Barrisurf LX	10	20	30	40	50
PEG-300	10	10	10	10	10
Coating rod/speed	2x3/10	2x2/10	2x2/10	2x2/10	2x0/10
	HEC-FCR 6	HEC-FCR 7	HEC-FCR 8	HEC-FCR 9	HEC-FCR 10
Coat weight (g/m ²) average	9.1	8.6	8.7	9.4	10.2
KIT flat	12	8	9	8	10
KIT creased	12	8	7	md7 cd8	md4 cd6
KIT folded	md1 cd2	1	0	0	md0 cd1

HVTR (g/m ² *d)	4	16	28	33	41
Blocking	1.4	1	1	1	1

Coating tests with CMC

Table 20

	CMC 1	CMC 2	CMC 3	CMC 4	CMC 5	CMC 6	CMC 7
CMC3	50						
CMC1		50					
CMC2			50				
Enzymatically hydrolysed CMC1 (Fibercare R)				50			
CMC2 (Fibercare R)					50		
Enzymatically hydrolysed CMC1 (Fibercare U)						50	
Enzymatically hydrolysed CMC 2 (Fibercare U)							50
HydroCarb HC 60	30	30	30	30	30	30	30
PEG 300	20	20	20	20	20	20	20
Coat weight (g/m ²)	7.3	7.3	8.5	6.9	6.9	7.3	7.5
KIT, flat	6	9	7	7	7	7	12
KIT, creased cd/md	5/4	5/4	3/2	5/4	6/5	4/3	7/6
KIT folded	2	2	2	1	2	3	4
WVTR (g/m ² *d)	114	112	111	96	123	98	108
Blocking	1	1	1	1	1	1	1

CMC coatings show more cracking at crease than the HEC samples showed.

Claims

1. A coating composition for a sheet like cellulosic fibrous web comprising one or more water-soluble cellulose derivatives selected from the group consisting of alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose, methyl cellulose (MC), and carboxymethyl cellulose hydrolyzed with an enzyme having cellulolytic activity, and having a weight average molecular weight MW is 20 000 Da - 120 000 Da, such as, 30 000 - 100 000 Da.
5
2. The coating composition of claim 1, wherein solids content of the coating composition is at least 20 weight-%.
10
3. The coating composition of claim 1 or 2, wherein viscosity of the coating composition is 50 - 3000 mPas measured at 23 °C using 100 rpm and Brookfield DV-E viscometer.
15
4. The coating composition of any of claims 1 to 3 or the coating of claim 1, wherein said coating composition comprises water-soluble cellulose derivatives in amount 20-100 weight-%, preferably 30-90 weight-%, more preferably 40-70 weight-% of the total solids content of the coating composition or the coating.
20
5. The coating composition of any of claims 1 to 4, wherein the coating composition further comprises one or more constituent(s) selected from the group comprising a plasticizer, pigment particle, starch, binder, thickener, cross-linker, lubricant, and dispersing agent; or the method of any of the previous claims, wherein one or more agents are selected from the group comprising a plasticizer, pigment particle, starch, binder, thickener, cross-linker, lubricant, and dispersing agent.
25
6. The coating composition of any of claims 1 to 5, wherein one or more water-soluble cellulose derivatives is/are selected from the group comprising or consisting of an alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose; and any combination thereof.
30
7. The coating composition of claim 6, wherein one or more water-soluble cellulose derivatives is/are selected from the group comprising or consisting of methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxymethyl cellulose (HMC), hydroxyethyl cellulose (HEC), methyl hydroxyethyl cellulose (MHEC), hydroxypropyl
35

cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), and any combination thereof.

5 8. A method of preparing a coating composition for a sheet like cellulosic fibrous web by enzymatically degrading one or more water-soluble cellulose derivatives, wherein the method comprises

- (a) providing an aqueous suspension of one or more water-soluble cellulose derivatives selected from alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose, methyl cellulose (MC), and carboxymethyl cellulose; and
- 10 (b) contacting said suspension with an enzyme having cellulolytic activity;
- (c) allowing to react at conditions conducive for activity of said enzyme; and
- (d) optionally removing excess of water; and
- (e) optionally adding one or more agents to the composition comprising degraded water-soluble cellulose derivatives.

