(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 725 137 A1**

(12) **EUROPEAN PATENT APPLICATION**

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

(51) Int Cl.:
D21H 21/16 *(2006.01)* ***D21H 19/82*** *(2006.01)*

(21) Application number: **12189885.2**

(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

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

(72) Inventor: **Pietikäinen, Reijo**
04420 Järvenpää (FI)

(74) Representative: **Berggren Oy Ab**
P.O. Box 16
Antinkatu 3 C
00101 Helsinki (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 water resistance of the fiber web is increased by decreasing water solubility of sizing agent used for production of the fiber web by using as sizing agent starch originating from grain or by using a chemical additive in the sizing agent which chemical additive creates bonds with reactive groups of the sizing agent and cross-links and/or decreases water solubility, in particular with an insolubilizer. The invention also relates to a method for producing a fiber web, in which a multilayer sizing process is used in which sizing agent is applied on the fiber web in at least two stages so that a layered sizing profile is achieve in the thickness direction and that in the multilayer sizing process the layers of sizing agent comprise in different layers sizing agents of at least two different compositions. The invention further relates to a process for producing a fiber web comprising sizing of the fiber web by sizing agent. In the sizing the sizing agent is provided in at least two stages of sizing to create a multilayer profile of the sizing agent onto the fiber web and that for at least one layer of the multilayer profile a sizing agent with decreased water solubility is used.

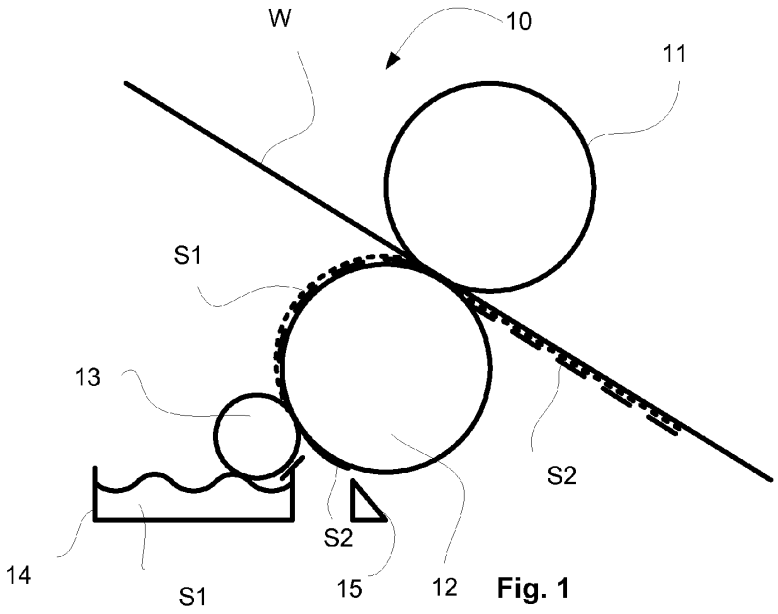

Fig. 1

EP 2 725 137 A1

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 and to a production line for producing fiber webs according to the preamble of claim 11.

[0002] As known from the prior art 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 precalender, 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 paper and board webs.

[0003] In moisture gradient calendering water is applied onto the web surface in order to soften and to plasticize surface layer fibers. The web needs to have certain hydrophilic nature and receptivity of water. On the other hand important factors are the process runnability and the reliability of the process, which might not be at desired level if the fiber web is not resistant enough to water. In order to achieve good process runnability and a reliable process and good calendered quality, the fiber web should be resistant to water to a certain extent such that the fiber web is not too hydrophobic and that a certain level of water receptivity is accomplished i.e. the fiber web is hydrophilic to a certain extent. One object of the invention is to create a method and a process for fiber web production in which the hydrophobic and hydrophilic properties are in balance and the fiber web provides good process runnability and a reliable process.

[0004] In fiber web production another important factor is the quality of the fiber web produced, for example smoothness, porosity and bulk are properties that have great influence in the end use quality of the fiber web. Simultaneously there exists need to achieve savings in raw materials used, for example need to make savings in used amounts of fibers, sizing agents and coating agents. One object of the invention is to create a method and a process for fiber web production in which good quality of the fiber web produced is achieved with simultaneous raw material savings.

[0005] In fiber web production adhesion and adherence of the fiber web to the surfaces of process devices contacting the fiber web, in particular contacting moist fiber web, may cause sticking and material picking problems. One further object of invention is to decrease the adhesion and adherence of the fiber web so that sticking problems in the process devices and in the devices used after the fiber web production are minimized, for example when the fiber web contacts steel or cast iron surfaces (calender rolls or metal belts, drying cylinders etc.), or aluminum surfaces (guide rolls) or polymer surfaces (guide rolls, calender rolls with soft covers) or rubber surfaces (guide rolls, rolls of reels or winders, surfaces of printing machines in printing processes).

[0006] 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 agent, for example starch or other glue chemicals. Sizing can be divided to internal sizing and surface sizing. In internal sizing the sizing agent is added to pulp in the wet end of the fiber web machine before forming. 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.

[0007] It is known that there are differences in solubility of different starch types due to their origin. Starch types originating from roots of plants (root starches) example potato starch and tapioca starch have higher solubility but starch types originating from grain (grain starch or cereal starch) for example maize starch and wheat starch have lower solubility.

[0008] In US patent publications 3145116, 3425896, 3545568, 5114999 and 6300393 are disclosed some known examples of insolubilizers for starches and for coating binders and for surface sizes. In addition US patent publication 6274001 discloses using lubricants in sizing process.

[0009] 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/ m^2 and boards manufactured in multiply technology and having a basis weight of 150 - 600 g/ m^2. 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.

[0010] 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.

[0011] Mechanical-pulp based, i.e. wood-containing printing papers include newsprint, uncoated magazine and coated magazine paper.

[0012] 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/m^2, 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/m^3, brightness (ISO 2470:1999) 57 - 63 %, and opacity (ISO 2470:1998) 90 - 96 %.

[0013] 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/m^2, 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/m^3, brightness (ISO 2470:1999) 62 - 70 %, and opacity (ISO 2470:1998) 90 - 95 %.

