(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 July 2017 (27.07.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/127004 A1

(51) International Patent Classification:
*D21C 9/14* (2006.01) *D21C 3/02* (2006.01)
*D21C 1/04* (2006.01)

(21) International Application Number:
PCT/SE2016/051253

(22) International Filing Date:
13 December 2016 (13.12.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1650050-6 18 January 2016 (18.01.2016) SE

(71) Applicant: **VALMET AB** [SE/SE]; Valmet AB, 851 94 Sundsvall (SE).

(72) Inventors: **WENNERSTRÖM, Maria**; Västra radiogatan 10A, 854 61 Sundsvall (SE). **NORDÉN, Solveig**; Södra järnvägsgatan 3, 852 37 Sundsvall (SE).

(74) Agent: **SAITTON, Hanna**; Valmet AB, 851 94 Sundsvall (SE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published**:

— *with international search report (Art. 21(3))*

WO 2017/127004 A1

(54) Title: CHLORINE DIOXIDE STAGE FOR CONTROLLING VISCOSITY IN DISSOLVING PULPS

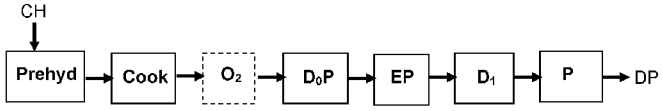


Fig. 1

(57) Abstract: The present invention relates to an improved process for producing dissolving pulp from a hydrolysis-kraft cooking process. The new process make it possible to control pulp viscosity in an efficient way by adding hydrogen peroxide to a first chlorine dioxide stage and by adjusting the charge of hydrogen peroxide could the total viscosity reduction be adjusted in a broad viscosity range enabling increased production in commercial dissolving processes using short D-(w)-E-(w)-P-(w) bleaching sequences converted to a DP-(w)-E-(w)-P-(w) bleaching sequence.

# Chlorine dioxide stage for controlling viscosity in dissolving pulps

The present disclosure relates in general to a method for producing dissolving pulp of low viscosity from lignocellulosic material. The dissolving process for producing low viscosity pulp conventionally contains a first hydrolysis stage followed by a kraft cooking stage, an optional oxygen delignification stage further reducing the lignin content and viscosity and thereafter bleaching for viscosity reduction and brightness increase.

## BACKGROUND

In the wood based pulping industry significant efforts have been made designing different processes for different grades of pulp.

In conventional kraft pulping the objectives have been to produce a pulp grade with high yield and high pulp strength having acceptable brightness level and stability. For fully bleached pulp grades ISO brightness above 88% is most often preferred, and if minimal brightness reversion is requested the residual content of lignin and hexenuronic acid must be kept low.

In recent years the pulping industry has strived to find alternative products for the wood material as the printing paper market declines in volume, and that new products may be found with better profit margins.

Dissolving pulp has emerged as a reborn alternative growing market for pulp mills and much attention has been given to modify the pulping processes to be able to produce different grades of dissolving pulp which is used to produce a multitude of products like Rayon-grade pulp or specialty pulps. The interest to find alternative textile materials to cotton has increased due to short term shortage and increase in costs for cotton and an increased competition in long term for land to grow an increasing demand of cotton on. Dissolving pulp can consist of cotton linters, pulp originating from wood or annual plants made by the sulfite process or the prehydrolysis kraft process. However, in pulp industry dissolving pulp is generally referred to as a bleached pulp produced from wood that has a high alpha cellulose content, typically over 92%, and only small content of hemicelluloses, typically below 10%. Hence, the wood yield of dissolving pulp from the process is typically low at about 35-40%. Dissolving pulp is used to manufacture various

cellulose-derived products such as rayon yarn for use in e.g. textile industry and specialty chemicals and materials such as cellulose acetate and carboxy methyl cellulose. When making rayon yarns the dissolving pulp is converted to cellulose xanthate which dissolves in caustic soda and the resulting viscous liquid is extruded in acidic baths to yield fibers. As an alternative process the dissolving pulp can be dissolved in ionic solvents to make extruding to fibers possible. For both these processes and the specific final product it is essential that the viscosity of the dissolving pulp is both low and within a specific range suitable for the process, in order to run derivatisation/dissolution process smoothly.

