



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
30.04.2014 Bulletin 2014/18

(51) Int Cl.:
D21H 21/16 (2006.01)

(21) Application number: **12189882.9**

(22) Date of filing: **25.10.2012**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

- **Heimonen, Jukka**
FI-33880 Lempäälä (FI)
- **Tynkkynen, Topi**
FI-01520 Vantaa (FI)
- **Vaitinen, Henri**
FI-04400 Järvenpää (FI)

(71) Applicant: **Metso Paper Inc.**
00130 Helsinki (FI)

(74) Representative: **Berggren Oy Ab**
P.O. Box 16
Antinkatu 3 C
00101 Helsinki (FI)

(72) Inventors:
• **Pietikäinen, Reijo**
FI-04420 Järvenpää (FI)

(54) **Method and production line and for producing fiber webs**

(57) The invention relates to a method for producing a fiber web, in which the fiber web (W) is surface sized with starch or other sizing agent in a sizer (20) and in which the fiber web (W) is calendered or correspondingly treated by contacting press-treatment. The fiber web is surface sized by applying low soluble starch, such as maize starch or wheat starch or barley starch or rice starch, or other sizing agent that is low soluble or not re-soluble in moisturizing. The invention also relates to a production line for producing fiber webs which comprises

a sizer (20) for surface sizing the fiber web (W) with starch or other sizing agent in a sizer and a calender (40; 60) or corresponding treatment device for calendering or correspondingly treating by contacting press-treatment the fiber web (W). The sizer (20) is provided with application means for surface sizing the fiber web (W) by applying low soluble starch, such as maize starch or wheat starch or barley starch or rice starch, or other sizing agent that is low soluble or not re-soluble in moisturizing.

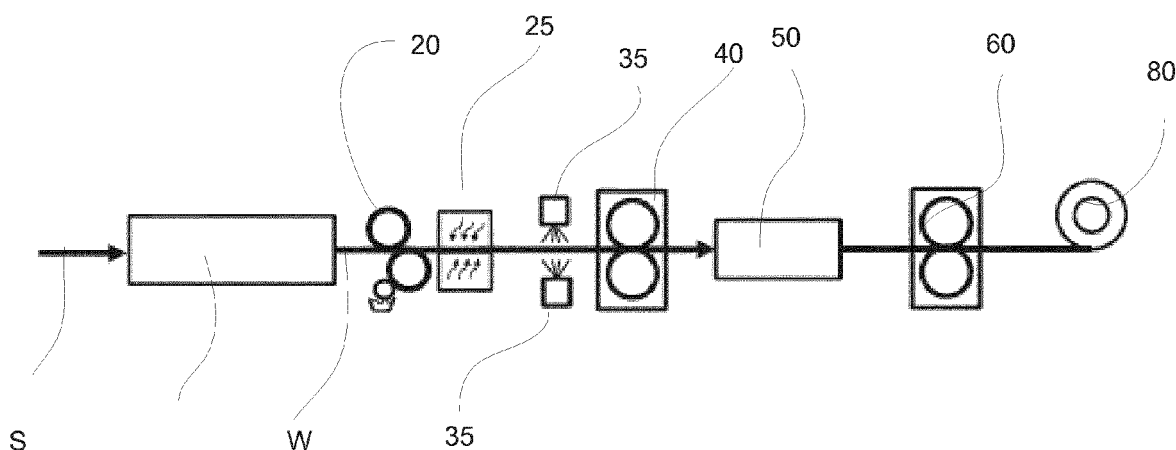


Fig. 8

Description

[0001] The invention relates to producing fiber webs, in particular paper and board webs. Especially the invention relates to a method for producing fiber webs according to the preamble of claim 1 or 2 and to a production line for producing fiber webs according to the preamble of claim 14.

[0002] As known from the prior art in fiber web producing processes typically comprise an assembly formed by a number of apparatuses arranged consecutively in the process line and forming process steps. A typical production and treatment line comprises a head box, a wire section and a press section as well as a subsequent drying section and a reel-up. The production and treatment line can further comprise other devices and/or sections for finishing the fiber web, for example a sizer, a pre-calender, a coating section, a final-calender. The production and treatment line also comprises at least one slitter-winder for forming customer rolls as well as a roll packaging apparatus. In this description and the following claims by term fiber web are meant for example a paper and board webs.

[0003] In production of fiber webs, for example of paper or board webs, sizing is used to alter the properties of a fiber web by adding sizing agents, for example starch or other sizing agents. In surface sizing the sizing agent is added onto the surface of the fiber web at the dry end of the fiber web machine. Surface sizing is used in production of many fiber web grades, for example of uncoated fine papers and of several board grades.

[0004] Pre-calendering is typically used for creating required surface properties for further treatment for example for coating. Final-calendering is generally carried out in order to improve the properties, like smoothness and gloss, of a web-like material such as a paper or board web. In calendering the web is passed into a nip, i.e. calendering nip, formed between rolls that are pressed against each other, in which nip the web becomes deformed as by the action of temperature, moisture and nip pressure. In the calender the nips are formed often between a smooth-surfaced press roll such as a metal roll and a roll coated with resilient material such as a polymer roll or between two smooth-surfaced rolls. The nips can be formed also by using instead one of rolls a belt or a shoe as known from prior art. Many different kinds of calenders to be used as a pre-calender and/or as an final-calender are known, for example hard nip calenders, soft nip calenders, supercalenders, metal belt calenders, shoe calenders, long nip calenders, multnip calenders etc.

[0005] Further web treatment producing web smoothing effect can be done in various hot pressing contact treatment processes, like Condebelt -drying, BoostDryer -drying, metal belt drying or treatment, Yankee cylinder drying, MG-cylinder drying etc. cylinder drying.

[0006] In web treatment processes where smoothening is desired the applied heat can be used to raise the

surface temperature of the fiber web to glass transition temperature, which causes the fibers to soften and conform to the surface of the roll. Moisture, for example water or steam can also be added before the nip to the surface to be treated to further lower the glass transition temperature. Thus the gradients in the temperature and moisture level tend to lower the glass transition temperature preferentially on the external surfaces of the fiber web and allow the web to achieve a desired smoothness without significant reduction in caliber.

[0007] In calendering and corresponding web treatment processes of moistened or moist fiber web, which has been sized with water soluble sizing agent like starch, a disadvantage is that the starch and associated fibers tend to pick and stick on the heated calender rolls and corresponding heated metal surfaces contacting the fiber web. This tends to be aggravated at higher nip loads and temperatures required for achieving high smoothness levels. The sticking and fiber pulling are caused by dissolving of starch or other binders that are added in to the web and may lead to runnability problems, roll contamination and calendered or treated quality reduction

[0008] In the contact drying or hot contact treatment processes the surfaces can be contaminated by stickies, fiber picking and binders in the web. In the beginning of drying section the web is wet (moist) which aggravates the problem.

[0009] In US patent publications 6645349 and 6905573 it is disclosed a method to use roll surface monitoring systems, for example camera systems, to detect the roll picking and contamination and control roll cleaning operation.

[0010] In WO publication 99/25921 is disclosed a method for detecting contamination that runs through a nip or nips in a calender, in which method vibrations occurring in connection with the constructions of calender are detected and processed. The source of unusual vibrations is located, which makes it possible to start eliminating the contaminations or to replace the damaged part.

[0011] In US patent publication 6274001 is disclosed a calendering method in which lubricant is applied to both sides of the web to prevent fiber sticking/picking in the hot nip. The lubricant may be applied by the sizer, by the moisturizing showers or by separate lubricant showers.

[0012] In US patent publications 3145116, 5114999 and 6300393 are disclosed some known examples of insolubilizers for starches and coating binders and surface sizes.

[0013] In fiber web production when fiber web is surface sized with water soluble starch and dried, the dried starch film easily dissolves in connection with moisture addition and can stick to the contacting surfaces. In pilot scale test it has been detected that even a small amount of starch deposits on roll surfaces can cause quality loss of a fiber web for example due to decreased smoothness. Due to the high water solubility of the starch the moisture addition before calendering has not been possible.

[0014] As known, the reactive part of a starch molecule is a hydroxyl group due to which one of the basic properties of starch is water solubility. Dried starch in sized fiber web is soluble in water and thus it sticks to for example calender rolls, if water is applied. This is preventing the use of water moisturizing in calendering of starch sized fiber webs even though the moisturizing before calendering would be very advantageous particularly due to enhanced moisture gradient calendering effect.

[0015] The water solubility of starch can be decreased by modifying starch or by adding chemicals that prevent solubility. It is known for example to decrease water solubility of a starch based binding agent of a coating medium by the above means in order to prevent starch dissolving due to water based printing colors in offset printing or to improve wet rub-off properties of fiber webs.

[0016] Sticking and picking problems at heated calender rolls may also occur with other sizing agents especially when moisturizing and/or high moisture content before calendering is used.

[0017] Paper and board are available in a wide variety of grades and can be divided according to basis weight in two categories: papers with a single ply and a basis weight of 25 - 300 g/m² and boards manufactured in multiply technology and having a basis weight of 150 - 600 g/m². It should be noted that the borderline between paper and board is flexible since board grades with lightest basis weights are lighter than the heaviest paper grades. Generally speaking, paper is used for printing and board for packaging.

[0018] The subsequent descriptions are examples of some values presently applied for fibrous webs, and there may be considerable variations from the disclosed values. The descriptions are mainly based on the source publication Papermaking Science and Technology, section Papermaking Part 3, edited by Jokio, M., published by Fapet Oy, Jyväskylä 1999, 362 pages.

[0019] Mechanical-pulp based, i.e. wood-containing printing papers include newsprint, uncoated magazine and coated magazine paper.

[0020] Newsprint is composed either completely of mechanical pulp or may contain some bleached softwood pulp (0 - 15 %) and/or recycled fiber to replace some of the mechanical pulp. General values for newsprint can be regarded as follows: basis weight 40 - 48,8 g/m², ash content (SCAN-P 5:63) 0 - 20 %, PPS s10 roughness (SCAN-P 76:95) 3,0 - 4,5 µm, Bendtsen roughness (SCAN-P 21:67) 100 - 200 ml/min, density 200 - 750 kg/m³, brightness (ISO 2470:1999) 57 - 63 %, and opacity (ISO 2470:1998) 90 - 96 %.

