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(54) **STARCH-COATED PAPER OR PAPERBOARD**

(57) There is provided a product comprising a paper substrate and a first coating provided on the substrate, wherein the first coating comprises starch and calcium carbonate pigment.

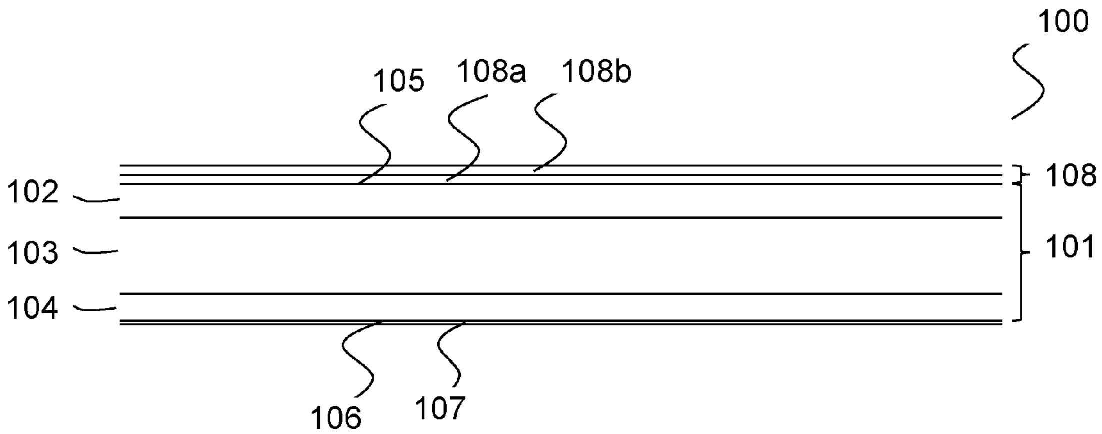

Fig. 1

Description

TECHNICAL FIELD

[0001] The present disclosure relates to the field of paper and paperboard intended to be covered by a polyolefin layer.

BACKGROUND

[0002] In manufacturing paper or paperboard, starch is sometimes coated onto a surface of the paper or paperboard for curl control or to prevent dusting/linting. Linting is when fibers from the paper come loose and are subsequently picked up by the printing unit, causing defects in the print. These fibers usually come from the non-coated side where the fibers are exposed.

SUMMARY

[0003] The inventor has noted that a problem of the above-mentioned starch coating is that the starch-coated surface has inferior adhesion to polyolefins. Accordingly, there may be a delamination problem after a polyolefin film has been laminated to a starch-coated paper or paperboard surface.

[0004] An objective of the present disclosure is to provide an alternative coating of that provides better adhesion to polyolefins.

[0005] To meet the objective, the present disclosure provides a product comprising a paper substrate, such as a paperboard substrate, and a first coating provided on the substrate, wherein the first coating comprises starch and calcium carbonate pigment, preferably in a dry weight ratio between 21:100 and 500:100.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006]

Fig 1 illustrates an embodiment of the product of the present disclosure.

Fig 2 illustrates another embodiment of the product of the present disclosure.

Fig 3 shows the set-up for measuring PE adhesion that is used in the examples section.

DETAILED DESCRIPTION

[0007] The present disclosure provides a product comprising a paper substrate and a first coating provided on the substrate, wherein the first coating comprises starch and calcium carbonate ($CaCO_3$) pigment.

[0008] The starch may be natural or modified starch. The starch may comprise dissolved starch molecules and/or starch particles that are not dissolved, but suspended in water.

[0009] Preferably, at least 90%, such as at least 95%, by dry weight of all the pigment in the first coating is calcium carbonate pigment.

[0010] The d_{50} of the calcium carbonate pigment maybe 0.60-0.80 μm and the d_{98} of the calcium carbonate pigment is preferably at least 2.8 μm, such as 2.9-4.0 μm. The d_{75} of the calcium carbonate pigment may be 1.0-1.4 μm

[0011] The skilled person working with calcium carbonate pigments is familiar with *d* values. For determining the *d* values, a Sedigraph 5100 or 5120 device from the company Micromeritics, USA, can be used. The particle size distributions given herein were determined using a Micromeritics Sedigraph III with software version V.1.04.

