

(19)



(11)

EP 2 876 207 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

27.05.2015 Bulletin 2015/22

(21) Application number: **13194313.6**

(22) Date of filing: **25.11.2013**

(51) Int Cl.:

D21H 25/06 (2006.01)	D21H 17/07 (2006.01)
D21H 17/20 (2006.01)	D21H 17/21 (2006.01)
D21H 17/33 (2006.01)	D21H 17/34 (2006.01)
D21H 17/35 (2006.01)	D21H 17/46 (2006.01)
D21H 17/52 (2006.01)	D21H 17/53 (2006.01)
D21H 17/70 (2006.01)	B27N 3/00 (2006.01)
B27N 3/04 (2006.01)	

(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: **CEPI aisbl**

1050 Brussels (BE)

(72) Inventor: **The designation of the inventor has not yet been filed**

(74) Representative: **Kinkeldey, Daniela**

**Bird & Bird LLP
Maximiliansplatz 22
80333 München (DE)**

(54) **DryPulp for cureformed paper**

(57) The present invention relates to a process comprising a non-water sheet forming technology using high concentration of cellulose fibres suspended in a high viscosity liquid.

EP 2 876 207 A1

Description

[0001] The present invention relates to a process comprising a non-water sheet forming technology using high concentration of cellulose fibres suspended in a high viscosity liquid.

BACKGROUND OF THE INVENTION

[0002] Today's paper machines require huge amounts of water for a number of reasons: the fibres need to be held at low concentration to avoid flocculation and to allow pumping as well as to enable a smooth formation as well as sufficient paper strengths. Removing the water at later stages requires a lot of energy. Tomorrow's paper machines should operate with in principle no water, which would eliminate the need for drying, the most energy intensive part of papermaking. In order to achieve this goal, a radically new technology for manufacturing has to be developed.

[0003] The dominant feature of a suspension composed of wood fibres and water is its inherent propensity to form bundles of mechanically entangled fibres, i.e. fibre flocs[1]. This is a feature closely connected to the concentration of fibres in water [2,3], which lies between 0.5-3% since higher concentration are not technically possible.

[0004] However, one possibility to avoid the flocculation of fibres that gives a poor sheet structure is to dramatically increase the viscosity of the fluid where the fibres are dispersed[2]. But, if only viscosity is increased dramatically the forces on the fibre surfaces levels will disintegrate the fibres[4]. If this detrimental effect can be avoided, it will allow forming at high concentration.

SUMMARY OF THE INVENTION

[0005] It is one object of the invention provide a new process, which overcomes the above outlined problems.

[0006] The present invention therefore provides a process for producing paper comprising

- a step (i) of treating fibres to protect them from shear,
- a step (ii) of suspending the fibres after step (i) in a viscous solvent to obtain a suspension,
- a step (iii) of forming a sheet with the suspension after step (ii),
- a step (iv) of removing solvent of the sheet after step (iii), and
- a step (v) of curing the sheet after step (iv) by curing.

[0007] By this process, paper will be made by applying an innovative non-water sheet forming technology using high concentration of cellulose fibres suspended in a high viscosity liquid. The biggest energy saving impact may result from eliminating not only the drying section, but also the needs for refining, vacuums in the process and huge flows in the white water recirculation. This would

mean 28% energy saving and 61% CO₂ saving. This process enables single or multi-layer structure, thus opening new opportunities for functionalization of paper as well as with significantly reduced capital investments.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Before the present invention is described in detail below, it is to be understood that this invention is not limited to the particular methodology, protocols and reagents described herein as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art.

[0009] Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

[0010] The term "resin" as used herein relates to any liquid, solid, semisolid or viscous substances of plant origin, such as copal, rosin, and amber, used principally in lacquers, varnishes, inks, adhesives, synthetic plastics, and pharmaceuticals and any physically similar synthetics, or chemically modified natural resins including thermoplastic materials such as polyvinyl, polystyrene, and polyethylene and thermosetting materials such as polyesters, epoxies, and silicones that may be used with fillers, stabilizers, pigments, and other components to form plastics.