[0021] Uncoated magazine paper (SC=supercalendered) usually contains mechanical pulp to 50 - 70 %, bleached softwood pulp to 10 - 25 %, and fillers to 15 - 30 %. Typical values for calendered SC paper (containing e.g. SC-C, SC-B, SC-A/A+) include basis weight 40 - 60 g/m², ash content (SCAN-P 5:63) 0 - 35 %, Hunter gloss (ISO/DIS 8254/1) < 20 - 50 %, PPS s10 roughness (SCAN-P 76:95) 1,2 - 2,5 µm, Bendtsen roughness

(SCAN-P 21:67) 100 - 200 ml/min, density 700 - 1250 kg/m³, brightness (ISO 2470:1999) 62 - 70 %, and opacity (ISO 2470:1998) 90 - 95 %.

[0022] Coated magazine paper (LWC = lightweight coated) contains mechanical pulp to 40 - 60 %, bleached softwood pulp to 25 - 40 %, and fillers and coaters to 20 - 35 %. General values for LWC paper can be regarded as follows: basis weight 40 - 70 g/m², Hunter gloss 50 - 65 %, PPS s10 roughness 0,8 - 1,5 µm (offset), 0,6 - 1,0 µm (roto), density 1100 - 1250 kg/m³, brightness 70 - 75 %, and opacity 89 - 94 %.

[0023] General values for MFC (machine finished coated) can be regarded as follows: basis weight 50 - 70 g/m², Hunter gloss 25 - 70 %, PPS s10 roughness 2,2 - 2,8 µm, density 900 - 950 kg/m³, brightness 70 - 75 %, and opacity 91 - 95 %.

[0024] General values for FCO (film coated offset) can be regarded as follows: basis weight 40 - 70 g/m², Hunter gloss 45 - 55 %, PPS s10 roughness 1,5 - 2,0 µm, density 1000 - 1050 kg/m³, brightness 70 - 75 %, and opacity 91 - 95 %.

[0025] General values for MWC (medium weight coated) can be regarded as follows: basis weight 70 - 90 g/m², Hunter gloss 65 - 75 %, PPS s10 roughness 0,6 - 1,0 µm, density 1150 - 1250 kg/m³, brightness 70 - 75 %, and opacity 89 - 94 %.

[0026] HWC (heavy weight coated) has a basis weight of 100 - 135 g/m² and can be coated even more than twice.

[0027] Pulp-produced, wood free printing papers or fine papers include uncoated - and coated - pulp-based printing papers, in which the portion of mechanical pulp is less than 10 %.

[0028] Uncoated printing papers (WFU) contain bleached birch wood pulp to 55 - 80 %, bleached softwood pulp 0 - 30 %, and fillers to 10 - 30 %. The values with WFU have a large variation: basis weight 50 - 90 g/m², Bendtsen roughness 250 - 400 ml/min, brightness 86 - 92 %, and opacity 83 - 98 %.

[0029] In coated printing papers (WFC), the amounts of coating vary widely in accordance with requirements and intended application, the following are typical values for once- and twice-coated, pulp-based printing paper: once-coated basis weight 90 g/m², Hunter gloss 65 - 80 %, PPS s10 roughness 0,75 - 2,2 µm, brightness 80 - 88 %, and opacity 91 - 94 %, and twice-coated basis weight 130 g/m², Hunter gloss 70 - 80 %, PPS s10 roughness 0,65 - 0,95 µm, brightness 83 - 90 %, and opacity 95 - 97 %.

[0030] Release papers have a basis weight within the range of 25 - 150 g/m².

[0031] Other papers include e.g. sackkraft papers and wallpaper bases.

[0032] Board making makes use of chemical pulp, mechanical pulp and/or recycled pulp. Boards can be divided e.g. in the following main groups cartonboards, containerboards and specialty boards. Cartonboards are mainly used for consumer product packaging and they

comprise boxboards, used for making boxes, cases, which boxboards include e.g. liquid packaging boards; FBB = folding boxboard, WLC = white-lined chipboard, SBS = solid bleached sulfate board, SUS = solid unbleached sulfate board and LPB = liquid packaging board. Containerboards comprise f. ex. linerboard and fluting board and other corrugated boards and specialty boards comprise wallpaper base, plaster board etc. Graphic boards are used for making e.g. cards, files, folders, cases, covers, etc. and wallpaper bases. Each end use sets its own demands on the mechanical and functional properties of boards. Basically a certain mechanical strength and stiffness, especially bending stiffness is required, and in the optimum structure middle-ply is very bulky, and top and back plies have high modulus of elasticity. Often also purity and cleanliness requirements are very high and also almost all boards have defined printing properties and for example the printing requirements of folding box board are usually very high and also high bulkiness is required of folding box board.

[0033] As known temperature and moisture gradient calendering utilize the Z-directional temperature and moisture profiles in the fiber web. The fiber plasticization, and therefore the deformation of web structure in calender nip compression, is more concentrated to the surface layers due to favorably adjusted moisture and temperature profiles in Z-direction. Particularly the moisture gradient calendering can offer very high smoothness while maintaining the inner web structure less compacted and thus keeping the bulk at a reasonable level. In the moisture gradient calendering the moisture gradient is in practice obtained by first drying the paper web to sufficiently dry and then applying water on to the web surface. Water is applied usually by water showers (spray nozzles). Water can be applied also by steam boxes (or pipes) and letting the steam to condensate at web surface, giving some moistening effect. Application of external water results almost always high moisture content at the surface. Moisture gradients in web thickness direction may arise also from one-sided heating, for example in Condebelt drying, hot metal belt and hot drying cylinder contacts. Moisture is transported from the hot side towards cooler side, and possibly condensing there at the cooler surface. In this case, redistribution of internal water results high local moisture content at the surface.

[0034] Starch sizing is used in order to improve paper web properties, in particular water resistance, water absorption properties, strength, internal strength and bending stiffness. In addition, runnability as well as dusting tendency can be affected favorably.

[0035] Starch based sizes, among some other sizing agents, are known to be water soluble. This will pose a major problem in moisture gradient calendering when sized paper is first moistened and soon after that calendered. It has been observed, that moistening of starch sized webs prior to hot calendering leads to problems like sticking, starch picking and deposit building on the calender roll surfaces. It is believed, that the applied wa-

ter is dissolving the dried starch film in the web surface layers. The dissolved starch can be transported, particularly with water movement, into a direct contact with roll surface. The mechanism of sticking and picking is not well known, but it can be assumed, that at hot roll surface the water is evaporated while the size (binder) remains at the surface contact. The binder is adhered to and possibly held by sticky bonds at the metal surface.

[0036] The root cause to the roll picking seems to be the water dissolving property of the binder. In order to solve the root cause in practical applications, it is important understand the binder chemistry in relation to its water dissolution.

[0037] For example, the source of starch, the ways of modifying starch, the use of various insolubilizers and way of dosing then is significantly affecting the water resistance and dissolution properties of starch. The root cause, the starch dissolution to water, can be approached in different ways. The most obvious solution is to use as small amounts of water as possible, but this is diminishing the benefits of the moisture gradient calendering. Ultimately, the starch dissolving and picking at the calender can be prevented when the process is arranged in such way that starch and water are not brought together in to a contact before calendering. If water-soluble starch needs to be used, sizing must then be done after the water-critical calendering.

[0038] An object of the invention is to create a method and a production line for producing fiber webs in which the above problems and disadvantages are eliminated or at least minimized.

[0039] A particular object is to prevent starch sticking from wet / moistened fiber web into the contacting surfaces, particularly hot drying surfaces and hot calendering surfaces.

[0040] In order to achieve the above objects the method for producing fiber webs according to the invention is mainly characterized by the features of claim 1 or 2 and the production line for producing fiber webs according to the invention is mainly characterized by the features of claim 14.

[0041] According to advantageous aspect of the invention to prevent or reduce starch dissolution chemicals (like insolubilizers) or other means, like starch modification is used. Preferably the soluble binder, like starch, is partially or fully, is replaced with other less soluble sizing agents. The sizing agent can also be a sizing agent with an insolubilizer additive for decreasing the solubility.

[0042] According to further advantageous aspects to prevent the binder from sticking to rolls, additional chemicals, like lubricants, roll surface passivation agents or cleaning chemicals, are applied either directly on the web, or mixed with moistening water or applied directly to the roll surface or mixed with sizing agent.

[0043] According to one aspect of the invention in production of fiber webs, in which the fiber web is surface sized and moisturized by water and/or by steam and calendered or correspondingly treated by pressure, the fiber

web is surface sized by applying low soluble starch, such as maize starch or wheat starch or barley starch or rice starch, or other sizing agent and the fiber web is moisturized and treated by contact pressure treatment, for example by calendering or drying. The starch can be natural starch or genetic modified starch.

[0044] Many starch properties, like viscosity, solubility and strength building characteristics are inherited from the starch composition and chemical structure at the molecular level. For example, the proportions of the amylose and amylopectin molecules, the degree of polymerization, and molecular weight of the polymer structure affect the end use properties. As is well known, the chemical nature and therefore the end use properties vary greatly depending on the source of the starch, for example giving higher solubility to the potato starch due to the higher amylopectin proportion, more branched molecular chains and in general more loose amorphous macromolecular structure.

[0045] The chemical structure and chemical characteristics of the starch can be modified also using means of genetic modifications. In this way, using genetically improved starch, it is possible to increase desired functionality and properties, like strength, and remove the less desired features, such as water solubility.

[0046] In order to avoid or reduce sizing agent dissolving and picking to the process surfaces, it is advantageous to keep the internal moisture content in the web as low as possible during the moistening and calendering stages of the sized web. Particularly, the lower base sheet moisture is reducing the picking risk and enhancing the moisture gradient calendering effect.

[0047] According to an advantageous aspect of the invention to prevent sizing agent to dissolve and pick to the process surfaces in fiber web treatment process, in which process fiber web is sized, and dried and possibly moisturized and thereafter treated in a contact treatment process, like calendering, after the sizing the fiber web is dried to the dryness 8% or less, preferably to 5 % or less, before the web is moistened and / or treated in surface treatment process, for example calendered.

[0048] According to one aspect of the invention in production of fiber webs, a starch size with chemical additive decreasing water solubility of the dried starch size is applied into the web and the fiber web is dried in which in at least one process step following the sizing water is added into the fiber web by water moisturizing means or by steaming means or by other corresponding moisturizing means, and/or

in at least one process step following the sizing the fiber web is treated by a hot surface contacting a side of the fiber web that is moist and sized, and/or

in at least one process step following the sizing the fiber web is dried and/or calendered by a hot surface.