For some dissolving pulp grades the required intrinsic viscosity in the finally bleached dissolving pulp must be as low as 350 ml/g and within a narrow acceptance range of only ±20 ml/g. This requires a low viscosity already after cooking or possibilities to lower the viscosity in a controlled manner and to a greater extent in subsequent delignification and/or bleaching stages. Examples of specification of higher grade dissolving pulps are Ethers (viscosity 470-600 ml/g), Nitrates (viscosity 550-650 ml/g), Acetates (viscosity 600-700 ml/g) and Viscose (viscosity 300-500 ml/g).

Historically and also in some existing dissolving pulp mills the bleaching chemicals chlorine and hypochlorite are used, for example in sequences as CEH and CEHD. Typically only one hypochlorite stage is required for viscosity control and the most important control parameters are hypochlorite charge and pH. However, today neither elemental chlorine nor hypochlorite are acceptable bleaching chemicals in a modern (ECF) bleach plant due to too high formation of chlorinated organics and chloroform.

Throughout this description, viscosity is used as the dominant pulp property for dissolving pulp. The viscosity number is expressed as intrinsic viscosity and measured in ml/g. A standard test method for intrinsic viscosity of cellulose could be found in ISO-standard ISO 5351.

Now, viscosity measurements is indicative for the average molecular weight of the cellulose polymers, i.e. the length of the cellulose chains. The length of the cellulose

chains impact the derivatisation and solubilisation process as well as the characteristics of the final product.

However, for dissolving pulp the viscosity is often about or below 900 ml/g after cook or at least below 800 ml/g after prebleaching, i.e. oxygen delignification or other pre bleaching stages (where kappa and viscosity reduction is an objective over increase in brightness) and below 600 ml/g after final bleaching. Most often the viscosity target for the final dissolving pulp is kept within a relatively narrow range, for example within 450-500 ml/g.

The problem with production of dissolving pulp is to reach the low viscosity of the final pulp requested and most often is extended and intensified cooking, i.e. both longer cooking time and tougher cooking conditions as of alkali charge and temperature, needed in order to obtain a low enough viscosity after the cook. A problem with extended cooking occurs if it is desired to increase the production in existing pulp mills as increased production results in decreased cooking time if the equipment is the same. This results in higher viscosity when the throughput of the lignocellulosic material increases. After cooking the pulp is normally oxygen delignified in order to further reduce lignin content and viscosity.

If the viscosity reduction does not reach a sufficient low level after cooking and oxygen delignification, it has with some standard bleaching sequences been found to be almost impossible to reach the final viscosity level by implementing tougher process conditions in final bleaching. Normally the viscosity reduction may be increased marginally in the order of 50 ml/g in final bleaching, by implementing tougher bleaching conditions in the final bleaching stages as of temperature and additional bleaching agents or increased charge of the standard bleaching agents used. Ozone stages are also capable of reducing viscosity to a larger extent, but this at expense of increased costs, especially in an existing bleaching plant.

When using a standard bleaching sequence as for example D0-EP-D1-P it has shown to be practically impossible to reach the viscosity target by intensifying the conditions in order to compensate the loss in viscosity reduction in the cook at increased production rate. Especially the D-stages do not respond with greater

viscosity reduction at tougher conditions. This is especially significant in bleaching lines where the bleaching stages are designed for lower temperatures below 100°C and thus may not designed as pressure vessels, which totally prevents an operator to increase temperature about 90°C.

## SUMMARY

The main objective problem with the present invention is to enable increased production of dissolving pulp in existing pulp mills while still being able to reach the lower viscosity requested in bleached dissolving pulp, and being able to control this low viscosity within a narrow range suitable for the final dissolving pulp grade. The invention is applied in ECF bleaching sequences not using any elemental chlorine nor hypochlorite as bleaching chemicals, i.e. so called C or H bleaching stages.