[0014] 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/m^2, Hunter gloss 50 - 65 %, PPS s10 roughness 0,8 - 1,5 μm (offset), 0,6 - 1,0 μm (roto), density 1100 - 1250 kg/m^3, brightness 70 - 75 %, and opacity 89 - 94 %.

[0015] General values for MFC (machine finished coated) can be regarded as follows: basis weight 50 - 70 g/m^2, Hunter gloss 25 - 70 %, PPS s10 roughness 2,2 - 2,8 μm, density 900 - 950 kg/m^3, brightness 70 - 75 %, and opacity 91 - 95 %.

[0016] General values for FCO (film coated offset) can be regarded as follows: basis weight 40 - 70 g/m^2, Hunter gloss 45 - 55 %, PPS s10 roughness 1,5 - 2,0 μm, density 1000 - 1050 kg/m^3, brightness 70 - 75 %, and opacity 91 - 95 %.

[0017] General values for MWC (medium weight coated) can be regarded as follows: basis weight 70 - 90 g/m^2, Hunter gloss 65 - 75 %, PPS s10 roughness 0,6 - 1,0 μm, density 1150 - 1250 kg/m^3, brightness 70 - 75 %, and opacity 89 - 94 %.

[0018] HWC (heavy weight coated) has a basis weight of 100 - 135 g/m^2 and can be coated even more than twice.

[0019] 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 %.

[0020] 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/m^2, Bendtsen roughness 250 - 400 ml/min, brightness 86 - 92 %, and opacity 83 - 98 %.

[0021] 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/m^2, 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/m^2, Hunter gloss 70 - 80 %, PPS s10 roughness 0,65 - 0,95 μm, brightness 83 - 90 %, and opacity 95 - 97 %.

[0022] Release papers have a basis weight within the range of 25 - 150 g/m^2.

[0023] Other papers include e.g. sackkraft papers and wallpaper bases.

[0024] 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.

[0025] 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 and the production line for producing fiber webs according to the invention is mainly characterized by the features of claim 11.

[0026] According to one aspect of the invention desired final web quality, good process runnability and process reliability is achieved by increasing water moisturizing of the fiber web during different process stages of the production and by increasing water resistance of the fiber web by decreasing water solubility of the sizing and/or bonding agents used in the production by using less dissolving sizing agent, in particular grain starch or synthetic starch or sizing agent with chemical additive which creates bonds with reactive or functional chemical groups of the sizing agent and cross-links and/or decreases water solubility, in particular with an insolubilizer. By this for example the loosening of sizing agent from the fiber web that disturbs the process and sticking of the loosened sizing agent to surfaces of the process devices contacting the fiber web is eliminated or at least minimized and the calendered quality is increased by moistening the web.

[0027] According to one aspect of the invention a new type of sizing process is created by providing a multilayer sizing process in which sizing agent is applied on the

fiber web in at least two stages so that a layered sizing profile is achieved in the thickness direction. Advantageously in the multilayer sizing process the layers of sizing agent comprise sizing agent layers of at least two different types, or compositions, preferably top layer i.e. the last applied layer is of less soluble sizing agent than in the other at least one sizing agent layer.

[0028] According to another advantageous aspect of the invention the sizing agent used for top layer is selected from the origin that is giving less water dissolving sizing agent. Particularly top layer sizing agent is grain starch or synthetic sizing agent.

[0029] According to one advantageous feature the water solubility of the sizing and/or bonding agents is decreased by using a chemical additive in the agent. In connection with this advantageous feature further advantageous features can be combined:

the chemical additive creates bonds with the reactive chemical groups of the sizing agent, for example with hydroxyl groups of starch or with other reactive groups of different types of sizing agents; for example:

- hydroxyl group -OH with starch, protein, casein, PVOH - Glyoxal, AZC, PZC,
- carboxyl group -COOH with protein, casein, latex - AZC, PZC,
- amine group -NH with casein - Glyoxal,

the chemical additive is cross-linking and/or water solubility decreasing chemical such as an insolubilizer,

preferably the chemical additive is di-aldehyde, for example glyoxal or its derivative,

preferably the chemical additive is inorganic, cross-linking zirconium based chemical such as ammonia-zirconium-carbonate or potassium-zirconium-carbonate or other zirconium salt,

preferably the chemical additive is metallic salt,

preferably the chemical is a lubricant, for example mineral oil, calcium-stearate, wax or polyethene-based emulsion,

preferably at least some part of sizing agent an unmodified starch is used,

preferably at least some part sizing agent a modified starch is used that is modified by

- cross-linking by organic cross-linker such as a di-aldehyde (for example glyoxal) or by inorganic cross-linker such as zirconium based cross-linker (for example AZC or PZC),
- cross-linking by a formaldehyde based chemical
- oxidation
- replacing hydroxyl-groups by a suitable group, for example by esterification or by etherifying

preferably modification is done before applying the sizing agent or in conjunction with applying the sizing agent,

preferably at least some part of the sizing agent is a mixture of starch and CMC, PVA, PVOH, latex, other synthetic glue chemical, pigment, filling agent, lubricant,

preferably at least some part of the sizing agent is synthetic or mixture of synthetic polymer and water soluble biopolymer

- especially in multilayer sizing in the top layer a part of the sizing agent is synthetic glue, for example poly-vinyl-acetate based glue or acrylate based glue or styrene- butadiene based glue,
- especially PVA or PVOH with insolubilizer decrease solubility,

preferably at least some part of the sizing agent is at least partly half-synthetic glue such as CMC (carboxyl-methyl-cellulose), for example with AZC or PZC for effective cross-linking,

preferably at least some part of the sizing agent is at least partly protein such as soy or casein or other non-synthetic glue,

preferably the above mentioned water soluble polymers or at least half-synthetic glues are treated by adding a solubility decreasing, to functional groups bonds creating, cross-linking chemical (such as glyoxal, AZC, PZC) in connection with application of the sizing agent.