[0049] According to an advantageous features in the method the calendering or treating the web by a hot surface; the surface temperature is in belt calendering 100 - 200 °C, in roll nip calendering 130 - 350 °C, in cylinder

or belt drying 80 - 200 °C is and the sizing is internal or surface sizing.

[0050] According to advantageous features sizing amount is per side 0,1 - 5 g/m² (solids), preferably for paper webs per side 0,1 - 2 g/m² and for board webs per side 0,5 - 3 g/m², web ingoing moisture 4 - 10 %, preferably 5 - 8 %, water application (moistening) 1 - 3 g/m² for paper webs for one side of the web and 2 - 6 g/m² for board webs for one side of the web, thermo roll temperature 130 - 350 °C, preferably 175 - 250 °C.

[0051] According to an advantageous feature at least one of the calendering surfaces is provided by oil-heated roll, and the sizing is internal or surface sizing.

[0052] According to one aspect the hot calendering is done by surfaces, wherein at least one of the surfaces is a high surface temperature roll, preferably a hot oil heated thermo roll, which has surface temperature over 150 °C, preferably over 175 °C. According to a very advantageous feature the hot roll is a high power shrink fitted thermo roll.

[0053] According to one aspect the calendering is done with metal belt calender, wherein the temperature of the metal belt is 100 - 200 °C.

[0054] According to one aspect the fiber web is dried and calendered in a metal belt contact zone, wherein at least one of the surfaces has surface temperature 100 - 200 °C. According to one aspect of the invention the water solubility of starch is decreased by additives provided in sizing process to create water resistant starch sizing in connection with hot calendering. In hot calendering the temperatures of calender rolls can be 130 °C - 350 °C and the rolls are advantageously heated by oil circulation. By the improved water resistance it is further possible to use water moisturizing. This provides for great quality advantages in particular in hot calendering. For example smoothness is improved, raw material can be saved and process can be designed simpler.

[0055] According to one aspect the additive decreasing water solubility of starch creates covalent or hydrogen bonds with the hydroxyl groups of the starch and/or works as a cross-linker. The additive is activated after it is applied by drying of the sized fiber web and by effect of the temperature. When activated, the additive creates bonds with the hydroxyl groups in the starch, cross-linking and passivizing the hydroxyl groups and thus preventing the adherence of water molecule bonding with them.

[0056] According to one inventive aspect a low soluble starch, for example corn starch, rice starch or wheat starch, or other sizing agent that is less soluble in moisturizing is used as sizing agent and thus sticking of the binder or sizing agent to the calender rolls or other corresponding contacting surface of a treatment device is avoided.

[0057] According to one advantageous feature the moisturizing is provided by water spray means just before calendering.

[0058] According to one aspect of the invention the sizing agent applied on the fiber web is modified by adding

insolubilizers and thus the dissolving and sticking of sizing agent onto the surfaces of calender rolls and other corresponding process surfaces of fiber web production line devices is decreased. When less soluble starch or sizing agent is used it is possible to use increased moisture addition and thus for example better calendering results are achieved.

[0059] According to an advantageous feature of the invention as additives for decreasing the solubility of starch or other sizing agent insolubilizers are used, for example zirconium based salts, such as AZC (Ammonium Zirconium Carbonate) or PZC (Potassium Zirconium Carbonate) or Glyoxal resins can be used. Also formaldehyde resins or CMC, polycarboxylic acids like citric acid can be used as insolubilizers.

[0060] According to an advantageous feature of the invention the surface sizing is done with spray sizing but also other sizing methods can be used.

[0061] According to an advantageous feature of the invention the fiber web production comprises following steps: sizing with starch or sizing agent with insolubiliser additive, drying of fiber web at drying section, moisturizing and calendering or corresponding contacting press treatment.

[0062] According to an advantageous feature of the invention the fiber web production comprises following steps: sizing with starch with additives decreasing water solubility, drying, water moisturizing and hot calendering.

[0063] According to an advantageous feature of the invention the fiber web production comprises applying starch or other sizing agent with additive insolubilizer on the fiber web before moisturizing at calender or before calendering.

[0064] According to an advantageous feature of the invention the fiber web production comprises following steps: sizing with starch or sizing agent with insolubilizer additive, contactless drying, contact drying or metal belt treatment or calendering.

[0065] According to one aspect of the invention the surface sizing with starch or other sizing agent is performed after calendering. Thus the sticking problems are avoided. Even though the sizing may increase the surface roughness, this can be compensated by calendering the fiber web to higher smoothness level than desired and thereafter by sizing reach the desired smoothness level. Particularly, a high solids content starch can be used to minimize the added water amount, thus reducing re-swelling and roughening of the fiber web.

[0066] According to an advantageous feature of the invention the fiber web production comprises following steps: internal (stock) sizing of the base fiber web with starch or other sizing agent, drying, calendering or corresponding contacting press treatment and surface sizing.

[0067] According to an advantageous feature of the invention the fiber web production comprises following steps: internal (stock) sizing of the base fiber web with starch or other sizing agent, drying, calendering or cor-

responding contacting press treatment, surface sizing, coating and final-calendering.

[0068] According to an advantageous feature as surface sizing method for example a film size-press, a spray-sizer or a pond-sizer can be used.

[0069] According to an advantageous feature as calender for example a hard nip calender, a soft calender, a multinip calender, a wet stack calender or a metal belt calender or a shoe calender can be used.

[0070] According to an advantageous feature moist fiber web is dried by contact drying and/or by belt drying.

[0071] According to an advantageous feature the surface sizing is performed in high dry solids content so that less water is applied on the surface of the fiber web. The solids content level is during sizing preferably 10 - 25 %. Thus the roughness increase after sizing is less. The sizing can even have a smoothness increasing effect if sizing is combined with a wet stack calender or with a hard nip calender.

[0072] According to some further aspects of the invention sticking problems can be decreased by using passivation and/or lubrication chemicals applied on the surface of the calender roll or the corresponding surface with sticking problems or by adding the passivation and/or lubrication chemical into the moisturizing agent at calender or before calender or by adjusting temperature and moisture amount. Lubricants or passivation chemicals can be: directly applied to the web before calendering, mixed with surface sizing agent, mixed with moisturizing water or directly applied to the calendering surface.

[0073] According to an advantageous feature of the invention as passivation and/or lubrication chemicals mineral oil or stearates can be used.

[0074] According to an advantageous feature of the invention the temperature of the web at ingoing to the calendering is 20 - 80 °C, preferably 30 - 50 °C.

[0075] According to an advantageous feature of the invention drying temperature of the sized web is over 60 °C, preferably over 80 °C, which ensures rapid curing of insolubilizers, added to the web.

[0076] According to an advantageous feature of the invention the size treated web is arranged to stay under drying conditions where the temperature is over 60 °C at least for 2 seconds.

[0077] According to an advantageous feature the size treated web is dried with high temperature impingement drying or in contactless airborne drying, preferably flotation dryer.

[0078] According to one example of the invention less soluble starch, for example corn starch, and minimized moisture amount, for example less than 2 g/m², and high roll temperatures, for example over 175 °C, advantageously over 200 °C, and optionally passivation and /or lubrication chemicals are used in combination to eliminate sticking problems.

[0079] The different advantageous aspects and features described above and in the claims can be combined in various ways to achieve further advantages.

[0080] By the invention many advantages are achieved for example sticking problems are eliminated, dust problems are minimized, increased cleanliness and better runnability is achieved. Also the lifetime of treatment device roll or belt, or their coatings is increased, since wearing and damaging pick due to sticking is decreased. The invention also makes it possible to use water moisturizing in increased amounts, and particularly enhanced moisture gradient calendering in hot calendering in production of starch sized fiber webs. Various kinds of calender types are utilizable, for example long nip calendering. The possibility of moisturizing also makes the calendering more efficient and thus quality results and production capacity improve. Further, the water resistance and strength properties (like surface strength and bending stiffness) of the fiber web are improved without reduction of water absorption or plasticization properties of the fiber web. Since by the passivation treatment of the starch, only the water solubility of the starch is reduced but the water absorption and hygroscopic nature of the fiber web is retained. The invention also provides the possibility of replacing more expensive sizing agents by starch in production lines comprising water moisturizing. Further important benefit is the possibility of controlling curl, controlling one-sidedness and/or web profiling by water moisturizing of starch sized fiber webs.

[0081] In the following the invention is described in more detail with reference to the accompanying drawing

in which in table 1 are listed some properties of dried starch films, and in which

in figure 1 is schematically comparison of starch picking test with two sheet base moistures, 5 and 10% respectively, before moisturizing and test result shows that higher base moisture indicates much higher picking,

in figure 2 is schematically shown test results of picking at various sizing amounts, using potato starch 0, 2.5, 3.5 g/m² (dry solids) on each side, in the test sheet moisture was 10 % before moisturizing and test results show that higher starch amount results much higher picking,

in figure 3 is schematically shown comparison of starch source test: potato vs. corn starch in the test surface sizing amount was 2 g/m², sheet base moisture was 8 % before moisturizing and moisturizing levels were 0 and 3 g/m² and calendering was done at 150 °C,

in figure 4 is schematically shown test results indicating the insolubilizer effect on calender roll picking, in the test sheets were sized with potato starch 2.1 g/m² with and without glyoxal insolubilizer and the sheet moisture was 8 % before moisturizing,

in figure 5 is schematically shown an example of a production line for producing fiber webs, which is an on-line paper or board making line for producing uncoated web,

in figure 6 is schematically shown an example of a production line for producing fiber webs, which is an on-line paper or board making line for producing coated web,

in figure 7 is schematically shown an example of a production line for producing fiber webs, which is an on-line paper or board making line with sizing for producing uncoated web,

in figure 8 is schematically shown an example of a production line for producing fiber webs, which is an on-line paper or board making line with sizing, for producing coated web,

in figure 9 is schematically shown an example of a production line for producing fiber webs, which is an off-line paper or board making line with sizing and coating,

in figure 10 is schematically shown an example of a production line for producing fiber webs, which is an off-line paper or board making line with sizing,

in figure 11 is schematically shown an example of a production line for producing fiber webs, which is an on-line paper or board making line with sizing,

in figure 12 is schematically shown an example of a production line for producing fiber webs, in which is an on-line paper or board making line with sizing and coating,

in figure 13 is schematically shown an example of a production line for producing fiber webs, in which is an on-line paper or board making line with integrated sizing, smoothening contact treatment, coating and calendering

in figure 14 is shown table 1.