[0012] The calcium carbonate pigment is preferably ground calcium carbonate (GCC).

[0013] The dry weight ratio of starch to calcium carbonate in the first coating may for example be between 10:100 and 500:100.

[0014] In the prior art, pigment coatings typically comprise 10-20 parts binding agent per 100 parts of pigment. In contrast thereto, a preferred embodiment of the first coating has 21-500 parts of starch per 100 parts of calcium carbonate pigment. In even more preferred embodiments, the lower limit for the proportion of starch is 25 or 33 parts per 100 parts of calcium carbonate pigment.

[0015] Accordingly, the dry weight ratio of starch to calcium carbonate in the first coating is between 21:100 and 500:100 in a preferred embodiment and between 25:100 and 500:100 in a more preferred embodiment.

[0016] In a particularly preferred embodiment, the dry weight ratio of starch to calcium carbonate in the first coating is between 33:100 and 300:100, such as between 50:100 and 500:100, such as between 150:100 and 500:100.

[0017] Starch and calcium carbonate pigment typically constitute at least 80% of the dry weight of the first coating. Preferably, they constitute at least 90% of the dry weight of the first coating and more preferably at least 95% of the dry weight of the first coating.

[0018] In addition to calcium carbonate and starch, the first coating may comprise a rheology modifier. The rheology modifier typically amounts to 0.05-2.0 %, such as 0.1-1.1%, of the dry weight of the first coating. The rheology modifier may for example be CMC or an acrylic co-polymer, such as an alkali-swellable emulsion (ASE) or a hydrophobically modified, alkali-swellable emulsion (HASE) or a high molecular weight starch or a polyvinyl alcohol.

[0019] According to the inventor's empirical testing, a coat weight no less than 0.5 g/m^2 is typically needed to obtain a significant reduction of the linting problem. The coat weight of the first coating is thus preferably at least 0.5 g/m^2 and may for example be between 0.5 and 20 g/m^2, such as between 0.5 and 15 g/m^2, such as between 0.5 and 10 g/m^2. In one embodiment, which is particularly relevant when the first coating is provided on the reverse side (discussed below), the coat weight is between 0.5 and 4.5 g/m^2, such as between 0.5 and 2.9 g/m^2, such as between 0.8 and 2.0 g/m^2. The first coating may be applied in two layers, in particular if the coat weight is higher, such as above 6 g/m^2.

[0020] In an embodiment, the paper substrate is a multi-layered linerboard or paperboard having a grammage according to ISO 536:2019 of 120-500 g/m^2, such as 150-500 g/m^2 or 120-300 g/m^2. The a multi-layered linerboard or paperboard typically has a density according to ISO 534:2011 of 550-900 kg/m3. Liquid packaging board (LPB) is preferred type of multi-layered paperboard. The LPB may have a basis weight according to ISO 536:2019 of 120-300 g/m^2, such as 125-260 g/m^2. Further, the LPB typically comprises hydrophobic size, e.g. rosin size, AKD and/or ASA. In one embodiment, the LPB comprises rosin size in combination with AKD or ASA. The hydrophobic size is preferably provided as internal sizing (i.e. added in the wet end of the paperboard machine).

[0021] If the paper substrate is intended to be printed on one side thereof (e.g. by water-based flexo or rotogravure, which are surface sensitive printing techniques), it is preferably the other side (the "reverse side") that is provided with the first coating. Further, a second coating may be provided of the side intended to be printed (the "printing side").

[0022] The second coating preferably comprises pigment and a polymeric binder. Examples of polymeric binders are styrene-butadiene copolymers, styrene-acrylate copolymers, other latex-forming polymers and starch. The styrene-acrylate copolymers are more preferred than the styrene-butadiene copolymers due to lesser health and environmental concerns.