15

9. The method of claim 8, wherein said one or more water-soluble cellulose derivatives is/are selected from the group comprising or consisting of methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxymethyl cellulose (HMC), hydroxyethyl cellulose (HEC), methyl hydroxyethyl cellulose (MHEC), hydroxypropyl cellulose (HPC) and hydroxypropylmethyl cellulose (HPMC) and any combination thereof.

20

10. The method of any of claim 8 to 9, wherein said enzyme having cellulolytic activity is a cellulase such as an endoglucanase enriched cellulase preparation.

25

11. The method of any of claims 8 to 11, wherein the aqueous suspension of one or more water-soluble cellulose derivatives during incubating / allowing to react at phase has a consistency of 2 - 20 wt.-% dry matter from the total weight of the total weight of said suspension.

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12. A coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web substrate, wherein the substrate has been coated with the coating composition of any of claims 1 to 7 or obtained by method of any of claims 8 to 11.

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13. The coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web of claim 12, wherein the substrate comprises

cellulosic or lignocellulosic fibres, or the substrate is a fibrous web, such as a paper, board, tissue or the like.

5 14. The coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web of claim 12 or 13, wherein the coated substrate or the product has KIT test value of at least 7, water vapor transmission rate (WVTR) less than 110 g/m²/d; decreased blocking tendency compared to a coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web with a coating obtained without enzymatic degradation; and/or increased
10 grease barrier properties compared to a coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web with a coating obtained without enzymatic degradation.

15 15. The coated sheet like cellulosic fibrous web or a product comprising said coated sheet like cellulosic fibrous web of any of claims 13 to 15, wherein the coating has a coat weight 3 – 25 g/m².

20 16. A method of coating a sheet like cellulosic fibrous web, wherein the method comprises applying the coating composition of any of claims 1 - 7 on said web.

25 17. A method of improving grease barrier properties of coating for a sheet like cellulosic fibrous web, wherein the method comprises

(a) providing an aqueous suspension of one or more water-soluble cellulose derivatives selected from alkyl cellulose, hydroxyalkyl cellulose, hydroxyalkyl alkyl cellulose, methyl cellulose (MC) and carboxymethyl cellulose; and

(b) contacting said suspension with an enzyme having cellulolytic activity; and
(c) allowing to react at conditions conducive for activity of said enzyme until said water-soluble cellulose derivatives have having a weight average molecular weight MW is 20 000 Da - 120 000 Da, such as, 30 000 -100 000 Da;

30 and

(d) optionally removing excess of water; and

(e) optionally adding one or more agents to the composition comprising hydrolysed water-soluble cellulose derivatives.

35 18. Use of the enzyme hydrolysed water-soluble cellulose derivatives having a weight average molecular weight MW is 20 000 Da- 120 000 Da, such as 30 000 Da - 100 000 Da as a coating composition for a sheet like cellulosic fibrous web.