[0082] In table 1 are listed some properties of dried starch films obtained from various cooked native starches and there are differences in solubility of different starch types, as can be seen from Table 1. For example potato starch and tapioca starch have high solubility but for example maize starch and wheat starch have lower solubility. In addition it is noted that rice starch is of low solubility. The applicant has noted in trial tests that potato starch that has high solubility in water tends to stick after moisture addition to calender rolls more easily than maize starch that has lower solubility. The potato starch has been found to stick after 1 - 2 g/m² or more moisture

addition but the maize starch only after 2 - 4 g/m² or more moisture addition in hot calendering contact. As previously explained in fiber web production where the fiber web is surface sized and thereafter moisturized at calendering or before calendering the starch types having high solubility in water proved in applicant's trial test to increase sticking problems and the starch types having low solubility in water solution proved to have decreased sticking problems.

[0083] Applicant has performed some trial tests and in figures 1 - 4 are schematically presented some results.

[0084] Starch dissolving and roll picking in a moisture gradient calendering was simulated using laboratory scale calendering equipment. The tests aimed to estimate the starch dissolving and picking in a quantitative way as water was applied on web surface prior a hot calender nip. Test material was typical surface sized board (250 g/m² folding boxboard). Sheets were cut from surface sized web containing 2 - 3.5 g/m² (dry amount) starch on both sides. Test sheets were conditioned into equilibrium moisture contents 5 %, 8 % and 10 %. Calendering was done at 150 °C temperature and water was applied by spray nozzles just before sheet entered calender nip. Water amount used was generally 0 - 5 g/m². Calendering test was started using clean surface in each condition. Test sheets were run using a single nip pass principle and the contact surface was then inspected immediately. Each condition was repeated 5 times with fresh sheets, without cleaning the surface. Starch and deposit picking at the contact surface was evaluated by inspecting the surface visually and by photography. The degree of picking was rated by several persons giving picking intensity values between 0...5, as follows: 0=picking free, 1= very small, 2= some, 3= medium, 4= severe, 5= very high picking. Observations were reported as averaged values. Based on research team's understanding and experience, the acceptable picking intensity in practical calendering situations should be < 0.5. Results are conservative, since they include deposit and starch picking and accumulation only from five (5) nip contacts, which is much less than picking and accumulation of repeated continuous nip rolling in real calender.

[0085] The figure 1 explains sheet base moisture effect on starch picking. In the figure 1, the bottom axis indicates used water amount and vertical axis indicates evaluated picking intensity value. As can be seen, higher basis moisture (10 %) gives higher picking compared to lower basis moisture (5%) at all moisturizing levels. Running without water (no moisturizing) is practically picking free in both cases. Calendering temperature was 150 °C. An acceptable picking level defined being < 0.5, one can see that picking free situation is obtained with < 1 g/m² moisturizing water in the case of 10 % base moisture and with < 2 g/m² moisturizing water with 5 % base moisture, respectively. Therefore sheet basis moisture before calendering is greatly affecting the picking at calendering.

[0086] In the figure 2 it can be seen further, that increase in sizing starch amount increase the picking in-

tensity clearly. The more starch is available to be solved into the water, more picking will take place.

[0087] In the figure 3 is presented further results, now comparing two starch sources at two moisturizing level. Sizing amount is 2 g/m² (dry starch) and base moisture 8%. As can be seen, potato starch, being more soluble to water, is giving clearly higher picking than corn starch.

[0088] In the figure 4 is presented further set of results, indicating the effect of insolubilizer. Sheets were sized using 2.1 g/m² potato starch, with and without insolubilizer. Insolubilizer used was glyoxal, mixed to starch after cooking and dilution. As can be seen, starch with glyoxal additive yield clearly less picking with all moisturizing levels. It can be concluded that the use of insolubilizer enables using more moisturizing, at least 2 g/m² or even more.

[0089] In figures 5 - 13 are schematically shown examples of production lines for producing fiber webs. In figure 5 is an on-line paper or board making line for producing uncoated web, in figure 6 is an on-line paper or board making line for producing coated web, in figure 7 is an on-line paper or board making line with sizing for producing uncoated web, in figure 8 is an on-line paper or board making line with sizing, for producing coated web, in figure 9 is an off-line paper or board making line with sizing and coating, in figure 10 is an off-line paper or board making line with sizing, in figure 11 is an on-line paper or board making line with calendering and sizing, in figure 12 is an on-line paper or board making line with pre-calendering, sizing, coating and final calendering and in figure 13 is an on-line paper or board making line with integrated sizing, smoothening contact treatment, coating and calendering. In the figures 5 - 13 same reference signs are used for corresponding parts and sections of the fiber web production line, unless otherwise mentioned.

[0090] The production and treatment line according to the examples of figure 5 - 13 comprises paper or board machine 10, which has a head box, a wire section and a press section as well as a subsequent drying section.

[0091] In the example of figure 5 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by moistening by a moistening device 35 of the fiber web W before calendering in a calender 40 and finally reeled in a reel-up 80 to a parent roll.

[0092] In the example of figure 6 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by moistening by a moistening device 35 before precalendering in a calender 40. There after the fiber web W is coated in a coating section 40 which comprises a coating device and drying section. The coating section 50 is followed by final calendering in the end calender 60 and finally the fiber web W is reeled in a reel-up 80 to a parent roll.

[0093] In the example of figure 7 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by sizing in a sizer

20 and dried thereafter by a drying device 25. Then the fiber web is moistened by moistening devices 35 before calendering in a calender 40 and finally the fiber web W is reeled in a reel-up 80 to a parent roll.

[0094] In the example of figure 8 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by sizing in a sizer 20 and dried thereafter by a drying device 25 and moistened by moistening devices 35 before precalendering in a calender 40. There after the fiber web W is coated in a coating section 40 which comprises a coating device and drying section. The coating section 50 is followed by final calendering in the end calender 60 and finally the fiber web W is reeled in a reel-up 80 to a parent roll.

[0095] In the example of figure 9 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by sizing in a sizer 20 and dried thereafter by a drying device 25 and reeled in a reel-up 80 to a parent roll. In the off-line finishing section the parent roll is unwound in an unwinder 85 and moistened by moistening devices 35 before calendering in a calender 40. There after the fiber web W is coated in a coating section 50 which comprises a coating device and drying section and at the end of the off-line part the fiber web W is reeled in a reel-up 80 to a parent roll.

[0096] In the example of the figure 10 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by sizing in a sizer 20 and dried thereafter by a drying device 25 and reeled in a reel-up 80 to a parent roll. In the off-line finishing section the parent roll is unwound in an unwinder 85 and moistened by moistening devices 35 before calendering in a calender 40 and at the end of the off-line part the fiber web W is reeled in a reel-up 80 to a parent roll.

[0097] In the example of the figure 11 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed by moistening by a moistening device 35 before precalendering in a precaler 40. Then the fiber web W is sized in a sizer 20 and dried thereafter by a drying device 25. The sizer 20 and its drying device 25 are followed by optional final calendering in the end calender 60 and finally the fiber web W is reeled in a reel-up 80 to a parent roll.

[0098] In the example of the figure 12 the fiber web W is guided from stock sizing S to the paper or board machine 10 with drying. The drying is followed and moistening by a moistening device 35 before precalendering in a calender 40. There after the fiber web W is sized in a sizer 20 and dried thereafter by a drying device 25. Then the fiber web W is coated in a coating section 50 which comprises a coating device and drying section. The coating section 50 is followed by final calendering in the end calender 60 and finally the fiber web W is reeled in a reel-up 80 to a parent roll.

[0099] In the example of the figure 13 the fiber web W is guided from stock sizing S to the paper or board machine 10 with integrated sizing and smoothening contact

drying and/or treatment with initial drying 15, which is followed by a sizer 20 and dried thereafter by a drying device 25 for predrying and curing. There after the fiber web is moistened by moistening devices 35 for control of water profile before drying in a drying section 45 comprising contact drying and/or smoothening metal belt treatment and curing. Then the fiber web W is coated in a coating section 50 which comprises a coating device and drying section. The coating section 50 is followed by final calendering in the end calender 60 and finally the fiber web W is reeled in a reel-up 80 to a parent roll.

[0100] The examples the fiber web the sizer 20 provided with application means by which low soluble starch or corresponding sizing agent is applied onto the fiber web. After the surface sizer 20 in some examples the fiber web is moisturized by at least one moisturizing device 35, for example by water moisturizing by sprays or by steam moisturizing with moisture amount of 1 - 10 g/m², preferably 1 - 5 g/m². The calenders 40, 60 of the examples can be for example a soft calenders or a hard nip calenders or a metal belt calenders or multinip calender. Preferably in the examples the possible insolubilizer is added as last step in size preparation, just before the application onto the web. The chemical additive amount is for example 1 - 8% of the dry solids content of the starch. The chemical is activated at drying section as water is removed and/or elevated temperature is enhancing the chemical additive curing. Due to the chemical the water solubility of the starch is lowered, which provides for the possibility of water moisturizing with greater water amounts without contamination of calender rolls. The water moisturizing with greater water amounts together with hot calendering improves the calendering results and the surface of the web when entering the coating is smoother. Thus the smoothness of the end product is better in relation to bulk and the amount of coating medium used can be decreased. The chemical additive has also strength improving effect and thus the amount of starch used can be decreased. The smoothening effect by the calender is improved and thus for example the Yankee cylinder can be removed from the production line without negative effect to the quality of the fiber web as the smoothening effect of the Yankee cylinder is no more so significant. By removing the Yankee cylinder the production speed of the production line can be increased for example by increasing the capacity (the length) of the drying section. The better smoothness and increased strength gives advantage in many ways. Increase in strength enables reduction of fiber raw materials, replacing some fiber material by cheaper filler material or by cheaper recycled fibers. Better calendering result (smoothness) enable reduction of calendering line load which means bulk savings. Bulk saving means more thickness and more bending stiffness. The better smoothness thus provides for bulk and raw material savings.

[0101] Overall the invention provides for the possibility of simple and cost effective line concept, for example

hard calender and water moisturizing in conjunction of efficient production line. This example is suitable for example in production of boards (FBB, liners etc.) and of uncoated or coated printing papers (WFU, LWC, MWC etc.).

[0102] In one example the starch sized fiber web is moisturized and end calendered. This example is suitable for example in production of wood-free sized paper grades, for example copy papers. The starch is used to improve strength properties and increasing surface strength, decreasing dusting etc. In particular wood containing or wood-free uncoated printing paper grades are sized or pigmented with insolubilized starch before moistening and calendering.