[0030] According to advantageous features of the invention the application of the sizing agent and/or the chemical additive of it is provided by:

preferably application in connection with sizing or with pigmenting sizing,

preferably before coating when coated fiber webs are produced,

preferably before hot contact treatment, for example before pre- or end calendering, in particular when

the temperature of the hot contact treatment surfaces is high, 140 - 350 °C and water moisturizing or steaming is used in connection with the treatment or prior to the treatment device, in particular the hot contact treatment is belt drying, belt calendering, hot machine calendering, hot soft calendering, multinip calendering,

for example in drying section, for example using spray application,

for example in connection with the fiber web production machine, after which a separate off-line calendering with water moisturizing is used, in this alternative the delay time from sizing to calendering is long and thus slower reacting (insolubilizer) chemicals such as glyoxal are advantageous,

preferably applying at on-line -production line, where delay time from sizing agent application to calendering is shorter, in this alternative advantageously faster reacting cross-linker or insolubilizers such as AZC or PZC are used.

[0031] The chemical additive dosing is preferably done by adding a chemical additive dosing stage after cooking and diluting stage to be last stage before applying the sizing agent with the chemical additive onto the fiber web. The dosing can be provided to an input container machine run tank or to an input feed line.

[0032] The chemical additive such as glyoxal or its derivate forms under dry and hot conditions covalent bonds with hydroxyl groups and with amino groups of the sizing agent, thus these are advantageous chemical additives when the sizing agent is starch or PVOH.

[0033] The chemical additives such as AZC and PZC react by forming bonds with hydroxyl groups but also with carboxyl groups, thus these are advantageous chemical additives when the sizing agent is synthetic glue (latex, styrene-acrylate, PVA) for strengthening and for decreasing water solubility.

[0034] According to advantageous features of the invention the application device used is:

pond sizer,

film transfer sizer,

non-contacting sizer, such as curtain or spray sizer.

[0035] According to an advantageous feature the solids content of the sizing agent is 5 - 35 %, preferably 5 - 15 %.

[0036] According to an advantageous feature the amount of sizing agent for one side of the web to be sized in 0,1 - 5 g/m^2 (as dry agent), preferably for paper web 0,1 - 2 g/m^2 for one side and for board 0,5 - 3 g/m^2 for one side.

[0037] According to an advantageous feature the curing speed and curing level of the chemical additive is controlled by controlling the temperature and the temperature influence time in sizing and sizing agent drying processes.

[0038] According to an advantageous feature the application is provided as one or two sided sizing, in which chemical addition is used for at least one side.

[0039] According to an advantageous aspect of the invention the sizing agent is provided to create a multilayer profile of the sizing agent onto the fiber web. According to advantageous features of the invention the multilayer sizing is provided such that:

the top layer is sized by sizing agent which has decreased properties of water solubility and of sticking when compared to the layer / layers of sizing agent in the layers below,

the top layer is sized by starch with chemical additive such that the water solubility of it is less than of the sizing agent layer / layers below; the chemical additive is dosed only to a part of the total amount of sizing agent to be applied and most preferably to the part that will form the top layer of the sizing agent layers,

the sizing agent to be used for the layer/layers not creating the top sizing layer on the fiber web has no or less chemical additives than the sizing agent to be used for the top layer,

the top layer is sized by a starch with lower water solubility preferably grain starches such as wheat or maize or barley starch and the layer /layers below is / are sized by a starch with higher water solubility preferably root starches such as potato or tapioca starch,

the sizing layers are provided on the fiber web by layering the sizing agent, for example in as least two stage process such that in the first stage/stages the more soluble sizing agent with higher penetration depth is applied onto the fiber web and in the second stage the less soluble sizing agent with lower penetration depth is applied onto the fiber web,

the lower layer / layers of the sizing agent is / are applied by film sizer, size press or similar process or by spray sizer with a pressing nip that provides for high penetration and the top layer of the sizing agent is applied by spray only or by curtain or other light or contactless application method that provides less penetration, but even and thin surface layer,

the lower layer / layers are of sizing agent with low viscosity and thus high penetration and the top layer is of sizing agent with high viscosity and thus with

lower penetration; the penetration profile in thickness direction can be controlled by viscosity agents like thickeners or by temperature or by dilution or by pH control,

the lower layer / layers of sizing agent are applied with lower solids content (5 - 15 % solids content) and the top layer of sizing agent is applied with higher solids content (10 - 35 % solids content).

[0040] According to advantageous features the process of multilayer sizing comprising at least two stages is for example:

first sizing stage, and second sizing stage and drying stage according to the wet-on-wet principle,

first sizing stage, drying stage, second sizing stage and drying stage according to the wet-on-dry principle.

[0041] According to an advantageous aspect of the invention the sizing agent and the sizing agent with the chemical additive decreasing the water solubility and/or decreasing sticking of the sizing agent are applied by multilayer technique such that the sizing agent with the chemical additive is applied last at the last sizing stage such that the sizing agent with the chemical additive forms for the top layer of the multilayered sizing agent. Thus less chemical additive is needed and cost savings are achieved.

[0042] According to an advantageous feature the chemical additive is applied mixed with the sizing agent or separately on top of the sizing agent, preferably using wet-on-wet technique such that the chemical additive concentration is greater on the surface than deeper in the web and the applied layers are dried simultaneously.

[0043] According to an advantageous example of the invention in the method the chemical additive is dosed with the sizing agent layer as a thin layer in wet-on-wet technique. The chemical additive will mix with the top layer of the sizing agent layer and thus smaller amount of chemical additive is needed.

[0044] According to an advantageous feature the chemical additive is cured as the fiber web is dried and water removed in the drying section after the sizing agent application. The drying at elevated temperature is speeding up the curing process.

[0045] The invention is applicable in production of various grades of paper or boards:

the invention is advantageous when producing coated printing or writing paper grades such as MWC, LWC, WFC or FCO,

the invention is advantageous when producing uncoated printing or writing paper grades such as WFU, book, news or SC,

the invention is advantageous when producing carton board grades such as FBB, SBS, LBP or WLC,

the invention is advantageous when producing container board grades such as liner or testliner or corrugating medium boards or special boards.