[0011] As used herein, a "viscous solvent" is a solvent having a dynamic viscosity of 0.01 to 1 kg/ms (Pa. s) measured with a viscometer at 20 °C.

[0012] Some documents are cited throughout the text of this specification. Each of the documents cited herein (including all patents, patent applications, scientific publications, manufacturer's specifications, instructions, DIN norms etc.), whether supra or infra, are hereby incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0013] As mentioned, the invention provides a process for producing paper comprising

a step (i) of treating fibres to protect them from shear,
 a step (ii) of suspending the fibres after step (i) in a
 viscous solvent to obtain a suspension,
 a step (iii) of forming a sheet with the suspension
 after step (ii),
 a step (iv) of removing solvent of the sheet after step
 (iii), and
 a step (v) of curing the sheet after step (iv) by curing.

[0014] In particular, the invention provides a process
 for producing paper comprising

a first process of preparing a suspension of fibres in
 a high viscosity solvent, wherein the suspended fi-
 bres have been modified to be protect from shear,
 and
 a second process of cureforming.

[0015] In particular, in step (i) a "shear reduction layer"
 or a drag-reducing (lubricating) layer is implemented to
 protect the fibres from shear. This may be done by cre-
 ating a low viscosity layer surrounding the fibre suspend-
 ed in a high viscosity liquid that will prevent flocculation
 and allow processing at high concentration.

[0016] The application relates to the use of two main
 technologies that are combined with the generic process
 of layered material structures:

1° Preparation of a suspension, the "DryPulp", hav-
 ing a high viscosity liquid/resin where the suspended
 fibres have been modified to have protective drag-
 reducing (lubricating) layers at the fibre surface.

2° Forming via a forming/casting process, i.e. "Cure-
 Forming", using the generic concept of layering for
 functionalised papermaking.

[0017] DryPulp technology

[0018] The first technology starts with dry (preferably
 <10% water content) fibres. Accordingly, the fibres used
 in step (i) have a water content of 0 to 20 wt%, preferably
 5 to 15 wt%, and more preferably 10 to 12 wt%. Moreover,
 the fibres used in step (i) may be obtained from recycled
 or from virgin pulp.

[0019] The fibres are mixed into a high viscosity liquid,
 i.e. a resin, at high fibre concentration (up to 40% of fi-
 bres). Specifically, the suspension obtained in step (ii)
 may have a fibre concentration of 10 and 45 wt.-%, pref-
 erably 20 to 40 wt.-% and more preferably 30 to 40 wt.-%.

[0020] The liquid/resin may be constituted of a bio-
 based polymer, oligomer or monomer, which can be
 cross-linked during the curing process in order to form a
 fixed structure. The resin should be seen as a generic
 technology platform. Similarly to the possibility to choose
 fibres raw material, the resin will be available in many
 variants targeted at different needs (bulk, opacity, mold-
 ability, printing, barrier properties ...) that all fulfils the
 base requirement for being able to be used to form a
 sheet structure at very high fibre concentrations without

excessive flocculation and without detrimental effects on
 the fibres.

[0021] The fibres may be modified chemically such that
 they will give rise to the protective "shear reduction layer"
 closest to the fibre surface. The possibility of modifying
 the resin to allow processing (rheology modification) has
 been exploited for processing within other areas such as
 e.g. in paints with excessive concentration of pigments
 or in biomass extrusion[5]. The resin and the fibres thus
 form a compatible system, which is called "DryPulp".

[0022] In step (i) amino acids may be used to protect
 the fibres from shear. Specifically, one possible embod-
 iment of this application is to use bio-based substances
 such as amino acids to functionalize the surface of the
 cellulosic fibre. These will modify the docking points and
 introduce bulky side chains that push the individual fibres
 apart. This will modify the viscosity of the medium in the
 proximity of the fibres.