[0103] In one example the starch sized fiber web is contact dried. The sizing by water resistant starch is followed by contact drying, either cylinder drying or drying-treatment by hot metal belt. The lower solubility of starch enables picking and contamination free operation

[0104] Above the invention has been described with reference to only some examples to which the invention is not to be narrowly limited and features of different examples can be combined in various ways.

Claims

1. Method for producing a fiber web, in which the fiber web (W) is surface sized with starch or other sizing agent in a sizer (20) and in which the fiber web (W) is calendered or correspondingly treated by contacting treatment, **characterized in that** the fiber web is surface sized by applying low soluble starch, such as maize starch or wheat starch or barley starch or rice starch, or other sizing agent that is low soluble or not re-soluble in moisturizing.
2. Method for producing a fiber web, in which the fiber web (W) is sized with starch or other sizing agent and in which the fiber web (W) is calendered or contact dried or correspondingly treated by contacting treatment, **characterized in that** the fiber web is sized by applying starch with chemical additive decreasing water solubility of the dried starch size and the fiber web is then dried.
3. Method according to claim 1 or 2, **characterized in that** the fiber web is surface sized by applying starch or other sizing agent, which is modified by using additives that decrease solubility in calendering.
4. Method according to claim 1 or 2, **characterized in that** passivation and/or lubrication chemicals are applied on the surface of the calender roll or the corresponding process surface and/or the passivation and/or lubrication chemicals are provided with the moisturizing agent at calender or before calender or that the passivation and/or lubrication chemicals are

added directly to the fiber web or passivation/lubrication chemicals are provided in mixed with the sizing agent.

5. Method according to claim 1 or 2, **characterized in that** fiber web is moisturized by water mist and/or by steam in a moisturizing device (35) after the sizing but before the calendering or the corresponding contacting treatment and the moisturizing is provided by water spray means or by steam-box means.
6. Method according to claim 1 or 2, **characterized in that** as additives for decreasing solubility of starch or other sizing agent insolubilizers are used, for example zirconium based salts, such as AZC (Ammonium Zirconium Carbonate), PZC (Potassium Zirconium Carbonate), Glyoxal, CMC, Citric acid, Polycarboxylic acid are used.
7. Method according to any of claims 1 - 6, **characterized in that** the sizing is by performed by spray sizing or by film sizing or by pond sizing.
8. Method according to claim 1 or 2, **characterized in that** the fiber web production comprises at least following steps: sizing with starch or sizing agent with insolubiliser additive, drying of fiber web, moisturizing and calendering or corresponding contacting press treatment.
9. Method according to claim 1 or 2, **characterized in that** the fiber web production comprises at least following steps: sizing with starch or sizing agent with insolubilizer additive, treatment in hot contact zone, drying and calendering.
10. Method according to claim 1 or 2, **characterized in that** the fiber web production comprises at least applying starch or other sizing agent with additive insolubilizer on the fiber web before moisturizing at calender or before calendering.
11. Method according to claim 1 or 2, **characterized in that** the fiber web production comprises at least following steps:
 - sizing with starch or sizing agent with insolubilizer additive, contactless drying, drying or metal belt treatment or calendering or
 - internal sizing of the base fiber web with starch or sizing agent, drying, calendering or corresponding contacting press treatment and surface sizing or
 - sizing of the base fiber web with starch or sizing agent, drying, calendering or corresponding contacting press treatment, surface sizing, coating and final-calendering or
 - sizing by starch with additives decreasing water

solubility and water moisturizing and hot calendering.

12. Method according to claim 1 or 2, **characterized in that** the surface sizing is performed in high dry solids content, preferably the solids content level during sizing is 10 - 25% so that less water is applied on the surface of the fiber web. 5
13. Method according to claim 2, **characterized in that** the chemical additive dosing is 1- 10 % from the dry solids content of the starch. 10
14. Production line for producing fiber webs which comprises a sizer (20) for surface sizing the fiber web (W) with starch or other sizing agent in a sizer and a calender (40; 60) or corresponding treatment device for calendering or correspondingly treating by contacting press-treatment the fiber web (W), **characterized in that** the sizer (20) is provided with application means for surface sizing the fiber web (W) by applying low soluble starch, such as maize starch or wheat starch or barley starch or rice starch, or other sizing agent that is low soluble or not re-soluble in moisturizing. 15
20
25
15. Production line according to claim 14, **characterized in that** the production line further comprises a moisturizing device (35). 30