[0046] The invention is applicable in new product lines as well as in modernizing projects of fiber web production lines, in particular in modernizing of drying sections, sizers or calenders. The line is modernized according to the simplest example of the invention by providing a dosing pump or corresponding means for the chemical additive in to the sizing.

[0047] The different advantageous aspects and features described above can be combined in various ways to achieve further advantages.

[0048] By the invention many advantages are achieved for example sticking problems are eliminated, dust problems are minimized, increased cleanliness and better runnability and better reliability are reached. Also the quality of the fiber web produced is improved as the strength and stiffness of the fiber web increases due to for example cross-linking and due to improved smoothness and porosity of the fiber web which further makes it possible to increase smoothness and decrease porosity provided by pre-calendering which further reduces the amount of coating agent needed. By the advantageous multilayer sizing savings are achieved in the amount needed for the desired result as the chemical additive or more expensive sizing agent can be used only in the top sizing layer and for the lower layer / layers more and cheaper sizing agent can be used. In the top layer sizing agent a higher concentration of chemical additive can be used.

[0049] It is advantageous to use lower ingoing temperature when leading the fiber web to a calender thus providing for stronger gradient calendering and savings in bulk. An advantageous process of sizing with chemical additive dosing, drying, cooling, moisturizing and calendering can be used. Particularly this improved gradient calendering process further enhances the benefits of this invention.

[0050] The utilization of the invention is very advantageous in connection of production of fiber webs in production lines where water moisturizing is used in connection with hot calendering. Particularly, benefits are realized as more water can be applied at moisturizing stage and therefore enhanced moisture gradient calendering effect is achieved together with temperature gradient calendering.

[0051] The benefits of the improved process achieved by the invention can be exploited at least in two ways as follows:

1. Thinner, lighter product, improved quality, like smoothness and strength, enable the reduction of fiber material, basis weight and thickness of fiber

web keeping functional end use properties unchanged, directly leading to material savings due to reduced material cost.

2. Improved quality potential, like smoothness and strength, enable to replace expensive fiber material with cheaper components, like recycled fiber of fillers etc., keeping thickness, bulk, basis weight and all other fiber grade specific properties substantially at same level, but same weight with cheaper materials with reduced production and material cost.

[0052] In the following the invention is described in more detail with reference to the accompanying drawing in which in figure 1 is schematically shown an example of one aspect of the invention in which the chemical additive or sizing agent is dosed onto a film transfer roll,
in which in figure 2 is schematically shown an example of one aspect of the invention in which the chemical additive or sizing agent is dosed onto a first sizing agent layer applied on the fiber web,
in which in figure 3 is schematically shown an example of a fiber web production line with on-line calendering,
in which in figure 4 is schematically shown an example of a fiber web production line and off-line calendering,
in which in figure 5 is schematically shown an example of one aspect of the invention with wet-on-wet sizing and
in which in figure 6 is schematically shown an example of one aspect of the invention wet-on-dry sizing.

[0053] In figures 1 - 6 same reference signs are used for indicating corresponding parts and part components of the example unless otherwise indicated.

[0054] In the examples of figures 1 and 2 the sizer is indicated by reference numeral 10. The sizer 10 comprises two sizing rolls 11, 12 in between of which a sizing nip is formed. From the sizing agent container 14 the sizing agent S1 is dosed by a film transfer roll/rod 13 onto the surface of one sizing roll 12 in this example of one side sizing. Naturally the examples are also suitable for two side sizing with corresponding means for the other side of the fiber web. From the surface of the sizing roll 12 the sizing agent S1 is applied onto the fiber web W passing through the sizing nip.

[0055] In figure 1 is schematically shown an example in which the second agent S2: for example a) lower solubility sizing agent as such or b) the sizing agent in which insolubilizer additives have been already mixed or c) solubility decreasing chemical additive, is applied with the sizing agent as a layer. The second agent S2 is dosed by dosing means 15 onto the surface of the sizing roll 12 before dosing the (first) sizing agent S1 by the film transfer roll/rod 13 such that the (first) sizing agent S1 remains on the top layer on the sizing roll 12 and then on the web the (first) sizing agent S1 is on the bottom and the second agent S2 is remaining in the top layer.

[0056] Alternatively, the agent S2 in the figure 1 can be understood to represent another (second) sizing agent (instead of chemical additive), having lower water solubility than the first sizing agent S1.

[0057] Second sizing agent S2 will be placed on the top layer, preventing the dissolving of bottom layer sizing agent S1, having greater water solubility.

[0058] In figure 2 is schematically shown an example where the second agent S2 is applied on the top of the first agent, which is being applied first on the web. The second agent S2 is applied by wet-on-wet technique.

[0059] By the second agent S2 is meant a chemical additive, which is mixed with the first sizing agent S1, when applied at the top by wet-on-wet technique.

[0060] Alternatively, the second agent S2 can be understood as an lower solubility sizing agent, being applied on top by wet-on-wet technique and forming a multilayer sizing layer.

[0061] Dosing means 15 can be rod, spray dosing/metering or corresponding means. Instead of the film transfer roll/rod 13 also for example spray dosing/metering application means can be used.

[0062] In figure 3 is schematically shown a fiber web production line comprising the beginning sections, a head box, a wire section, a press section and a drying section of the fiber web machine, generally indicated by reference numeral 50, followed by a sizer 10 for application of a sizing agent onto the fiber web W and a dryer 20 for drying the sizing agent. There after an on-line calender 30 with a pre-moisturizing unit 35 is located. In this example the delay time from sizing agent application at the sizer 10 to calendering at the calender 30 is short, for example several seconds, in this alternative advantageously fast curing cross-linker or insolubilizers such as AZC or PZC are used as the chemical additives of the sizing agent.

[0063] In figure 4 is schematically shown a fiber web production line comprising the beginning sections, a head box, a wire section, a press section and a drying section of the fiber web machine, generally indicated by reference numeral 50, followed by a sizer 10 for application of a sizing agent onto the fiber web W and a dryer 20 for drying the sizing agent. At the end of the production line the fiber web is reeled-up to a parent roll 40. There after the parent roll 40 is transferred to an off-line calender 30 with a pre-moisturizing unit 35. In this example the delay time from sizing agent application at the sizer 10 to calendering at the calender 30 is long, for example from tens of minutes to several hours, and thus slower curing (insolubilizer) chemical additives of the sizing agent such as glyoxal are advantageous.