- CureForming technology

[0023] By using the second technology, the DryPulp
 will allow forming of a thin sheet without excessive flocc-
 ulation due to the high viscosity of the resin. Hence a
 fibre network similar to paper that is made today can be
 formed with up to 40% fibre content. There are several
 methods of sheet forming and one possible embodiment
 is to use a technology combining continuous resin casting
 with today's forming technology. The DryPulp is formed
 as a sheet, containing up to 40% fibres. After forming the
 sheet solvent is removed. Preferably, in step (iv) the sol-
 vent is removed by pressing the sheet e.g. subjected the
 sheet to a pressing stage where resin is removed similarly
 to today's pressing operation where water is removed.
 Compared to water the resin is not bound within the fibres
 and can thus easily be removed by the pressing opera-
 tion. Typically, after step (iv) the sheet has a fibre con-
 centration of 50 and 90 wt.-%, preferably 60 to 85 wt.-%
 and more preferably 70 to 80 wt.-%. Moreover, after the
 pressing operation the web may contain up to 80% fibres.

[0024] In step (v) the curing may be carried out by
 chemical additives, ultraviolet radiation, electron beam,
 heat or any combination thereof. The curing may cause
 cross-linking within the resin as well as between resin
 and the cellulose fibres. Curing can be made in several
 steps affecting different properties such as the resin only
 or the resin-protective layer interface. The resin-protect-
 ive layer-fibre system will allow reversal of the curing,
 which will allow recycling of the resin as well as of the
 fibres.

[0025] To generate a controlled amount of bulk and
 thus stiffness depending of the product requirements to
 the formed sheet, the use of air or other gases as ex-
 panding elements within the sheet may be applied. This
 could be achieved either by having micro-capsules of air
 and gas within the resin that are activated during treat-
 ment in the pressing (crushed) or through substances
 that generates gas bubbles under the influence of the

curing process or some other external forcing. One possibility is to use Sodium Bicarbonate to form gas bubbles[6]. This activation will generate carbon dioxide and the sheet will expand generating a bulky material. This is already used in speciality paper grades where an active energy beam is irradiated onto a foamable composition containing an acid generating agent and Sodium Bicarbonate. The irradiating energy generates an acid that activates the Sodium Bicarbonate that, in turn, generates the bubbles/foam.

Layered structure and functionalization

[0026] Moreover, the sheet may be formed as a layered product. Typically, the layered product is formed by first forming simultaneously, e.g. in one nozzle, or separately at least two layers and then bringing the layers together. This will allow optimization towards desired product properties as well as addition of new functionalities. As an example, if a smooth surface is required, the expansion can be limited to take place within the middle layer of a three layered sheet, i.e. coating will be achieved during the forming process. Micro-bubbles may also be used in the final sheet in order to achieve opacity, which would remove the need for fillers.

Carbon emission reduction

[0027] This process for paper and board products will contribute to decarbonisation through the energy savings gained from the elimination of the excessive need for vacuum, the friction losses in pressing and the drying of the base paper as well as drying of coating layers. As an example, the drying process in paper making alone consumes about half of the energy and today has the largest CO₂ impact.

[0028] An estimate of the energy demand for the process is as follows:

Curing of resins using heat in e.g. filter manufacturing, are made at temperatures up to 200°C.

This means that all material needs to be brought to that temperature. Given that the starting point is room temperature this means that one ton of material has to be heated about 180°C.

Assuming that the DryPulp has a specific heat capacity about the same as cellulose this gives that about 75 kWh/t is needed, given by: Since the concentration in the forming process is significantly high, the amount of mass (fibres+resin) that has to be pumped is less compared to traditional papermaking. On the other hand the viscosity goes up and the effective reduction in energy consumption for the DryPulp handling (a.k.a the stock preparation and forming) will only be 50%[1]. The total energy demand for the complete "paper machine", including drives, winding etc. will be 200 kWh/t. In addition, the energy demand for recycling will be re-