35

40

45

50

55

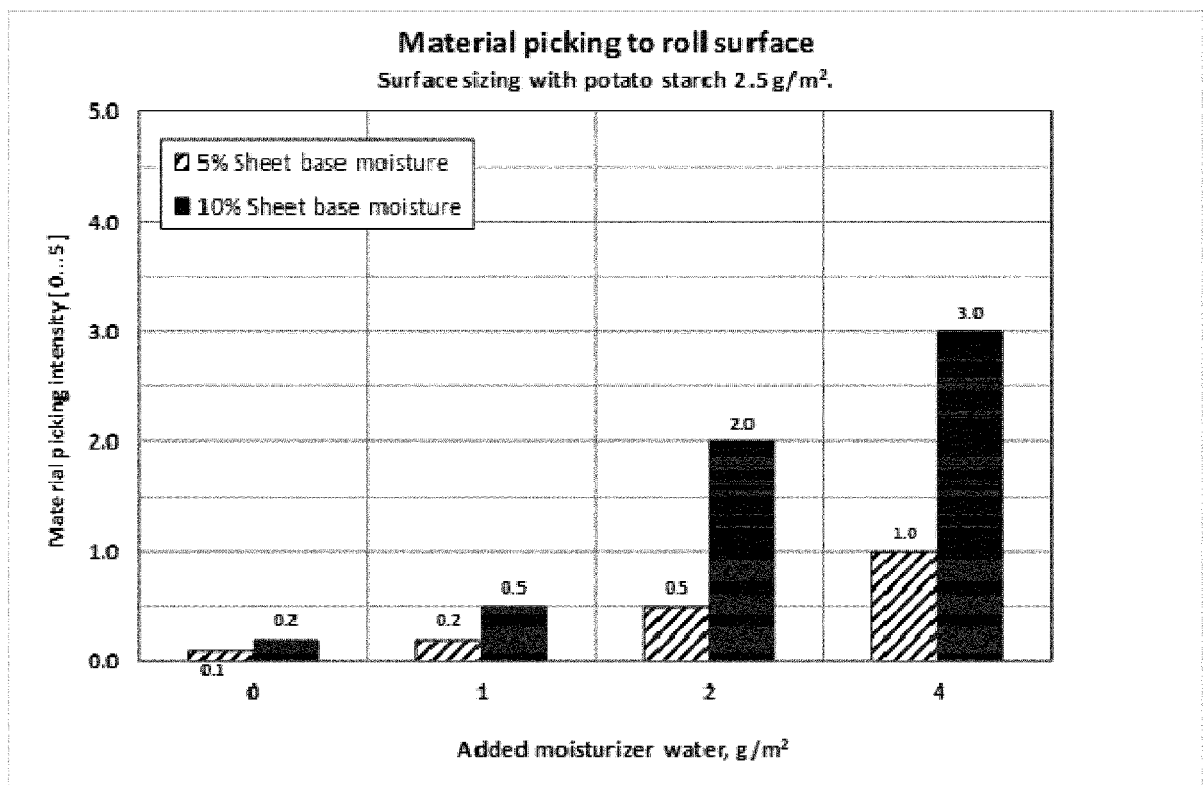


Fig. 1

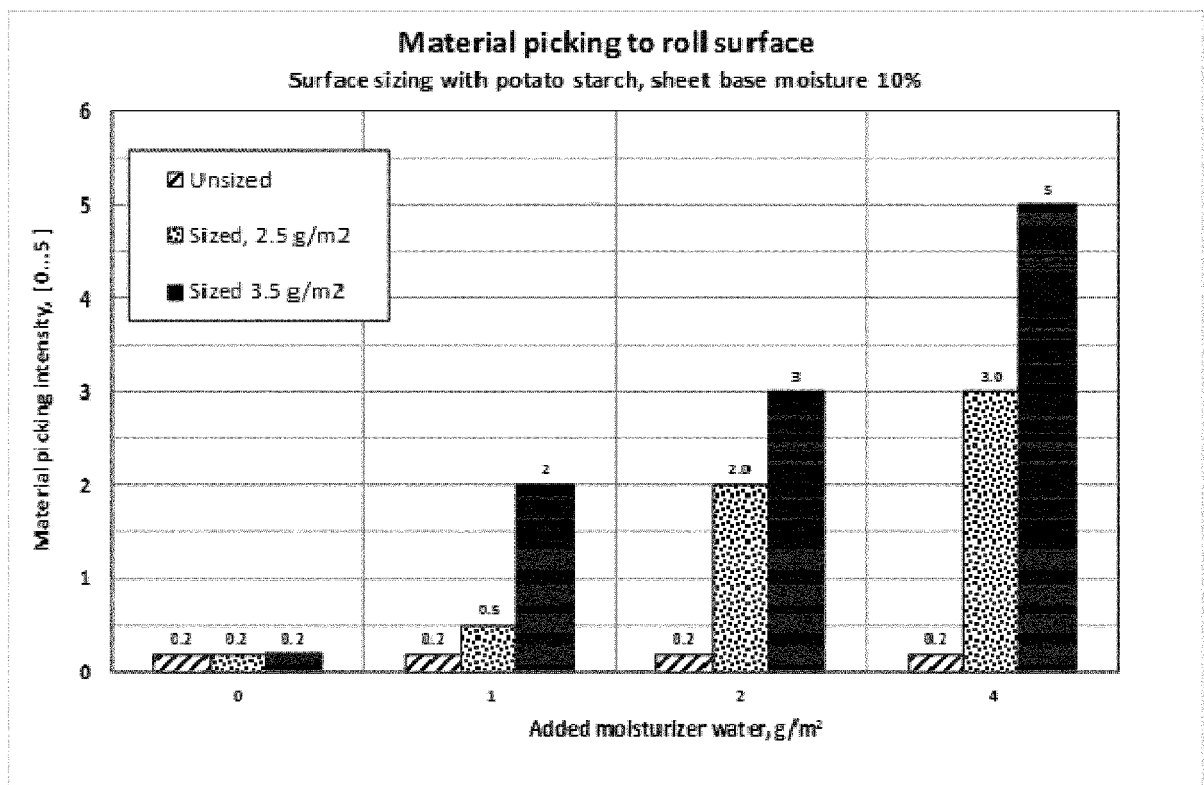


Fig. 2

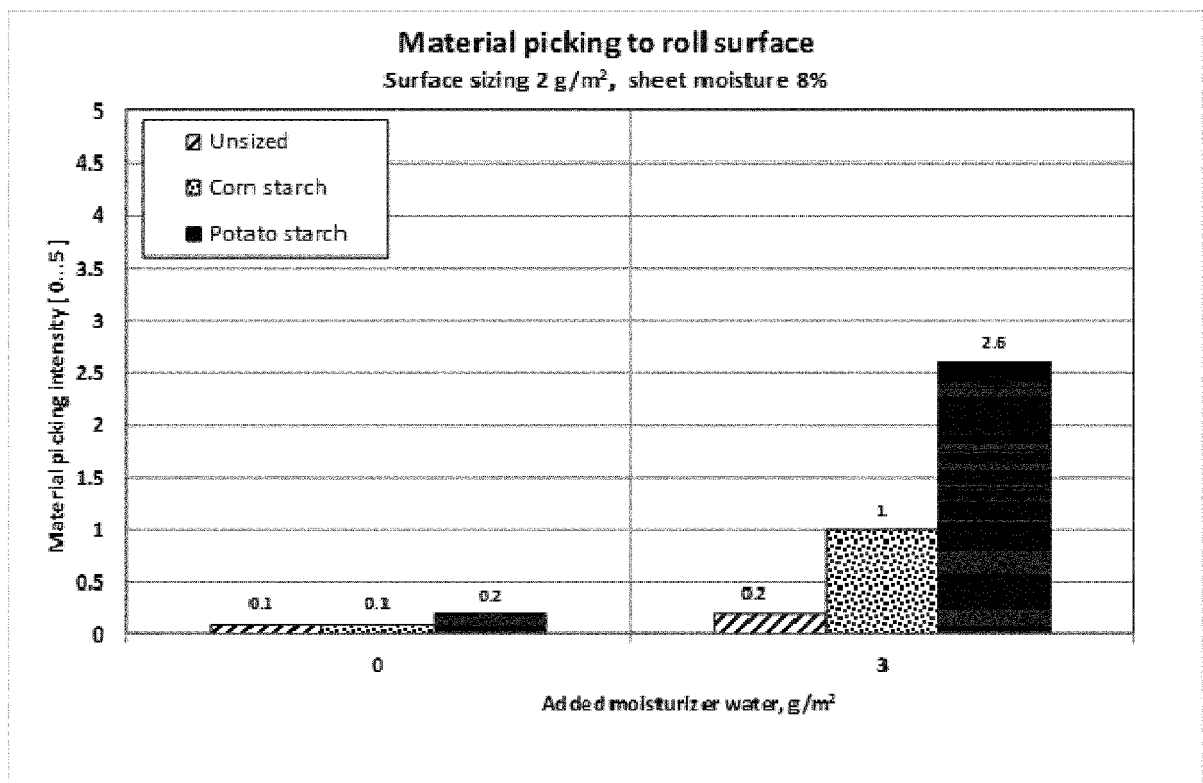


Fig. 3

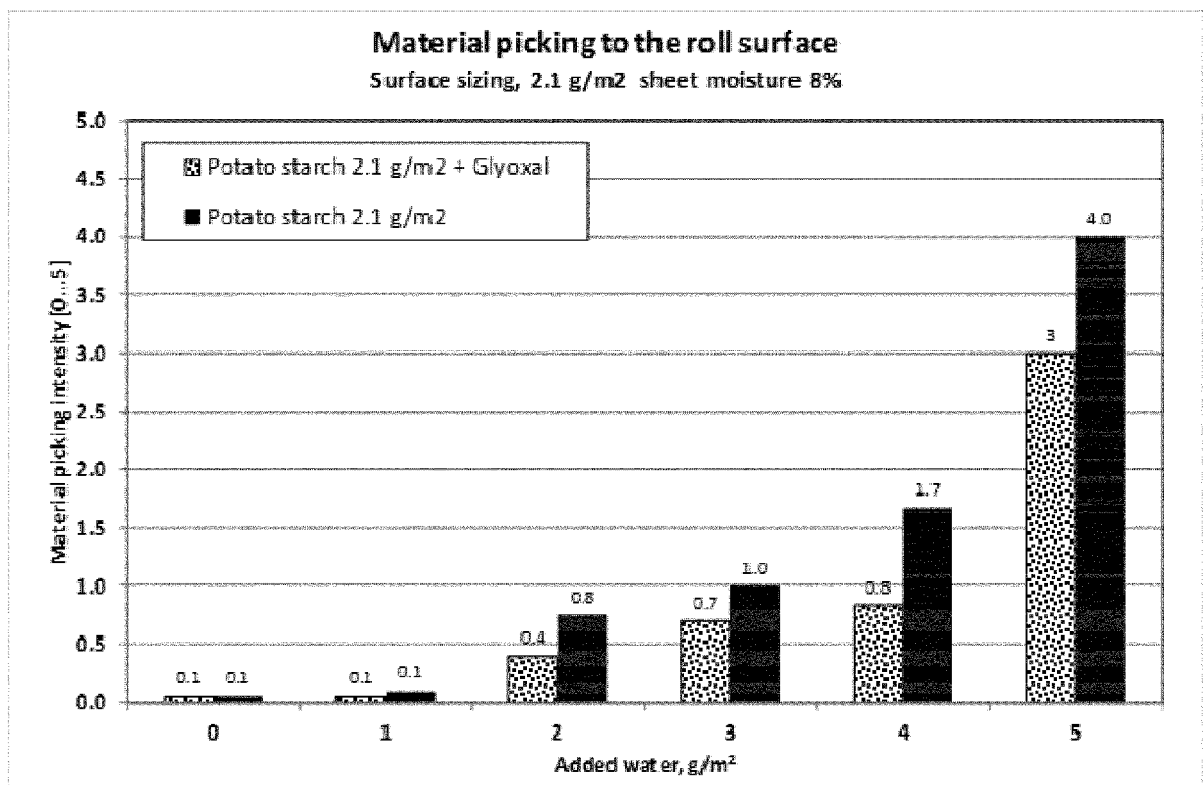


Fig. 4

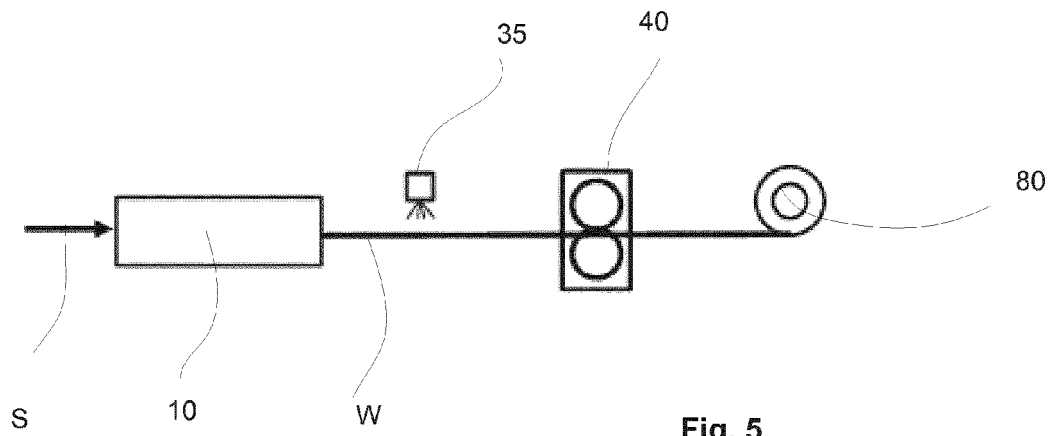


Fig. 5

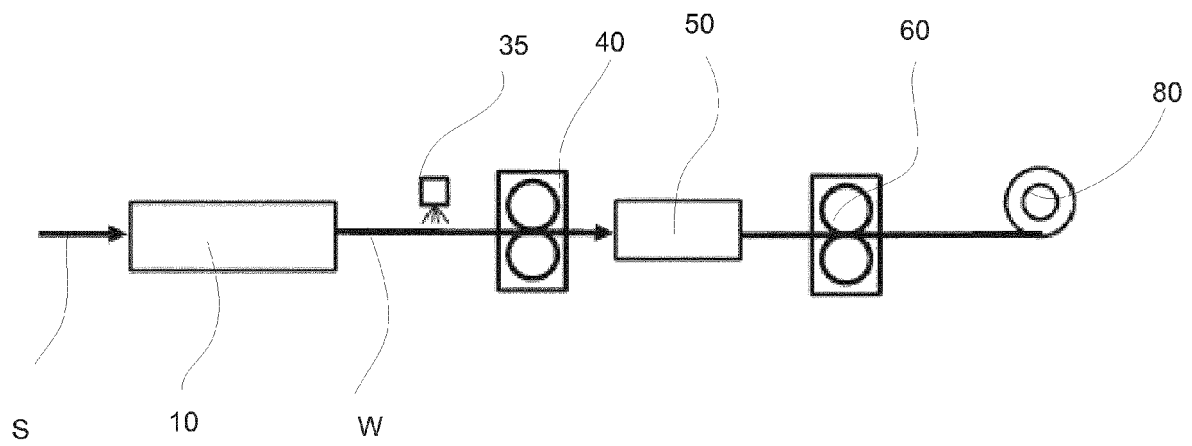


Fig. 6

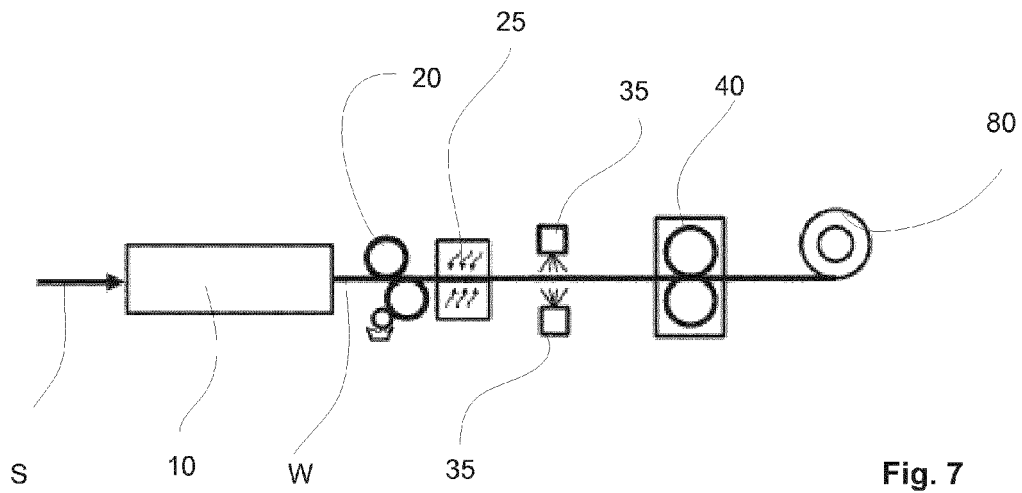


Fig. 7

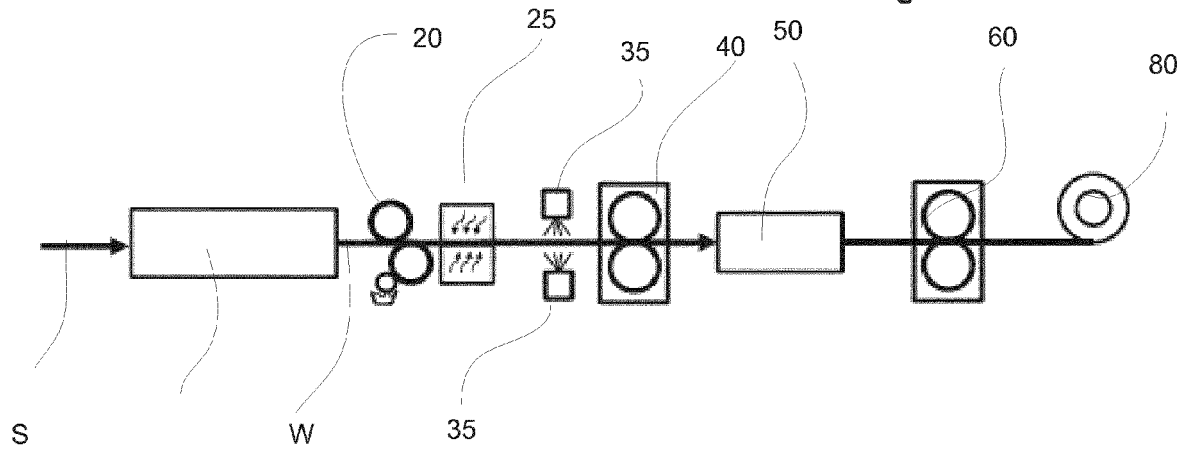


Fig. 8

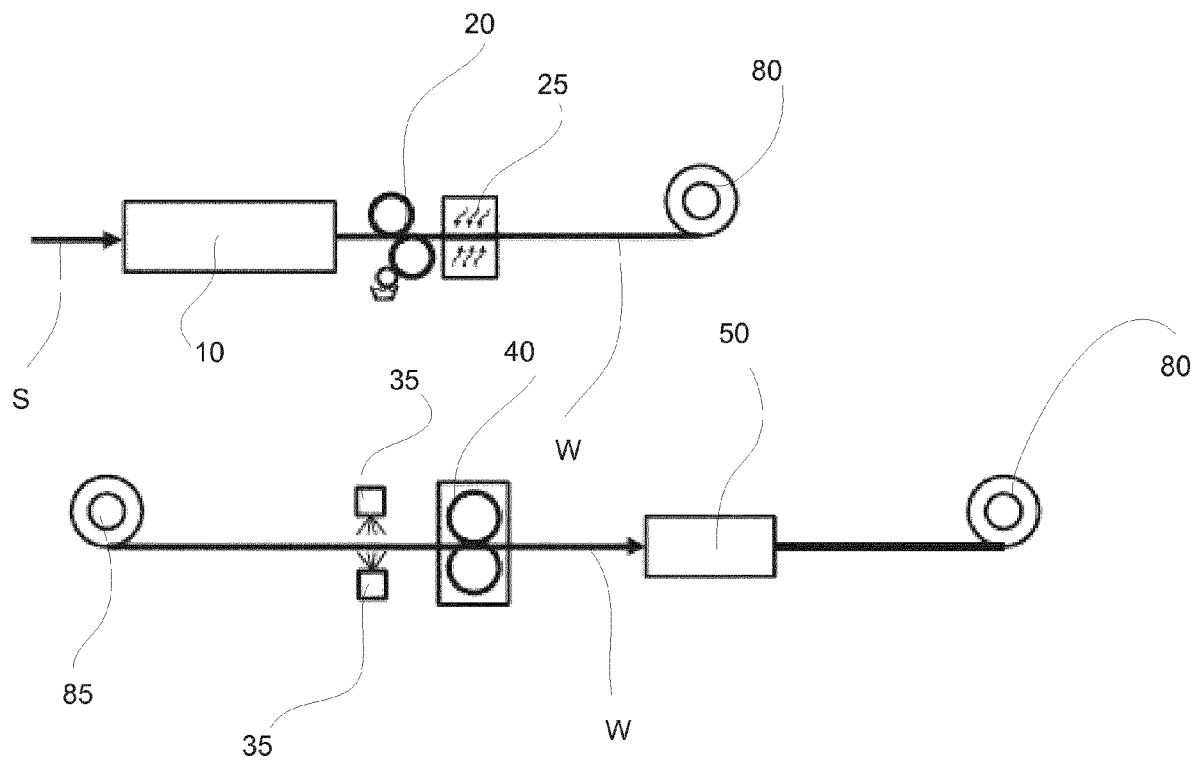


Fig. 9

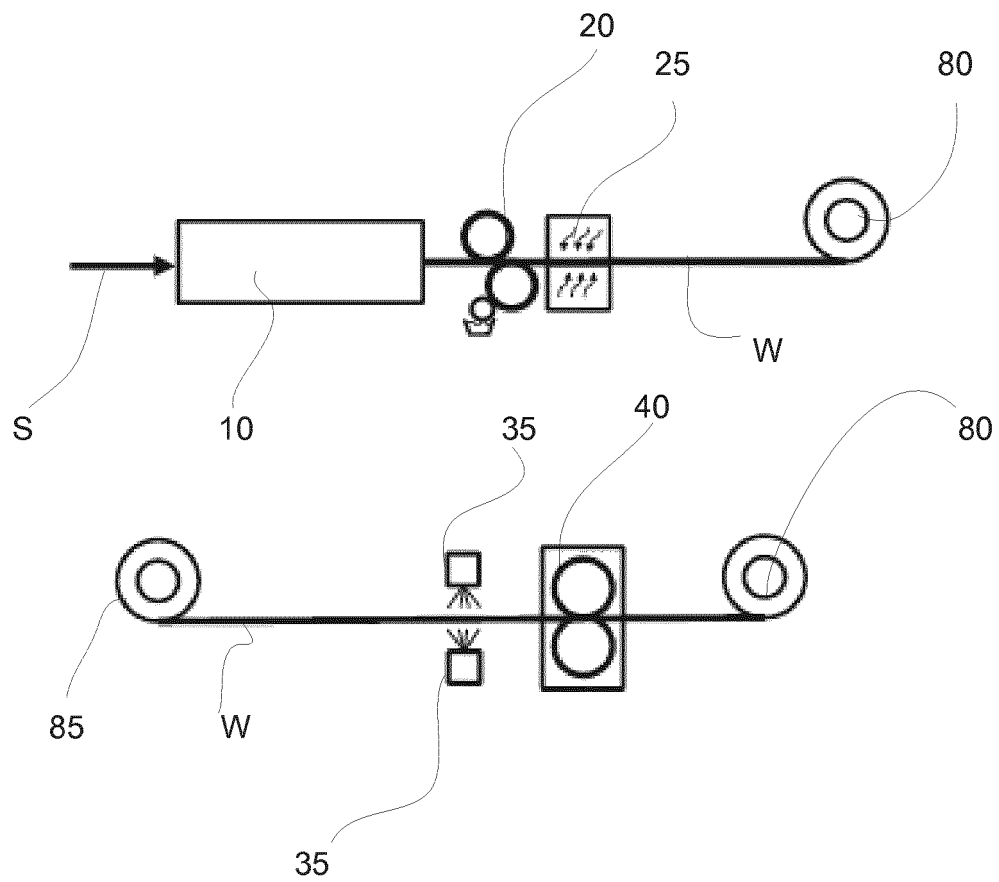


Fig. 10

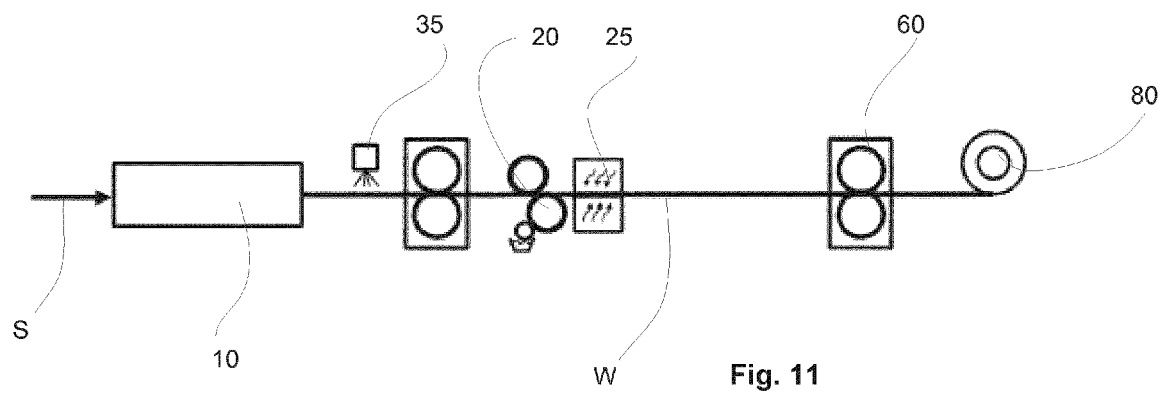


Fig. 11

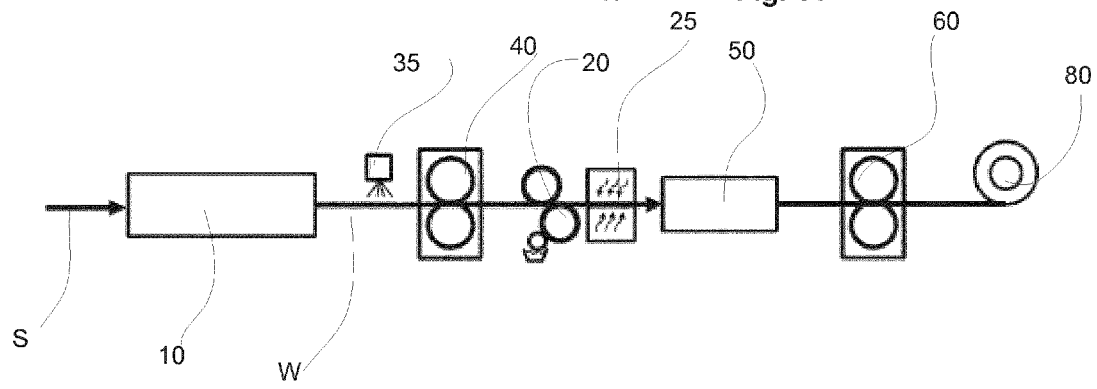


Fig. 12

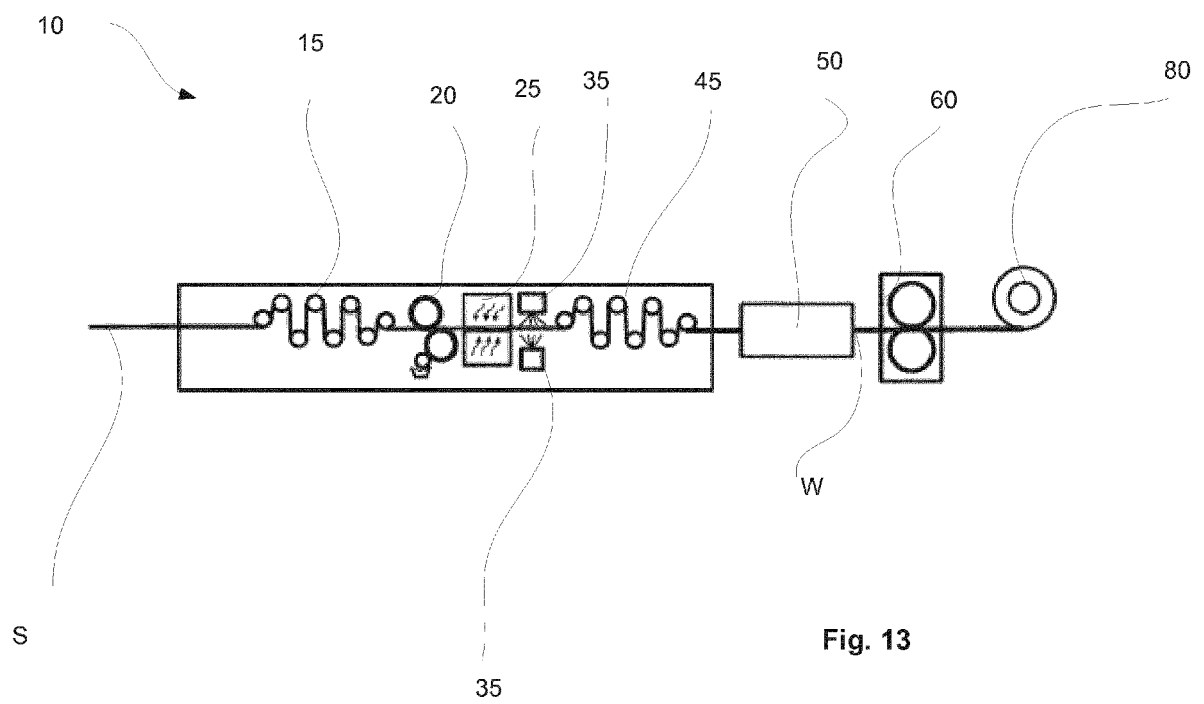


Fig. 13

Table 1

Properties	Potato starch	Maize starch	Wheat starch	Tapioca starch	Waxy maize starch
Clarity; gloss; transparency;	high	low	low	high	high
Smoothness; continuity	high	low	low	high	high
Flexibility: plasticity; toughness; folding endurance	high	low	low	high	high
Internal strength; tensile strength; film strength	high	low	low	high	high
Film solubility: susceptibility to rewetting	high	low	low	high	high

Fig. 14



EUROPEAN SEARCH REPORT

Application Number
EP 12 18 9882

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	US 6 300 393 B1 (HUDSON ALICE P [US] ET AL) 9 October 2001 (2001-10-09) * column 1, lines 23-43 * * column 7, lines 38-54; claims 1-23 *	1-4,6, 8-11	INV. D21H21/16
X,D	US 6 274 001 B1 (MOHAN K KRISHNA [US]) 14 August 2001 (2001-08-14) * claims 1-8 *	14	
X	US 2011/240242 A1 (KOENIG MICHAEL F [US] ET AL) 6 October 2011 (2011-10-06) * paragraphs [0002], [0033]; claims 1-25; figures 1,2 *	1,7,8, 11,14	
X	WO 99/41453 A1 (HERCULES INC [US]) 19 August 1999 (1999-08-19) * page 9, lines 3-13; claims 1-35 * * page 12, lines 8-16 *	1,7,8,14	
X	WO 00/58412 A1 (PENFORD CORP [US]) 5 October 2000 (2000-10-05) * claims 1-32 *	1	TECHNICAL FIELDS SEARCHED (IPC)