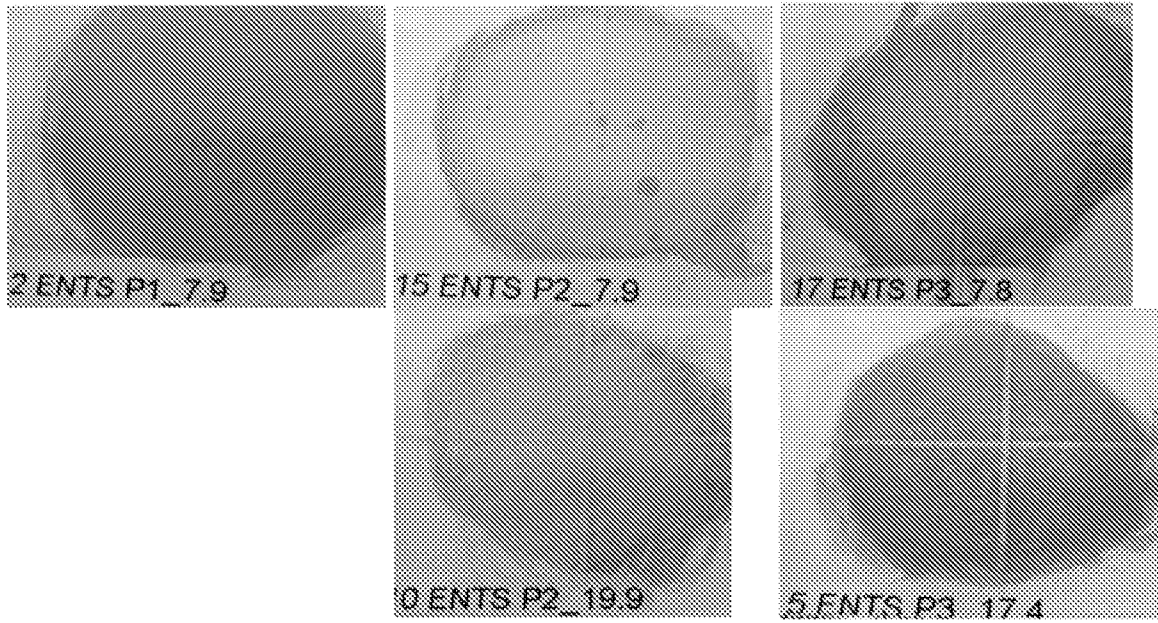


Figure 1.

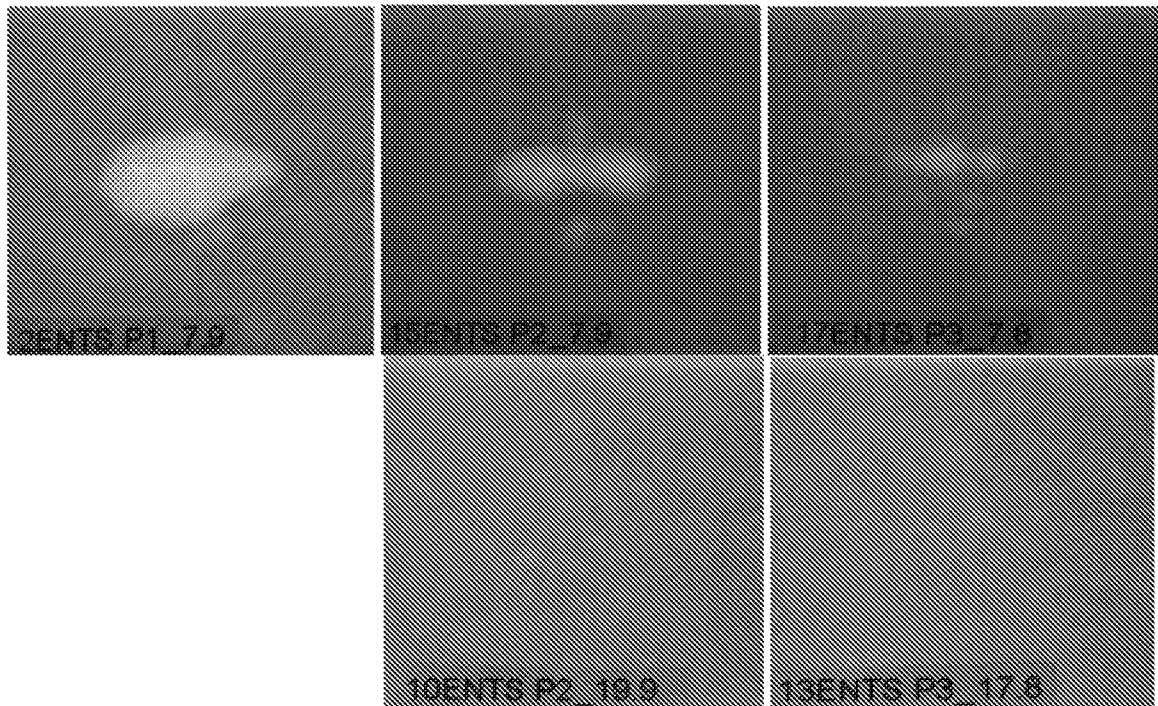


Figure 2.