The invention is based upon the assumption that larger viscosity reductions may be implemented in the $D_0$-stage if agents with strong chain cleavage abilities located close to or neighboring to cellulose are increased. This can be achieved by e.g. an increase in hydroxyl radical formation. It is well known in the pulping industry that the formation of hydroxyl radicals during oxidation are reducing pulp viscosity but no prior art has tried to increase this effect in order to control the viscosity of pulp in general, and especially not in dissolving pulp production.

In the most general approach the invention relates to a method for producing low viscosity dissolving pulp from lignocellulosic material, said dissolving process comprising a first acidic hydrolysis process followed by a kraft cooking process reaching a kappa number in the washed cooked pulp below 30, said cooked and washed pulp subsequently further delignified in an optional oxygen delignification stage and finally bleached in 2-5 bleaching stages, and wherein the final target viscosity of the bleached dissolving pulp is primarily controlled by combining chlorine dioxide and hydrogen peroxide bleaching in a first chlorine dioxide stage, often referred to as a $D_0$-stage.

The first chlorine dioxide stage is conventionally in a position where the lignin content is still measured, and typically lies above a kappa number of 4-8, typically 10-20, and often referred to a pre-bleaching stage. After the $D_0$ position the

kappa number is so low that instead ISO brightness is measured. Characteristic reaction kinetics in a $D_0$ stage is that the charge of chlorine dioxide could most often not be controlled by measuring residual levels of chlorine dioxide as all charge is consumed due to surplus of organic material consuming chlorine dioxide.

The combination of chlorine dioxide and hydrogen peroxide in a first chlorine dioxide stage may obtain a reduction of viscosity in the range of 200-350 ml/g, where at least 90-170 ml/g is contributed to the chlorine dioxide charge per se and at least 60-130 ml/g is contributed to the hydrogen peroxide charge per se.

It has surprisingly been found that the first chlorine dioxide stage is possible to adjust whereby a large range of viscosity reduction could be obtained. Hence, the total production may be increased in any existing mills, which increased production is compensated by increased viscosity reduction in the bleach plant. A commercial dissolving line with Cook-O-D-E-P may then be easily be converted to a Cook-O-DP-E-P, and meet the increasing viscosity that may result from production increases, and where the first chlorine dioxide stage, $D_0$, is gradually changed to a DP stage with increasing additional charge of hydrogen peroxide.

More specifically the inventive method is applied for producing low viscosity dissolving pulp from lignocellulosic material, said dissolving process comprising a first acidic hydrolysis process followed by a kraft cooking process reaching a kappa number in the washed cooked pulp below 30, said cooked and washed pulp subsequently further delignified in an optional oxygen delignification stage and finally bleached in 2-5 stages containing at least a first chlorine dioxide stage ($D_0$), and wherein the final target viscosity of the bleached dissolving pulp is primarily controlled by adjusting the conditions in the first chlorine dioxide stage using $H_2O_2$-charge and additionally pH and temperature, obtaining a basic viscosity reduction in the first chlorine dioxide stage by the chlorine dioxide charge in the range of 90-170 ml/g by said adjustment of time and temperature in the first chlorine dioxide stage , said first chlorine dioxide stage being further reinforced by hydrogen peroxide addition in order to obtain an additional viscosity reduction in said first chlorine dioxide stage in the range 60-130 ml/g at least.

Further, the inventive method comprises following steps in sequence;

a) subjecting comminuted cellulosic material for an acidic hydrolysis process wherein at least 20% of the original hemicellulose content of the lignocellulosic material is degraded in the hydrolysis process,

b) subjecting the hydrolysed lignocellulosic material to a kraft cook and extracting and washing out dissolved organic material obtaining a washed and cooked pulp,

c) subjecting the oxygen delignified washed pulp for bleaching in a first chlorine dioxide stage ($D_0$), wherein the charge of bleaching chemicals in the chlorine dioxide stage-stage is

c1) a chlorine dioxide charge equal to or above kappa factor 1, that is 1 x kappa number kg active Cl/adt, and

c2) an $H_2O_2$-charge equal in the range 1-8 kg/odt.

In a preferred embodiment the conditions of the first chlorine dioxide stage is as follows

c3) a retention time of at least 60 min, preferably 90 min and at the most 120 min in said first chlorine dioxide stage;

c4) an initial temperature established equal to or above 85°C and 95°C at the most.