[0023] The dry weight ratio of polymeric binder to pigment in the second coating is preferably between 10:100 and 20:100. The pigment of second coating preferably comprises or consists of calcium carbonate and/or clay. A suitable example of the second coating is the pigment coating disclosed in WO 2018/189283, which provides satisfactory PE adhesion in combination with satisfactory printing properties.

[0024] The coat weight of the second coating is typically 5-30 g/m^2, such as 6-25 g/m^2, such as 7-22 g/m^2, such as 8-20 g/m^2. In one embodiment, the coat weight of the first coating is at least 50% lower than the coat weight of the second coating. In a preferred embodiment, the coat weight of the first coating is 0.5-2.9 g/m^2 at least 60% lower than the coat weight of the second coating.

[0025] In one embodiment, not only the first, but also the second coating comprises starch and calcium carbonate pigment, preferably in a dry weight ratio between 21:100 and 500:100. This embodiment is advantageous when there is a need to reduce linting and obtain a strong polyolefin adhesion on both sides. This coating layer may improve the printing properties compared to uncoated paper, however if the printing properties requirements are high then a different coating can be employed for the print side.

[0026] The product discussed above may further comprise a polyolefin layer, such as a polyethylene (PE) layer, provided on the first coating. When the second coating is provided, the product may also comprise a second polyolefin layer (e.g. PE layer) provided on the second coating. The surface of the second coating may be printed before the second polyolefin layer is applied.

[0027] An embodiment of the product of the present disclosure is illustrated in Fig 1. The product 100 comprises a multilayered paperboard substrate 101 comprising a printing layer 102, a middle layer 103 and a reverse layer 104. The paperboard substrate 101 thus has a printing side 105 and a reverse side 106. A first coating 107 is provided on the reverse side 106. The dry content of the first coating 107 consists essentially of starch, calcium carbonate pigment and rheology modifier. The dry weight ratio of starch to calcium carbonate pigment is between 21:100 and 500:100. The rheology modifier amounts to 0.05-2.0 % of the dry weight of the first coating 107. The coat weight of the first coating 107 is in the range of 0.5-2.9 g/m^2. A second coating 108 is provided on the printing side 105. The second coating has two sublayers 108a and 108b (typically applied in two subsequent coating steps). The coat weight of the second coating 108 is in the range of 7-22 g/m^2. The composition of the sublayers 108a and 108b may be the same or different, but both comprise polymeric binder and pigment in a dry weight ratio between 10:100 and 20:100. The upper surface of the uppermost sublayer 108b is intended to be printed. The first coating 107 is intended to be covered by a polyolefin layer.

[0028] Another embodiment of the product of the present disclosure is illustrated in Fig 2. The product 200 comprises a multilayered paperboard substrate 201 comprising a first outer layer 202, a middle layer 203 and a second outer layer 204. A first coating 207 is provided on the outer surface of the first outer layer 202 and a second coating 208 is provided on the outer surface of the second outer layer 204. The dry content of each of the first coating 207 and the second coating 208 consists essentially of starch, calcium carbonate pigment and rheology modifier, wherein the dry weight ratio of starch to calcium carbonate pigment is between 21:100 and 500:100. The rheology modifier amounts to 0.05-2.0 % of the dry weight of the first coating 207 and the second coating 208. The coat weight of each of the first coating 207 and the second coating 208 is in the range of 0.5-2.9. The first coating 207 and the second coating 208 are intended to be covered by a polyolefin layer. Further, the coatings 207, 208 result in improved bending stiffness (since the starch improves the tensile strength of the outer layers 202, 204.