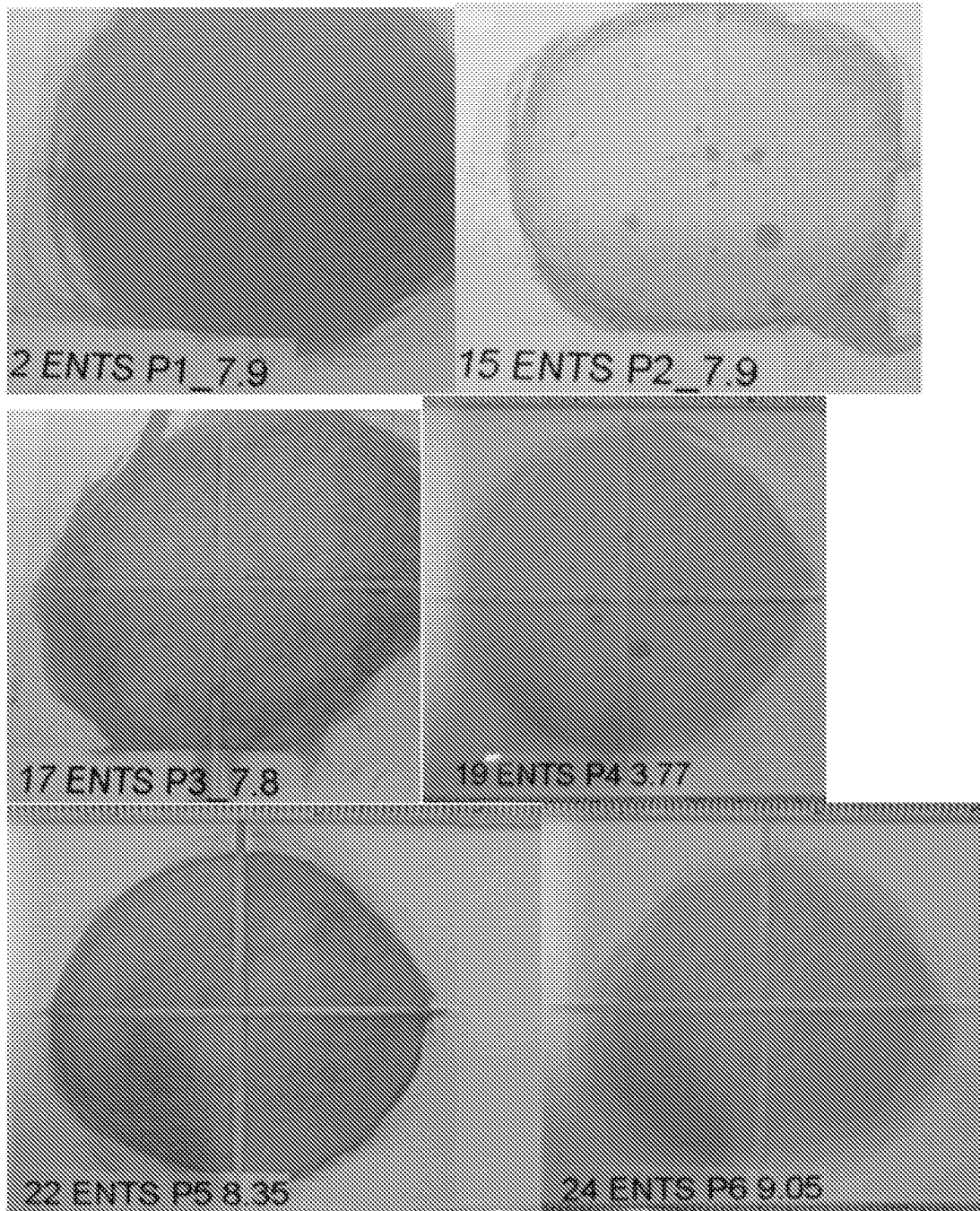


Figure 3.