[0064] In figure 5 is schematically shown an example in which the fiber web W is multilayer sized by wet-on-wet technique by two sizers 10A, 10B, each of which applies a layer of sizing agent onto the fiber web W such that the second layer is applied onto the first layer and only there after the sizing agent layers are dried in a common dryer 20. The sizing agents for each layer have different compositions.

[0065] In figure 6 is schematically shown an example in which the fiber web W is sized by wet-on-dry technique

by two sizers 10A, 10B, each applying layer of sizing agent onto the fiber web W such that the second layer is applied by the second sizer 10B only after the first sizing agent layer has by dried by the first dryer 20A. The second layer of the sizing agent is dried by the second dryer 20B located after the second sizer 20B. In this example each sizer 10A, 10B is followed by its own dryer 20A, 20B. The sizing agents for each layer have different compositions.

[0066] 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 water resistance of the fiber web is increased by decreasing water solubility of sizing agent used for production of the fiber web by using less water dissolving sizing agent, in particular grain starch or synthetic sizing agent or by using a chemical additive in the sizing agent which chemical additive creates bonds with reactive groups of the sizing agent and cross-links and/or decreases water solubility, in particular with an insolubilizer.

2. Method for producing a fiber web, **characterized in, that** in the method a multilayer sizing process is used in which sizing agent is applied on the fiber web in at least two stages so that a layered sizing profile is achieved in the thickness direction and that in the multilayer sizing process the layers of sizing agent in different layers advantageously comprise sizing agent of at least two different composition, preferably of at least two different solubility.

3. Method according to claim 1 or 2, **characterized in, that** in the method the sizing agent is applied in at least two stages of sizing to create a multilayer profile of the sizing agent onto the fiber web.

4. Method according to any of claim 1 - 3, **characterized in, that** the multilayer profile is created by multilayer sizing and that in the top layer of the multilayer profile is used a less water soluble sizing agent than in the at least one other sizing agent layer and that the sizing agent of the top layer is a sizing agent with lower solubility, for example with chemical additive, or that the sizing agent of the top layer is lower solubility grain starch.

5. Method according to claim 1, **characterized in, that** the chemical additive creates bonds with reactive groups of the sizing agent, in particular with hydroxyl groups or amino groups of the sizing agent.

6. Method according to any of claims 1or 3, **characterized in, that** as the insolubilizer chemical additive is used di-aldehyde or inorganic, cross-linking chemical zirconium based chemical or other insolubilizer or a lubricant.

7. Method according to claim 4, **characterized in, that** as the cross-linking chemical an organic cross-linker or an inorganic cross-linker or a formaldehyde based chemical is used.

8. Method according to any of the previous claims 1 - 7, **characterized in that** the solids content of the sizing agent is 5 - 35 %, preferably 5 - 15 %.

9. Method according to claim 2, **characterized in that** in the multilayer profiling of the sizing agent the top layer is sized by sizing agent which has decreased properties of water solubility and of sticking and picking to a roll when compared to the corresponding properties of sizing agent in the layers below and/or the top layer is sized by starch with chemical additive such that the water solubility of it is less than of the sizing agent layer / layers below and that the chemical additive is dosed only to a part of the total amount of sizing agent to be applied and most preferably to the part that will form the top layer of the sizing agent layers and/or the sizing agent to be used for the layer/layers not creating the top sizing layer on the fiber web has no or less chemical additives than the sizing agent to be used for the top layer and/or the top layer is sized by a starch with lower water solubility such as wheat or maize or barley starch and the layer / layers below is / are sized by a starch with higher water solubility such as potato or tapioca starch.

10. Method according to claim 2, **characterized in that** the sizing layers are provided on the fiber web by layering the sizing agent in at least two sizing stages such that in the first sizing stage/stages the more soluble sizing agent with higher penetration depth is applied onto the fiber web and in the last sizing stage the less soluble sizing agent with lower penetration depth is applied onto the fiber web.

11. Process for producing a fiber web comprising sizing of the fiber web by sizing agent, **characterized in that** in the sizing the sizing agent is provided in at least two stages of sizing to create a multilayer profile of the sizing agent onto the fiber web and that for at least one layer of the multilayer profile a sizing agent with decreased water solubility is used.

12. Process according to claim 11, **characterized in that** the sizing agent is applied by a pond sizer or by a film transfer sizer or by a non-contacting sizer such as curtain or spray sizer.

13. Process according to claim 11, **characterized in**

that lower layer / layers of the sizing agent is / are applied by size press that provides for higher penetration and top layer of the sizing agent is applied by spray only or by curtain or other contactless or light application method that provides for less penetrating layer and more even surface layer.

14. Process according to claim 11, **characterized in that** the application of the sizing agent and the chemical additive of it is provided by application in connection with sizing or with pigmenting sizing or before coating when coated fiber webs are produced and/or before hot contact treatment, advantageously belt drying, belt calendering, hot machine calendering, hot soft calendering or multinip calendering, in particular when the temperature of the treatment device surfaces is high, 140 - 350 °C and water moisturizing or steaming is used prior or in connection with the hot contact treatment and/or in drying section.

15. Process according to claim 2, **characterized in that** in the sizing agent with chemical additive is dosed on a sizing agent layer by wet-on-wet technique.