X	US 2008/163993 A1 (VARNELL DANIEL F [US]) 10 July 2008 (2008-07-10) * paragraphs [0045], [0050], [0069]; claims 1-9; examples 3-6 *	1,11,14	D21H
X	WO 00/49226 A1 (STORA KOPPARBERGS BERGSLAGS AB [SE]; HAAKANSSON PHILIP [SE]) 24 August 2000 (2000-08-24) * claims 1-11 *	1	
X	EP 1 338 699 A1 (AKZO NOBEL NV [NL]) 27 August 2003 (2003-08-27) * claims 1-19 *	1	
	----- -/--		
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 18 April 2013	Examiner Karlsson, Lennart
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

 1
EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number
EP 12 18 9882

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 603 727 A1 (NAT STARCH CHEM INVEST [US]) 29 June 1994 (1994-06-29) * claims 1-9; examples 1-8 *	1,6	
X	US 5 460 645 A (PANDIAN VERNON E [US] ET AL) 24 October 1995 (1995-10-24) * claims 1-20; examples 1-7 *	1-3,6,7,14	
X	US 3 425 896 A (HART ROBERT T) 4 February 1969 (1969-02-04) * claim 1.9 *	1-3,6,11,14	
A,D	US 5 114 999 A (HUI SAI H [US] ET AL) 19 May 1992 (1992-05-19) * the whole document *	1-15	
A,D	US 3 145 116 A (ZIENTY MITCHELL F) 18 August 1964 (1964-08-18) * the whole document *	1-15	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
Place of search Munich		Date of completion of the search 18 April 2013	Examiner Karlsson, Lennart
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

1
EPO FORM 1503 03.02 (P04C01)

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

EP 12 18 9882

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-04-2013

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6300393	B1	09-10-2001	CA 2254228 A1 US 6300393 B1	17-05-1999 09-10-2001
US 6274001	B1	14-08-2001	NONE	
US 2011240242	A1	06-10-2011	CA 2794948 A1 CN 102906332 A EP 2553168 A1 US 2011240242 A1 WO 2011123214 A1	06-10-2011 30-01-2013 06-02-2013 06-10-2011 06-10-2011