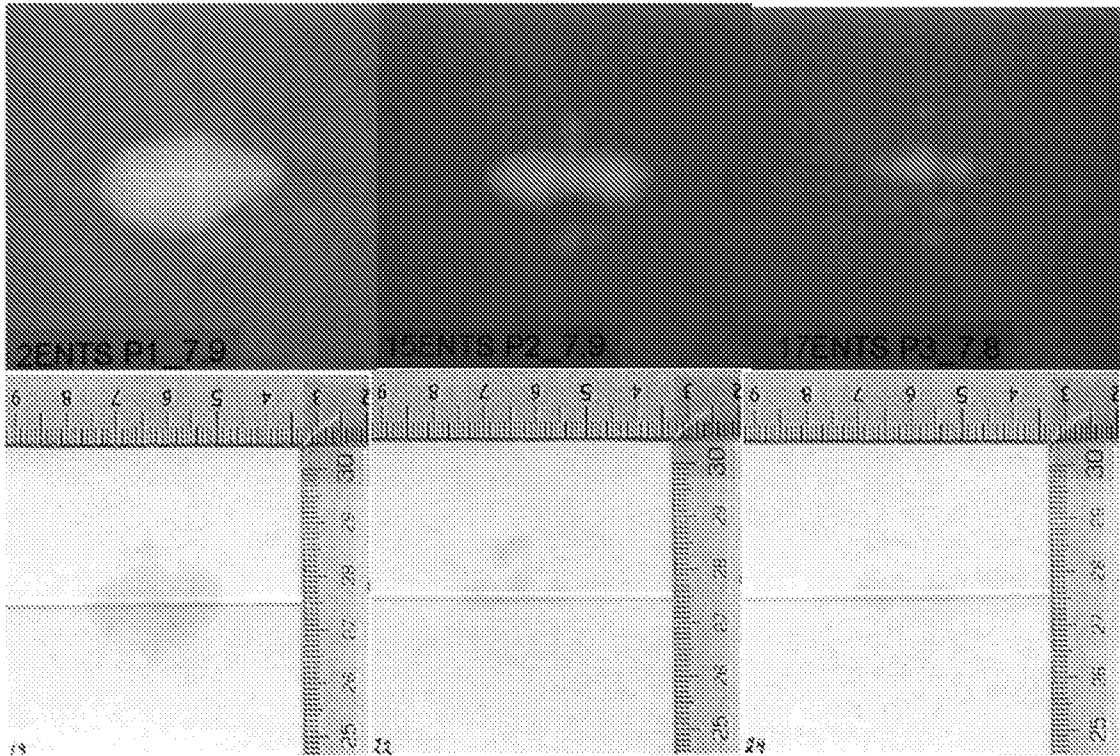


Figure 4.