Additionally the washed and cooked pulp may also be subjected to an oxygen delignification stage with a subsequent washing obtaining an oxygen delignified and washed pulp before being subjected to the first chlorine dioxide stage. However, in some dissolving line the kappa number from the cook may be sufficiently low, whereby this oxygen delignification stage may be omitted, but strongly preferred if the mill is subject to major production increases.

More specifically, the bleaching sequence is preferably a D-(w)- E-(w)-P-(w) sequence, where the viscosity control is made in the first chlorine dioxide stage (D) using different charge of peroxide addition converting the bleaching sequence to a (DP)-(w)- E-(w)-P-(w) sequence .

In summary the inventive method use the conditions in the first chlorine dioxide (D)-stage are used as a primary control for the final viscosity of dissolving pulp, enabling total viscosity modifications in the first chlorine dioxide stage in the range 200-350 ml/g by altering charge of hydrogen peroxide, chlorine dioxide, temperature and pH.

The cooking process according to the inventive method could equally well take place in a batch digester or a continuous digester. If the production is increased in an existing batch digester the cooking time needs to be reduced so that each batch digester may be emptied more frequently. If the production is increased in an existing continuous digester is normally the retention time in the digester reduced and thereby is the viscosity reduction decreased. The reduced retention time in batch or continuous digesters may in part be compensated by increasing the temperature, but this at high costs as this requires addition of steam capable of increasing the temperature at the normal cooking temperature at about 140-170°C.

The oxygen delignification can take place in one or two successive treatment vessels. The (DP)-stage can take place in one treatment vessel.

## BREIF DESCRIPTION OF THE DRAWINGS

Figure 1 Show an example of a complete fiberline for manufacturing dissolving pulp;

Figure 2 Show an oxygen delignification stage followed by (DP)-stage;

Figure 3 Show impact of $H_2O_2$ charge in (DP) on pulp viscosity;

Figure 4 Show impact of $H_2O_2$ charge in (DP) on ISO brightness;

Figure 5 Show the development of viscosity and brightness in a O(DhtP)(EP)(DP) sequence using the invention; and

Figure 6 Show the correlation between charge of chlorine dioxide and brigthness in a O(DhtP)(EP)(DP) sequence using the invention..

## DETAILED DESCRIPTION

The process will be further described with reference to the accompanying Figures and Tables. It should however be noted that the invention is not limited to

the embodiments described below and shown in the drawings, but may be modified within the scope of the appended claims.

The invention is related to a method for producing low viscosity dissolving pulp from lignocellulosic material, said dissolving process comprising a first acidic hydrolysis process followed by a kraft cooking process reaching a kappa number in the washed cooked pulp below 30, said cooked and washed pulp subsequently further delignified in an oxygen delignification stage and finally bleached in 2-5 bleaching stages. The principle layout of such a dissolving process is shown in Figure 1. Lignocellulosic material, preferably wood chips (CH), are fed to a first hydrolysis stage (Prehyd), followed by a kraft cooking stage (Cook), and thereafter oxygen delignification ($O_2$), before final bleaching in a first chlorine dioxide/peroxide bleaching stage, (DP) an extraction stage, (EP), a second chlorine dioxide bleaching stage, (D1), and finally a peroxide stage, (P) or chlorine dioxide stage, D2 from which the dissolving pulp is fed out. The first stage Prehyd+Cook+$O_2$ are more or less standard stages but the final bleaching stages could have other configurations than the (DP)-EP-D1-P sequence.

Typically the first stage following oxygen delignification is an acidic stage (A, D or Z) followed by alkaline extraction (E, (EP), (EOP)) and an acidic bleaching stage (D) before an optional alkaline bleaching stage (such as P stage). Such alternative configurations could be; Z-D-EP-D or Z-D-P or D0-EP-D1-D2 or D0-(EP)-D-P or A-D-(EP)-D or (DP)-(EP)-(DP)-D.