WO 9941453	A1	19-08-1999	AU 2241199 A AU 2470099 A BR 9907959 A CA 2319104 A1 CN 1291249 A EP 1055030 A1 ID 26077 A JP 2002503772 A NO 20004073 A PL 342320 A1 WO 9941452 A1 WO 9941453 A1 ZA 9901270 A	30-08-1999 30-08-1999 24-10-2000 19-08-1999 11-04-2001 29-11-2000 23-11-2000 05-02-2002 09-10-2000 04-06-2001 19-08-1999 19-08-1999 17-08-1999
WO 0058412	A1	05-10-2000	AU 4044500 A CO 5190728 A1 US 6290814 B1 WO 0058412 A1	16-10-2000 29-08-2002 18-09-2001 05-10-2000
US 2008163993	A1	10-07-2008	US 2008163993 A1 WO 2008086029 A2	10-07-2008 17-07-2008
WO 0049226	A1	24-08-2000	AU 2952100 A EP 1185735 A1 PL 349844 A1 SE 513602 C2 SE 9900520 A SK 11202001 A3 US 6585859 B1 WO 0049226 A1	04-09-2000 13-03-2002 23-09-2002 09-10-2000 18-08-2000 03-12-2001 01-07-2003 24-08-2000
EP 1338699	A1	27-08-2003	NONE	
EP 0603727	A1	29-06-1994	AT 150502 T BR 9305197 A	15-04-1997 28-06-1994

EPO FORM P0459

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

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

EP 12 18 9882

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-04-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
		CA 2112197 A1	24-06-1994	
		DE 69309018 D1	24-04-1997	
		DE 69309018 T2	19-06-1997	
		DK 0603727 T3	01-09-1997	
		EP 0603727 A1	29-06-1994	
		ES 2100438 T3	16-06-1997	
		FI 935804 A	24-06-1994	
		JP 2975517 B2	10-11-1999	
		JP H06212595 A	02-08-1994	
		PH 29961 A	16-09-1996	
		US 5368690 A	29-11-1994	
		US 5523339 A	04-06-1996	
		ZA 9309561 A	03-10-1994	

US 5460645	A	24-10-1995	AU 3244095 A	09-04-1996
			US 5460645 A	24-10-1995
			WO 9609345 A1	28-03-1996

US 3425896	A	04-02-1969	GB 1024881 A	06-04-1966
			US 3425896 A	04-02-1969

US 5114999	A	19-05-1992	NONE	

US 3145116	A	18-08-1964	GB 927448 A	29-05-1963
			US 3145116 A	18-08-1964

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- US 6645349 B [0009]
- US 6905573 B [0009]
- WO 9925921 A [0010]
- US 6274001 B [0011]
- US 3145116 A [0012]
- US 5114999 A [0012]
- US 6300393 B [0012]

Non-patent literature cited in the description

- Papermaking Science and Technology. Fapet Oy, 1999, 362 [0018]