EXAMPLES

[0029] A two-layered paperboard having a white (bleached) top/print layer and a brown (unbleached) reverse layer was provided. Both layers were formed from kraft pulp and the basis weight of the paperboard was 192 g/m^2. In a trial series, the paperboard was coated on the reverse side with compositions comprising pigment, starch (Perfectafilm A150 from Avebe) and rheology modifier (Rheocoat 66 SN from Coatex, which is an alkali-swellable emulsion of acrylic copolymer) in different ratios. The pigment was talc (C15 B2 from Elementis), $CaCO_3$ (HydroCarb 90 (HC90) from OMYA) or clay (Kaovit from Thiele, which is a delaminated kaolin clay). The compositions tested are shown in Table 1 below.

[0030] HC90's particle size curve gives the following Sedigraph values: d_{50} = 0.70 μm, d_{75} = 1.2 μm and d_{98} = 3.2 μm. Kaovit's particle size curve gives the following Sedigraph values: d_{50} = 0.85 μm and d_{75} = 2.0 μm.

[0031] The trial series was run in a gravure pre-metered size press (manufactured by UMV coating) in direct offset mode by coating the reverse side, which usually faces the inside of a package formed from the board. Coat weight was measured as an average by a traversing frame consisting of ash sensor, moisture sensor and basis weight sensor in a 2-frame system, one frame before coating and the other frame after the coating and drying. The difference between the average basis weight sensors output, corrected for moisture content, was used as the measurement of basis weight increase, i.e. coat weight in this case. The average value is taken from several measurement points in both cross and machine direction during the coating trial. The measuring frame was supplied by Honeywell.

[0032] In the trials, it was aimed for a coat weight of 2.0 +/- 1.0 g/m^2. It was expected, due to density differences between mineral/pigment and polymer, that higher percentage of mineral/pigment would yield higher coat weight (this by generating higher normal force on the metering element and in the nip). It takes long time to correct for these differences and hence the +/- 1.0 g/m^2 tolerance was accepted for the coat weight. Ideally the coat weight is as low as possible while still covering the fibers of the paper to prevent linting. The solids content was kept at approximately 20% or lower so that the coat weight would not be too high.

[0033] The pigment-coated paperboard was then extrusion-coated with low density polyethylene (LDPE CA8200 from Borealis). The extrusion die was set to 320 °C. A_3 sized samples of the pigment-coated paperboard were taped to a 820 mm wide 70 g/m^2 kraft paper to get a carrier to take the sheets through the machine. The coat weight was 40 g/m^2 divided between two slots in the die. Ozone was used just before the nip to further oxidize the polymer melt and a pre-treatment of corona at 12kW before the extrusion station was employed to the paper and paperboard samples on the surface to be coated. Line speed was 100m/min, press roll was set to 3.2 kp/cm^2 and the chill roll surface was set to 20 °C.

[0034] After extrusion coating, F_{max} (the maximum force determined in a peel test), which represents "PE adhesion", was measured. The method of measuring F_{max} is described in more detail below. The results of the F_{max} testing are shown in Table 1 below.

Table 1.

Sample		1	2	3	4	5
Coating comp.	$CaCO_3$ (parts by dry weight)	100	100	100	100	100
	Clay (parts by dry weight)					
	Talc C15 B2 (parts by dry weight)					
	Starch (parts by dry weight)	10	13	33	100	300
	RheoCoat 66 (parts by dry weight)	1	1	1	1	1
Dry matter content (wt.%)		20	20	19	18	14
Viscosity (mPas)		100	90	130	290	320
Coat weight (g/m²)		2.8	2.5	2.2	1.5	1.4
F_{max} (N)		3.6	3.7	3.8	3.9	4.3

Table 1 continued.

Sample		6	7	8	9	10
Coating comp.	HC 90 (parts by dry weight)	75	25			
	Kaovit (parts by dry weight)	25	75	100	100	
	Talk C15 B2 (parts by dry weight)					100
	Starch (parts by dry weight)	33	33	33	100	100
	RheoCoat 66 (parts by dry weight)	1	1	1	1	1
Dry matter content (wt.%)		20	19	20	20	19
Viscosity (mPas)		150	150	170	340	470
Coat weight (g/m²)		2.5	2.4	2.5	2.6	1.5
F_{max} (N)		3.3	3.0	2.9	3.4	2.9

[0035] As shown in Table 1, a composition comprising 100 parts of $CaCO_3$ and 100 part of starch (sample 4) resulted in significantly higher F_{max} than a composition comprising 100 parts of clay or talc and 100 parts of starch (sample 9 or 10). It is also noted that F_{max} increases with an increased proportion of starch in the $CaCO_3$/starch mixtures, which may be considered surprising given the inferior polyolefin adhesion of surfaces coated with starch only. Another beneficial effect of an increased proportion of starch is that lower coat weights are enabled.