In **Figure 2** is the first (DP)-stage shown in more detail before the final bleaching FB, with washing stages shown between O and (DP). Mixing positions are indicated for charge of acid ($H_2SO_4$), Steam (ST), chlorine dioxide ($ClO_2$) and hydrogen peroxide ($H_2O_2$). The charges are not necessarily made with individual mixers for each charge, and additional points of different media can be done in another order.

**EXPRIMENTAL DATA FROM ALTERING CONDITIONS IN THE $D_0$-STAGE**

The pulp studied was a hardwood (Russian Birch) pulp which after hydrolysis and cook had a kappa number of 12.8, an intrinsic viscosity of 1205 ml/g and an ISO

brightness of 41.7 %. After oxygen delignification the kappa number was 4.3, intrinsic viscosity 874 ml/g and ISO brightness 59.1%.

The oxygen delignified pulp was bleached with the sequences $D_0$-(EP)-$D_1$-P and (DP)-(EP)-$D_1$-P with conditions shown in the table below.

*Table 1 Bleaching conditions*

| | | $D_0$ | (DP) | (EP) | $D_1$ | P |
|---|---|---|---|---|---|---|
| **Pulp consistency** | % | 12 | 12 | 12 | 12 | 12 |
| **Temperature** | °C | 70/90 | 90 | 90 | 75 | 90 |
| **Kappa factor** | | 2 | 2 | - | - | - |
| **$H_2SO_4$** | kg/odt | 0, 3 | 0, 3 | - | 0-2.5 | - |
| **NaOH** | kg/odt | - | - | 5 | - | 4 |
| **$H_2O_2$** | kg/odt | 0 | 1-4 | 3 | - | 3 |
| **Time** | min | 60/120 | 120 | 60 | 60 | 90 |

The oxygen-delignified pulp with kappa number 4.3 and viscosity 874 ml/g was bleached $D_0$-(EP) with varied time and temperature in $D_0$ with end pH 2.1, **Table 2**.

After 60 minutes at 90 °C the viscosity loss was 110 ml/g after $D_0$-(EP). The maximum viscosity loss, 171 ml/g, was reached after 120 minutes at 90 °C in $D_0$.

*Table 2 Bleaching $D_0$-(EP) with varied time and temperature in $D_0$*

| | | After O | $D_0$-(EP) | $D_0$-(EP) | $D_0$-(EP) |
|---|---|---|---|---|---|
| **Time in $D_0$** | min | | 60 | 60 | 120 |
| **Temp. in $D_0$** | °C | | 70 | 90 | 90 |
| **$H_2SO_4$** | kg/odt | | 3 | 3 | 3 |
| **pH in $D_0$** | | | 2.1 | 2.1 | 2.1 |
| **Kappa number** | | 4.3 | 1.5 | 1.5 | 1.5 |
| **Viscosity** | ml/g | 874 | 784 | 764 | 703 |
| **Δ viscosity** | ml/g | | **90** | **110** | **171** |
| **ISO brightness** | % | 59.1 | 81.5 | 81.4 | 80.2 |

Bleaching with hydrogen peroxide addition in the $D_0$-stage, that is a (DP)-stage, made it possible to reduce the viscosity further. The maximum viscosity loss after (DP)-(EP), 302 ml/g, was reached after 120 minutes at 90 °C in (DP) with 3 kg/odt $H_2O_2$ and end pH 2.1, **Table 3**.

When the (DP)-stage was performed at higher end pH, 3.2, the viscosity loss was lower, 232 ml/g.

Pulp brightness after (DP)-(EP) was slightly higher than after D-(EP). The bleaching efficiency was thus the same or slightly better for pulps bleached (DP)-(EP) as for pulp bleached D-(EP).