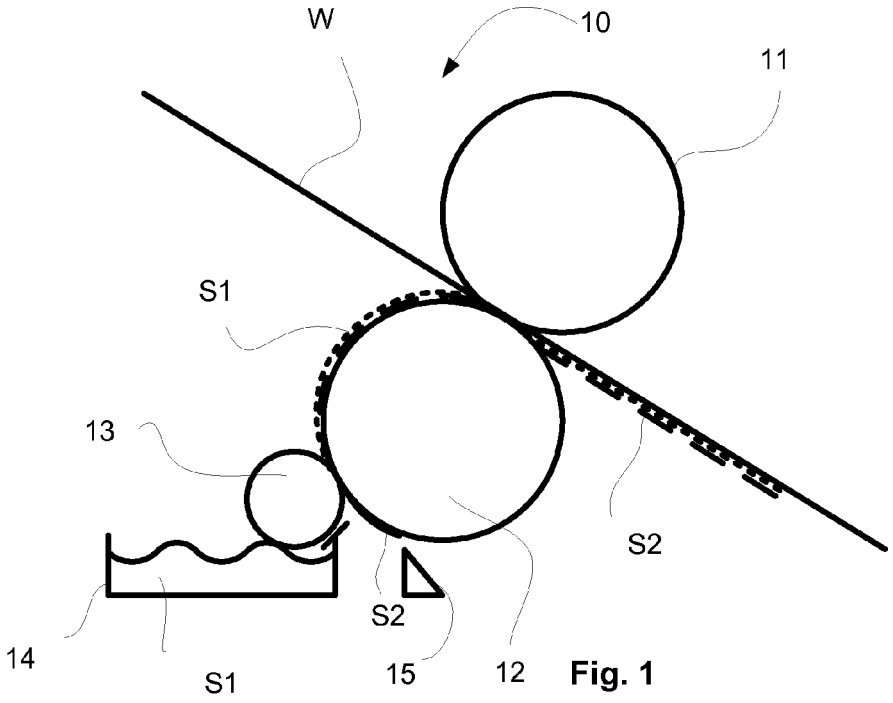

Fig. 1

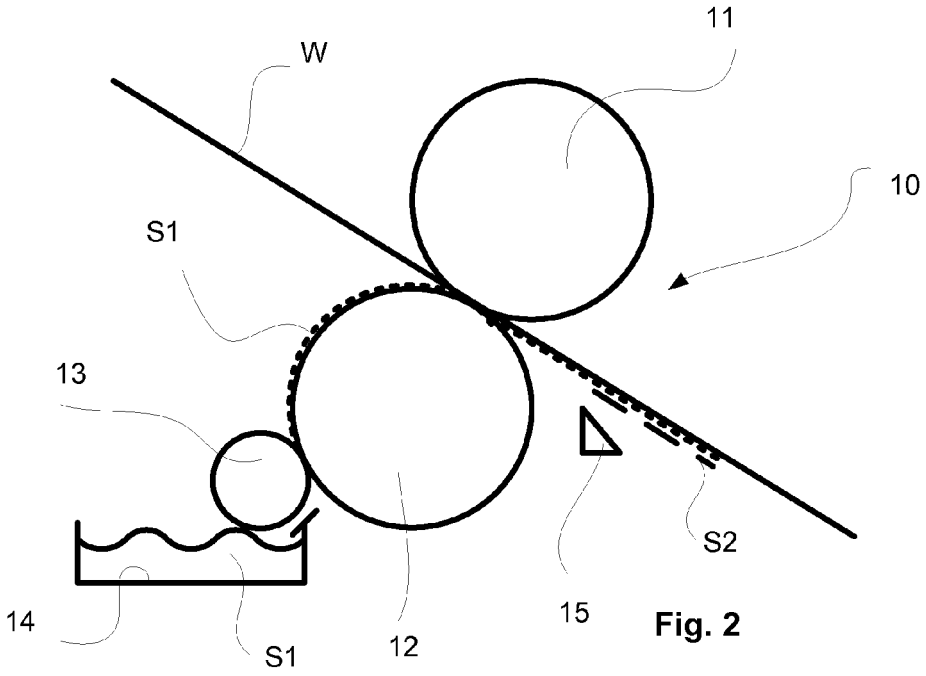

Fig. 2

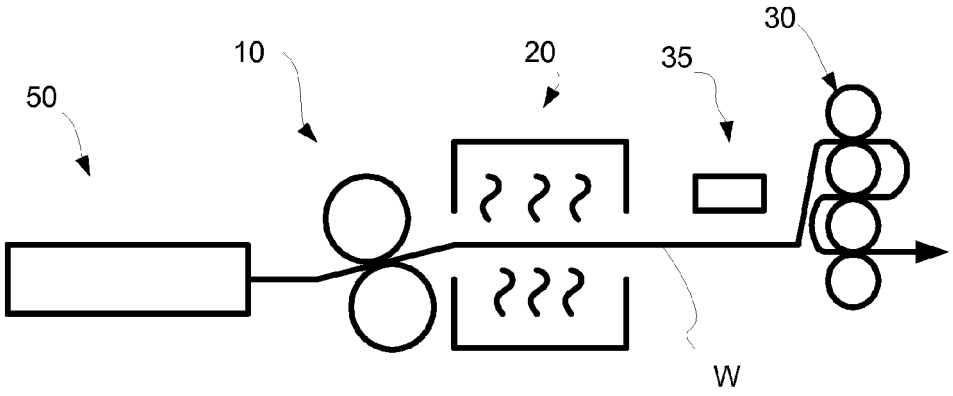

Fig. 3

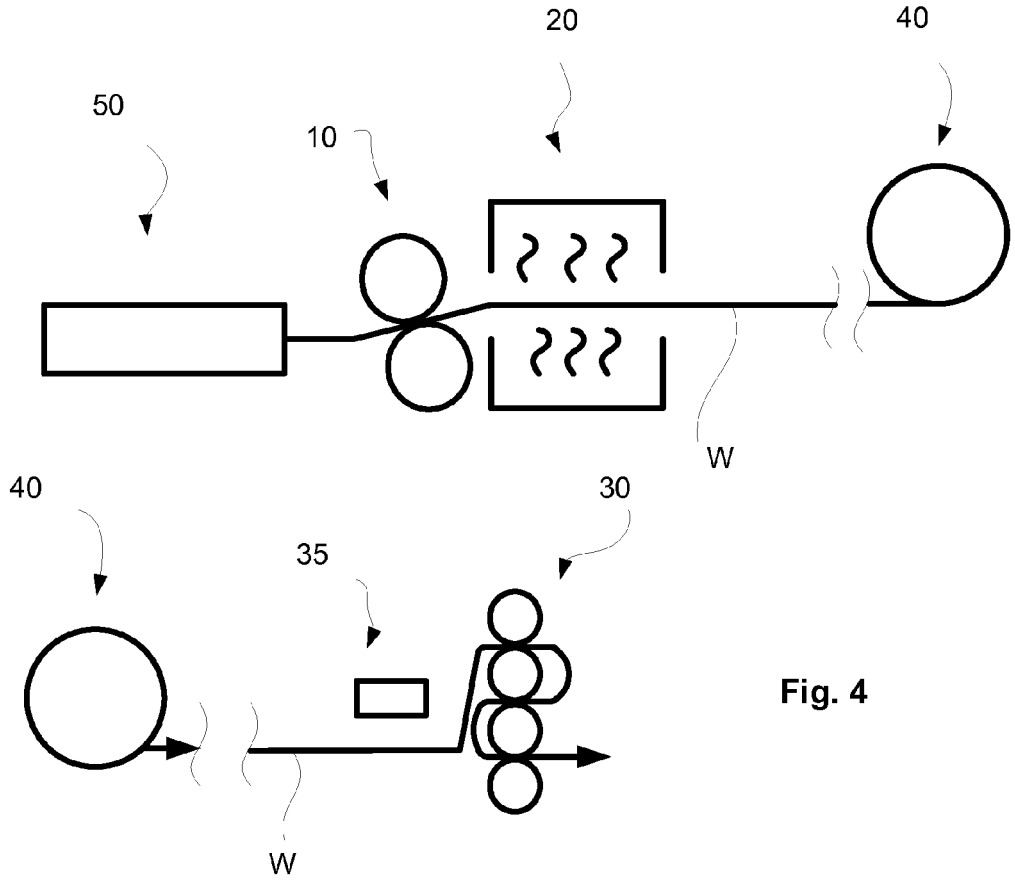

Fig. 4

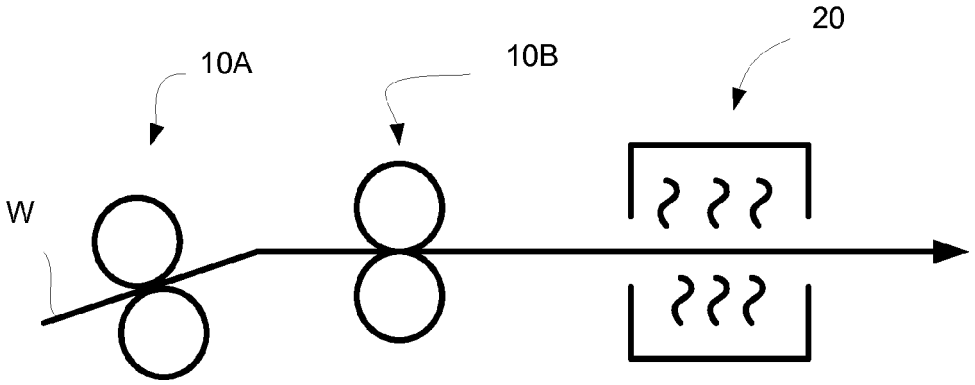

Fig. 5

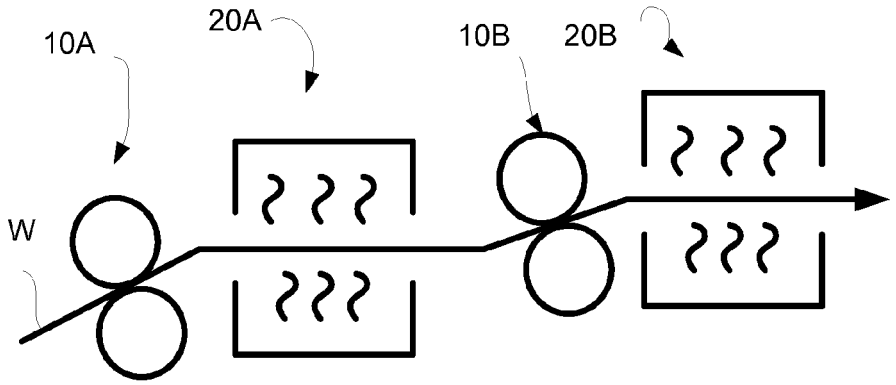

Fig. 6

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 12 18 9885

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, line 23 - line 43 *	1,5-7	INV. D21H21/16 D21H19/82
X	US 2011/240242 A1 (KOENIG MICHAEL F [US] ET AL) 6 October 2011 (2011-10-06) * claims 1-25; figures 1,2 *	1	
X	WO 99/41453 A1 (HERCULES INC [US]) 19 August 1999 (1999-08-19) * claims 1-35 *	1	
X	WO 00/58412 A1 (PENFORD CORP [US]) 5 October 2000 (2000-10-05) * claims 1-32 *	1	
X	US 2008/163993 A1 (VARNELL DANIEL F [US]) 10 July 2008 (2008-07-10) * claims 1-19; examples 3-6 *	1	
X	WO 00/49226 A1 (STORA KOPPARBERGS BERGSLAGS AB [SE]; HAAKANSSON PHILIP [SE]) 24 August 2000 (2000-08-24) * claims 1-11; examples 1-4 *	1,5-7	TECHNICAL FIELDS SEARCHED (IPC) D21H
X	EP 1 338 699 A1 (AKZO NOBEL NV [NL]) 27 August 2003 (2003-08-27) * claims 1-19 *	1	
X	EP 0 603 727 A1 (NAT STARCH CHEM INVEST [US]) 29 June 1994 (1994-06-29) * claims 1-9 *	1,5-7	
X	WO 03/056102 A1 (METSO PAPER INC [FI]; FORS STEFAN [FI]; GROEN JOHAN [FI]; RAUTIAINEN P) 10 July 2003 (2003-07-10) * page 8, lines 8-32; claims 1-15 *	2,3	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	30 October 2013	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