Method of measuring PE adhesion

[0036] The method described below is designed to determine how well a final product, such as a liquid package, performs when subjected to mechanical stress by measuring the cohesion of the coating layer. The instrument used for the method is made by Instron, but any quality tensile tester will suffice.

1. An extrusion-coated sample, 50-100 cm x web width, was sampled.
2. A cut was gently made in the PE film in the cross direction (CD), relative to the production direction (MD).
2b. In this specific case there was a need to add a 50mm width PTFE tape to the paperboard before coating with polyolefin to get a place to start, i.e. a non-adhered portion of the polyolefin film.
3.15 mm * 15 cm samples were cut to get the delaminated film in the one end (15 mm CD and 15 cm MD)
4. The samples were placed one at the time onto the wheel, as depicted in Fig 3, with double adhesive tape 3M 410 and the non-adhered portion of the polyolefin film was attached to the clamp positioned 90 degrees in relation to the movement of the paper sample. The clamp exerted a pulling force upwards at a specified speed and at the same time the force (i.e. the delamination resistance of the sample) was monitored. The wheel was moved during the measurement to maintain 90° angle. In case of very high values for delamination, the film may stretch or rupture. This was the case here, so a tape (Scotch Tape 371 PP clear) was attached on top of the PE film to make it stronger. Thereby interference caused by stretching or rupturing the PE film was avoided when the adhesion force between the paper coating and the PE film was measured.

5. Pulling upwards with the Instron was started and the force (N) and extension (mm) was recorded. The measurement length was 15 mm. For each sample, four measurements in MD and four measurements in anti-MD were made.
6. The maximum value for each measurement was read. "F_{max}" was calculated as an average of the eight maximum values.

Claims

1. A product comprising a paper substrate and a first coating provided on the substrate, wherein the first coating comprises starch and calcium carbonate pigment.

2. The product of claim 1, wherein the dry weight ratio of starch to calcium carbonate in the first coating is between 10:100 and 500:100.

3. The product of claim 2, wherein the dry weight ratio of starch to calcium carbonate in the first coating is between 21:100 and 500:100.

4. The product of claim 3, wherein the dry weight ratio of starch to calcium carbonate in the first coating is between 25:100 and 500:100.

5. The product of claim 4, wherein the dry weight ratio of starch to calcium carbonate in the first coating is between 33:100 and 300:100.

6. The product of claim 4, wherein the dry weight ratio of starch to calcium carbonate in the first coating is between 50:100 and 500:100.

7. The product of claim 6, wherein the dry weight ratio of starch to calcium carbonate in the first coating is between 150:100 and 500:100.

8. The product of any one of the preceding claims, wherein starch and calcium carbonate pigment constitute at least 80% of the dry weight of the first coating, such as at least 90% of the dry weight of the first coating, such as at least 95% of the dry weight of the first coating.

9. The product of any one of the preceding claims, wherein the coat weight of the first coating is between 0.5 and 4.5 g/m^2, such as between 0.5 and 2.9 g/m^2, such as between 0.8 and 2.0 g/m^2.

10. The product of any one of the preceding claims, wherein the paper substrate is a multi-layered linerboard or paperboard having a grammage according to ISO 536:2019 of 120-500 g/m^2, such as 150-500 g/m^2 or 120-300 g/m^2.

11. The product of claim 10, wherein the paper substrate is liquid packaging board.

12. The product of any one of the preceding claims, wherein the paper substrate has a printing side and a reverse side and the first coating is provided on the reverse side and a second coating is provided on the printing side.