duced by 50%, coating will not be necessary since the product is coated in the forming process, and the absence of water removes energy costs for effluent treatment. Based on this, the technology will have an estimated total energy demand of 330 kWh/t. Looking at manufacturing of all paper and packaging grades (excluding sanitary and household), the energy demand of the papermaking process (excluding pulp production), is about 1550 kWh/t on average. Since the new process only requires 330 kWh/t, as indicated above, this results in a reduction in energy demand by 79%. If the whole sector is considered, including pulp production as well as sanitary and household grades, this translates to a reduction in energy demand of 28%. Similarly, the process will cause 66 kg CO₂/t emissions compared to today's 370 kg/t for the manufacturing of paper and packaging grades (excluding pulp production and the sanitary and household grades), giving a reduction of 82%. For the whole sector this means a reduction by 61%.

[0029] Various modifications and variations of the invention will be apparent to those skilled in the art without departing from the scope of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in the relevant fields are intended to be covered by the present invention.

REFERENCES

[0030]

- 1 Mason, S.G. (1948) "The Flocculation of Cellulose Fibre Suspensions", Pulp Paper Mag. Can. 99-104.
- 2 Kerekes (2009) "Rheology of fibre suspensions in papermaking: An overview of recent research", Nordic Pulp and Paper Research Journal, vol 21, issue 5, 2006, 598-612.
- 3 Schmid, C.F., Klingenberg, D.J. (2000) "Mechanical Flocculation in Flowing Fiber Suspensions", Physical Review Letters, 84 (2), pp. 290-293.
- 4 Suzuki, K., Okumura, H., Kitagawa, K., Sato, S., Nakagaito, A.N. & Yano, H. (2013) "Development of continuous process enabling nanofibrillation of pulp and melt compounding", Cellulose, vol. 20, no. 1, pp. 201-210.
- 5 Scott, C.T., Samaniuk, J.R., Klingenberg, D.J. (2011) "Rheology and extrusion of high-solids biomass", Tappi Journal, 10 (5), pp. 47-53.
- 6 Patent WO2011001791 A1, "Wood Powder-Containing Resin Molded Product and Method for Producing the Same".

Claims

1. A process for producing paper comprising
 - a step (i) of treating fibres to protect them from shear, 5
 - a step (ii) of suspending the fibres after step (i) in a viscous solvent to obtain a suspension,
 - a step (iii) of forming a sheet with the suspension after step (ii), 10
 - a step (iv) of removing solvent of the sheet after step (iii), and
 - a step (v) of curing the sheet after step (iv).
2. The process according to claim 1, wherein the fibres used in step (i) have a water content of 0 to 20 wt%, preferably 5 to 15 wt%, and more preferably 10 to 12 wt%. 15
3. The process according to claim 1 or 2, wherein the fibres used in step (i) are obtained from recycled or from virgin pulp. 20
4. The process according to any of the preceding claims, wherein the viscous solvent is selected from uncured resins, and is preferably selected from polymers, oligomers or monomers. 25
5. The process according to any of the preceding claims, wherein in step (i) amino acids are used to protect the fibres from shear. 30
6. The process according to any of the preceding claims, wherein the suspension obtained in step (ii) has a fibre concentration of 10 and 45 wt.-%, preferably 20 to 40 wt.-% and more preferably 30 to 40 wt.-%. 35
7. The process according to any of the preceding claims, wherein the sheet is formed as a layered product in step (iii). 40
8. The process according to claim 7, wherein the layered product is formed by first forming simultaneously or separately at least two layers and then bringing the layers together. 45
9. The process according to any of the preceding claims, wherein in step (iv) the solvent is removed by pressing the sheet. 50
10. The process according to any of the preceding claims, wherein after step (iv) the sheet has a fibre concentration of 50 and 90 wt.-%, preferably 60 to 85 wt.-% and more preferably 70 to 80 wt.-%. 55
11. The process according to any of the preceding claims, wherein in step (v) the curing is carried out

by chemical additives, ultraviolet radiation, electron beam, heat, or any combination thereof.