3

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 12 18 9885

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 0 754 800 A2 (WESTVACO CORP [US]) 22 January 1997 (1997-01-22) * claims 1-12; figure 1 *	2,3	
X	US 3 413 190 A (AYCOCK ALBERT J ET AL) 26 November 1968 (1968-11-26) * claim 1; figures 1-2 *	2,3,9,12	
X	WO 2010/114467 A1 (KORSNAES AB PUBL [SE]; LARSSON JOHAN [SE]; AKSBERG REIN [SE]; TUFVESSO) 7 October 2010 (2010-10-07) * claims 1-20 *	2,3	
X	US 2012/121872 A1 (KOENIG MICHAEL F [US]) 17 May 2012 (2012-05-17) * paragraph [0093]; claims 1-23 *	2,3	
A,D	US 3 425 896 A (HART ROBERT T) 4 February 1969 (1969-02-04) * 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	TECHNICAL FIELDS SEARCHED (IPC)
A	EP 2 402 168 A1 (CANON KK [JP]) 4 January 2012 (2012-01-04) * the whole document *	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	30 October 2013	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

3

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

Application Number
EP 12 18 9885

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

Europäisches Patentamt
European Patent Office
Office européen des brevets

LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 12 18 9885

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1, 3-8

The first group of inventions pertains to a method for producing a fiber web, in which water resistance of the fiber web is increased by decreasing water solubility of sizing agent used for production of the fiber web by using less water dissolving sizing agent, in particular grain starch or synthetic sizing agent or by using a chemical additive in the sizing agent which chemical additive creates bonds with reactive groups of the sizing agent and cross-links and/or decreases water solubility, in particular with an insolubilizer.

---

2. claims: 2-4, 6-15

The second group of inventions refers to a method for producing a fiber web, characterized in, that in the method a multilayer sizing process is used in which sizing agent is applied on the fiber web in at least two stages so that a layered sizing profile is achieved in the thickness direction and that in the multilayer sizing process the layers of sizing agent in different layers advantageously comprise sizing agent of at least two different composition, preferably of at least two different solubility.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 18 9885

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.

30-10-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6300393 B1	09-10-2001	CA 2254228 A1	17-05-1999
		US 6300393 B1	09-10-2001
US 2011240242 A1	06-10-2011	CA 2794948 A1	06-10-2011
		CN 102906332 A	30-01-2013
		EP 2553168 A1	06-02-2013
		JP 2013524031 A	17-06-2013
		KR 20130029072 A	21-03-2013
		US 2011240242 A1	06-10-2011
		WO 2011123214 A1	06-10-2011
WO 9941453 A1	19-08-1999	AU 2241199 A	30-08-1999
		AU 2470099 A	30-08-1999
		BR 9907959 A	24-10-2000
		CA 2319104 A1	19-08-1999
		CN 1291249 A	11-04-2001
		EP 1055030 A1	29-11-2000
		ID 26077 A	23-11-2000
		JP 2002503772 A	05-02-2002
		NO 20004073 A	09-10-2000
		PL 342320 A1	04-06-2001
		WO 9941452 A1	19-08-1999
		WO 9941453 A1	19-08-1999
		ZA 9901270 A	17-08-1999
WO 0058412 A1	05-10-2000	AU 4044500 A	16-10-2000
		CO 5190728 A1	29-08-2002
		US 6290814 B1	18-09-2001
		WO 0058412 A1	05-10-2000
US 2008163993 A1	10-07-2008	US 2008163993 A1	10-07-2008
		WO 2008086029 A2	17-07-2008
WO 0049226 A1	24-08-2000	AU 2952100 A	04-09-2000
		EP 1185735 A1	13-03-2002
		PL 349844 A1	23-09-2002
		SE 513602 C2	09-10-2000
		SE 9900520 A	18-08-2000
		SK 11202001 A3	03-12-2001
		US 6585859 B1	01-07-2003
		WO 0049226 A1	24-08-2000
EP 1338699 A1	27-08-2003	NONE	
EP 0603727 A1	29-06-1994	AT 150502 T	15-04-1997
		BR 9305197 A	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 9885

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.

30-10-2013

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
WO 03056102 A1	10-07-2003	AT 462836 T	15-04-2010
		AU 2002346769 A1	15-07-2003
		CA 2469065 A1	10-07-2003
		CN 1617965 A	18-05-2005
		EP 1454016 A1	08-09-2004
		JP 4413010 B2	10-02-2010
		JP 2005513302 A	12-05-2005
		US 2005089641 A1	28-04-2005
		WO 03056102 A1	10-07-2003
EP 0754800 A2	22-01-1997	CA 2181332 A1	18-01-1997
		DE 69606929 D1	13-04-2000
		DE 69606929 T2	02-11-2000
		EP 0754800 A2	22-01-1997
		FI 962883 A	18-01-1997
		JP 3202921 B2	27-08-2001
		JP H09104083 A	22-04-1997
		US 5747141 A	05-05-1998
		US 5916637 A	29-06-1999
US 3413190 A	26-11-1968	NONE	
WO 2010114467 A1	07-10-2010	CN 102378725 A	14-03-2012
		EP 2414253 A1	08-02-2012
		JP 2012522907 A	27-09-2012
		SE 0900437 A1	03-10-2010
		US 2012114959 A1	10-05-2012
		WO 2010114467 A1	07-10-2010
US 2012121872 A1	17-05-2012	US 2012121872 A1	17-05-2012
		WO 2012067976 A1	24-05-2012

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 9885

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.

30-10-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3425896 A	04-02-1969	GB 1024881 A	06-04-1966
		US 3425896 A	04-02-1969
US 3145116 A	18-08-1964	GB 927448 A	29-05-1963
		US 3145116 A	18-08-1964
EP 2402168 A1	04-01-2012	CN 102310675 A	11-01-2012
		EP 2402168 A1	04-01-2012
		JP 2012030573 A	16-02-2012
		US 2011318508 A1	29-12-2011

EPO FORM P0459

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

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 3145116 A **[0008]**
- US 3425896 A **[0008]**
- US 3545568 A **[0008]**
- US 5114999 A **[0008]**
- US 6300393 B **[0008]**

Non-patent literature cited in the description

- Papermaking Science and Technology. Fapet Oy, 1999, 362 **[0010]**