13. The product of claim 12, wherein the second coating comprises pigment and a polymeric binder.

14. The product of claim 13, wherein the dry weight ratio of polymeric binder to pigment in the second coating is between 10:100 and 20:100.

15. The product of any one of claims 12-14, wherein the coat weight of the second coating is at least 100% higher than the coat weight of the first coating.

16. The product of any one of the preceding claims, further comprising a polyolefin layer, such as a polyethylene (PE) layer, provided on the first coating.

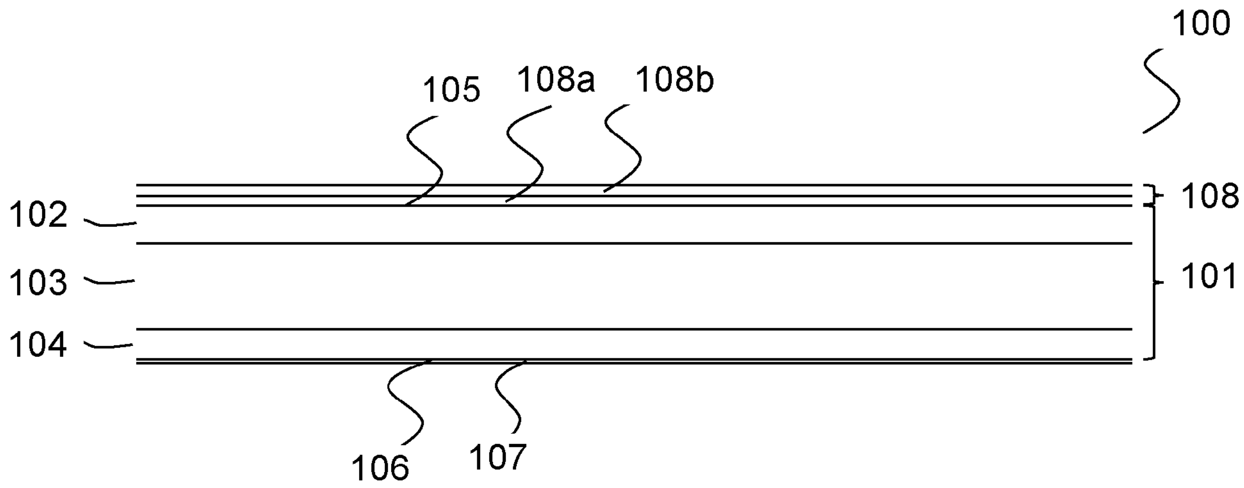
100
105
108a
108b
108
102
103
101
104
106
107