*Table 3 Bleaching with the sequences $D_0$-(EP) and (DP)-(EP)*

| | | After O | $D_0$-(EP) | (DP)-(EP) | (DP)-(EP) |
|---|---|---|---|---|---|
| **Time in D/(DP)** | min | | 120 | 120 | 120 |
| **Temp. in D/(DP)** | °C | | 90 | 90 | 90 |
| **$H_2SO_4$** | kg/odt | | 3 | 0 | 3 |
| **pH in D/(DP)** | | | **2.1** | **3.2** | **2.1** |
| **$H_2O_2$ in D/(DP)** | kg/odt | | 0 | 3 | 3 |
| **Kappa number** | | 4.3 | 1.5 | 1.6 | 1.6 |
| **Viscosity** | ml/g | 874 | 703 | 642 | 572 |
| **Δ viscosity** | ml/g | | **171** | **232** | **302** |
| **ISO brightness** | % | 59.1 | 80.2 | 81.5 | 81.2 |

The $H_2O_2$ charge was varied from 0-4 kg/odt when bleaching for 90 and 120 minutes at 90°C in (DP). In **Figure 3** viscosity is shown versus $H_2O_2$ charge. The results show that the viscosity is reduced with increased $H_2O_2$ charge, from 700 ml/g when bleaching without $H_2O_2$ to 560 ml/g when bleaching with 4 kg $H_2O_2$/odt. Bleaching for 90 and 120 minutes in (DP) showed similar results.

ISO brightness increased slightly with increased $H_2O_2$-charge, **Figure 4**.

In Figure 5 is shown the development of viscosity and brightness in an O(DhtP)(EP)(DP) sequence using the invention; and in Figure 6 is shown the correlation between charge of chlorine dioxide and brightness in an O(DhtP)(EP)(DP) sequence using the invention.

## CLAIMS

1. A method for producing low viscosity dissolving pulp from lignocellulosic material, said dissolving process comprising a first acidic hydrolysis process followed by a kraft cooking process reaching a kappa number in the washed cooked pulp below 30, said cooked and washed pulp subsequently further delignified in an optional oxygen delignification stage and finally bleached in 2-5 stages containing at least a first chlorine dioxide stage ($D_0$), and wherein the final target viscosity of the bleached dissolving pulp is primarily controlled by adjusting the conditions in the first chlorine dioxide stage using $H_2O_2$-charge and additionally pH and temperature, obtaining a basic viscosity reduction in the first chlorine dioxide stage by the chlorine dioxide charge in the range of 90-170 ml/g by adjustment of time and temperature in the first chlorine dioxide stage , said first chlorine dioxide stage being further reinforced by hydrogen peroxide addition in order to obtain an additional viscosity reduction in said first chlorine dioxide stage at least in the range 60-130 ml/g.

2. Method according to claim 1, said dissolving process comprising following steps in sequence;

a) subjecting comminuted cellulosic material for an acidic hydrolysis process wherein at least 20% of the original hemicellulose content of the lignocellulosic material is degraded in the hydrolysis process,

b) subjecting the hydrolysed lignocellulosic material to a kraft cook and extracting and washing out dissolved organic material obtaining a washed and cooked pulp,

c) subjecting the washed and cooked pulp for bleaching in a first chlorine dioxide stage ($D_0$), wherein the charge of bleaching chemicals in the chlorine dioxide stage-stage is

c1) a chlorine dioxide charge equal to or above kappa factor 1, that is 1 x kappa number kg active Cl/adt, and

c2) an $H_2O_2$-charge equal in the range 1-8 kg/odt:

3. Method according to claim 2 wherein the conditions of the first chlorine dioxide stage is as follows

c3) a retention time of at least 60 min, preferably 90 min and at the most 120 min in said first chlorine dioxide stage;

c4) an initial temperature established equal to or above 85°C and 95°C at the most.

4. Method according to claim 2, wherein the washed and cooked pulp is subjected to an oxygen delignification stage with a subsequent washing obtaining an oxygen delignified and washed pulp before being subjected to the first chlorine dioxide stage.

5. Method according to claim 2 wherein the bleaching sequence is a D-(w)- E-(w)-P-(w) sequence, where the viscosity control is made in the first chlorine dioxide stage (D) using different charge of peroxide addition converting the bleaching sequence to a (DP)-(w)- E-(w)-P-(w) sequence .

6. Method according to claim 1 wherein the conditions in the first chlorine dioxide (D)-stage are used as a primary control for the final viscosity of dissolving pulp, enabling total viscosity modifications in the first chlorine dioxide stage in the range 200-350 ml/g by altering charge of hydrogen peroxide, chlorine dioxide, temperature and pH.