12. The process according to any of the preceding claims comprising a further step of using air or other gases as expanding elements within the sheet.
13. The process according to claim 13, wherein the further step comprises introducing micro-capsules of air or the other gases within the viscous solvent.
14. The process according to claim 13, wherein the further step comprises introducing substances that generate gas bubbles under the influence of step (v) or other external forcing.



EUROPEAN SEARCH REPORT

 Application Number
 EP 13 19 4313

5

10

15

20

25

30

35

40

45

50

55

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	US 6 582 648 B1 (REIF GEORG [AT]) 24 June 2003 (2003-06-24)	1,4,11	INV. D21H25/06
Y	* column 5, line 64 - column 6, line 5 * * claims 1-26 *	1-14	D21H17/07 D21H17/20 D21H17/21

X	WO 2012/084846 A2 (BAYER MATERIALSCIENCE AG [DE]; BAYER MATERIALSCIENCE LLC [US]; SOMMER) 28 June 2012 (2012-06-28)	1,3,4,11	D21H17/33 D21H17/34 D21H17/35
Y	* claims 1-12 *	1-14	D21H17/46 D21H17/52 D21H17/53

X	US 2013/078437 A1 (SYMKESEN STEFAN HENRI DOMINIQUE MARIA [BE] ET AL) 28 March 2013 (2013-03-28)	1	D21H17/70 B27N3/00 B27N3/04
Y	* claims 1,8 *	1-14	

X	DE 44 13 619 A1 (WKP WUERTEMBERGISCHE KUNSTSTO [DE]) 8 June 1995 (1995-06-08)	1	
Y	* claims 1-7 *	1-14	

			TECHNICAL FIELDS SEARCHED (IPC)
			D21H
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 27 March 2014	Examiner Ponsaud, Philippe
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	

EPO FORM 1503 03.82 (P04C01)

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

EP 13 19 4313

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.

27-03-2014

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6582648 B1	24-06-2003	AT 208252 T AU 9265898 A CA 2303300 A1 DE 19738953 C1 DE 19881279 D2 EP 1011940 A1 ES 2167937 T3 JP 2001515802 A US 6582648 B1 WO 9912711 A1	15-11-2001 29-03-1999 18-03-1999 04-03-1999 18-01-2001 28-06-2000 16-05-2002 25-09-2001 24-06-2003 18-03-1999
WO 2012084846 A2	28-06-2012	CA 2822324 A1 CN 103270216 A EP 2655739 A2 KR 20140008327 A TW 201303113 A US 2012160437 A1 WO 2012084846 A2	28-06-2012 28-08-2013 30-10-2013 21-01-2014 16-01-2013 28-06-2012 28-06-2012
US 2013078437 A1	28-03-2013	EP 2574476 A1 NL 2007494 C US 2013078437 A1	03-04-2013 02-04-2013 28-03-2013
DE 4413619 A1	08-06-1995	NONE	

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

- WO 2011001791 A1 [0030]

Non-patent literature cited in the description

- **MASON, S.G.** The Flocculation of Cellulose Fibre Suspensions. *Pulp Paper Mag. Can.*, 1948, 99-104 [0030]
- **KEREKES.** Rheology of fibre suspensions in paper-making: An overview of recent research. *Nordic Pulp and Paper Research Journal*, 2006, vol. 21 (5), 598-612 [0030]
- **SCHMID, C.F. ; KLINGENBERG, D.J.** Mechanical Flocculation in Flowing Fiber Suspensions. *Physical Review Letters*, 2000, vol. 84 (2), 290-293 [0030]
- **SUZUKI, K. ; OKUMURA, H. ; KITAGAWA, K. ; SATO, S. ; NAKAGAITO, A.N. ; YANO, H.** Development of continuous process enabling nanofibrillation of pulp and melt compounding. *Cellulose*, 2013, vol. 20 (1), 201-210 [0030]
- **SCOTT, C.T. ; SAMANIUK, J.R. ; KLINGENBERG, D.J.** Rheology and extrusion of high-solids biomass. *Tappi Journal*, 2011, vol. 10 (5), 47-53 [0030]