Fig. 1

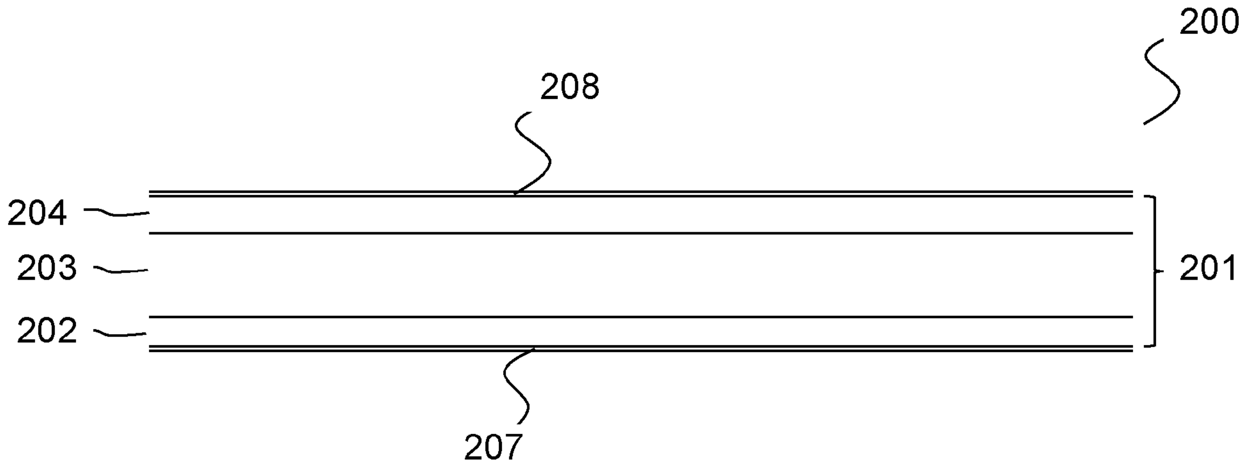
200
208
204
203
201
202
207

Fig. 2

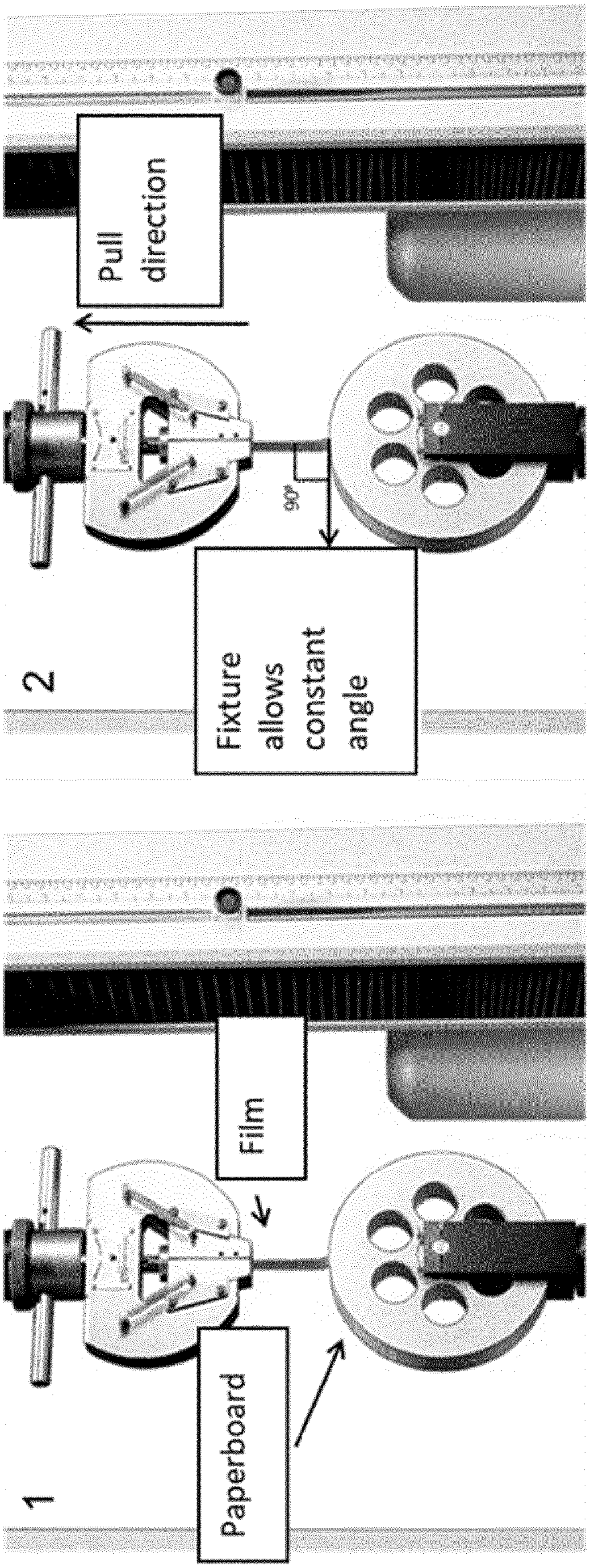
2
Pull direction
90°
Fixture allows constant angle
1
Film
Paperboard

Fig. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 21 21 0830

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
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CATEGORY OF CITED DOCUMENTS

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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