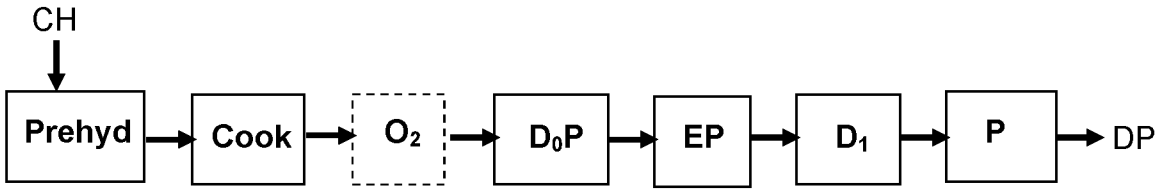


Fig. 1

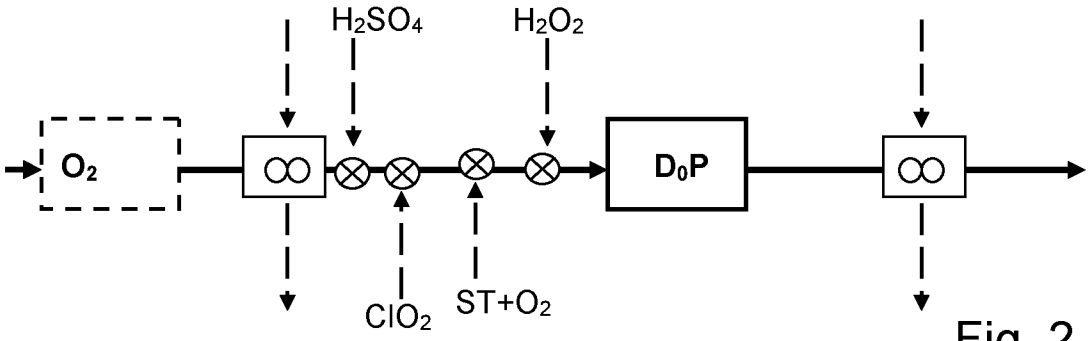


Fig. 2

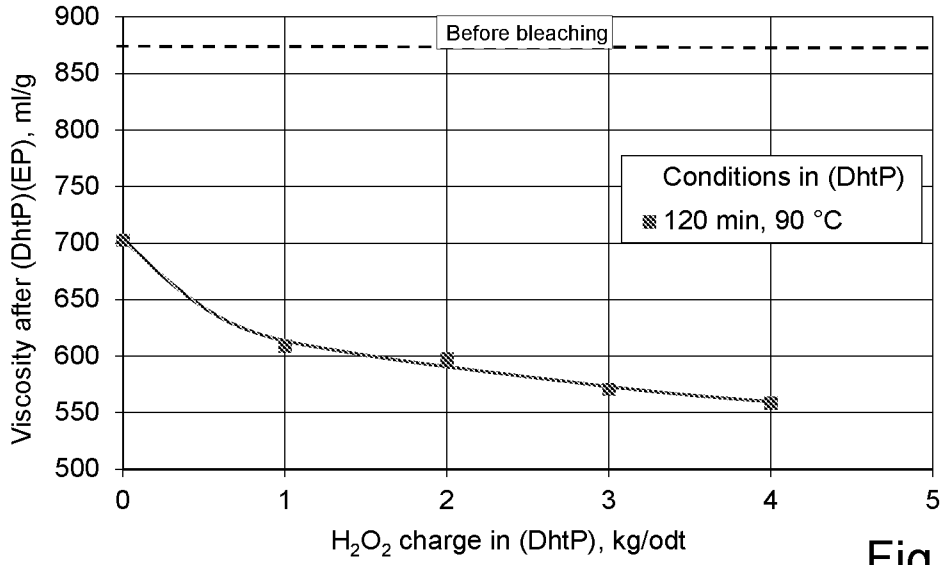
Before bleaching
Conditions in (DhtP)
120 min, 90 °C
Viscosity after (DhtP)(EP), ml/g
900
850
800
750
700
650
600
550
500
0
1
2
3
4
5
H2O2 charge in (DhtP), kg/odt