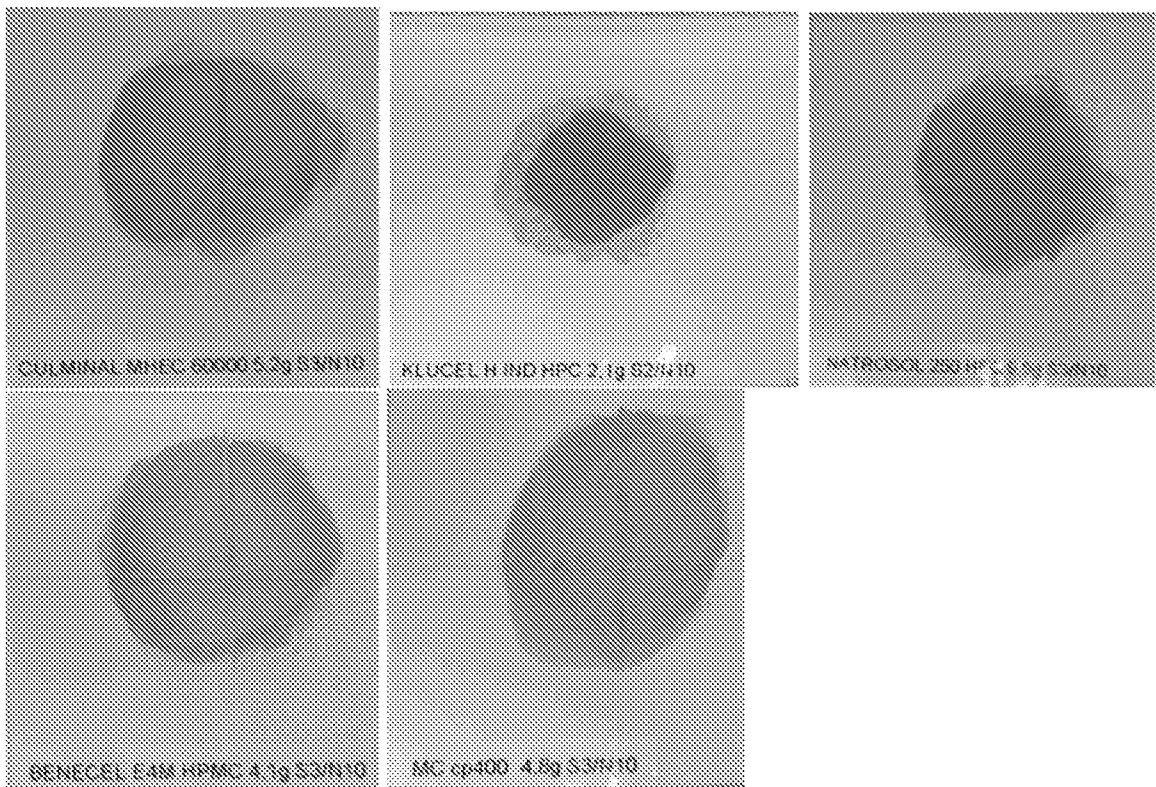


Figure 5 (continues in the next page).

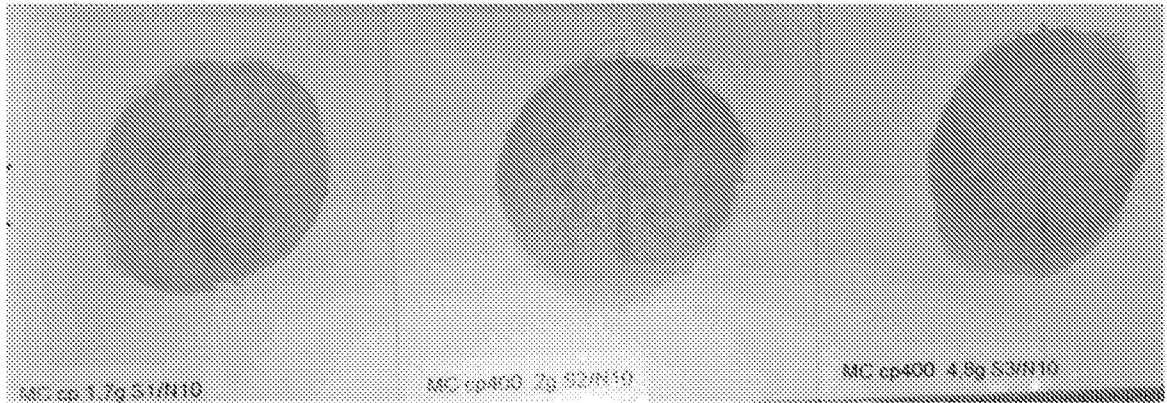


Figure 5 (continues from the previous page).

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2022/050697

A. CLASSIFICATION OF SUBJECT MATTER		
INV. D21H17/00	D21H17/25	D21H17/26
D21H19/52	D21H21/16	D21H17/27
D21H19/34		
ADD.		
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) D21H		
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 practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"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 "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 "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 "&" document member of the same patent family	
Date of the actual completion of the international search	Date of mailing of the international search report	
15 December 2022	04/01/2023	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Karlsson, Lennart	

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