Fig. 3

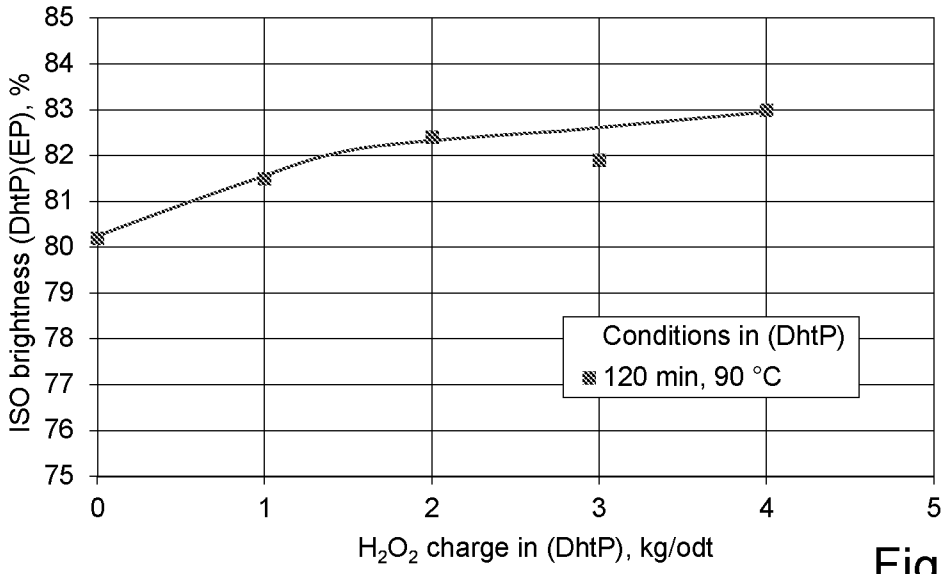
Conditions in (DhtP)
120 min, 90 °C
ISO brightness (DhtP)(EP), %
85
84
83
82
81
80
79
78
77
76
75
0
1
2
3
4
5
H2O2 charge in (DhtP), kg/odt

Fig. 4

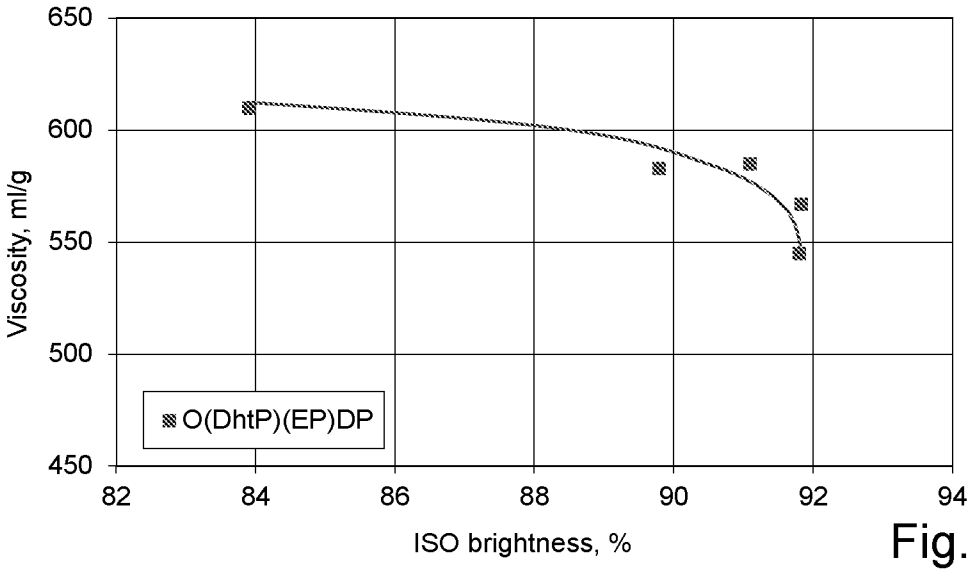
650
600
550
500
450
Viscosity, ml/g
82
84
86
88
90
92
94
ISO brightness, %
O(DhtP)(EP)DP

Fig. 5

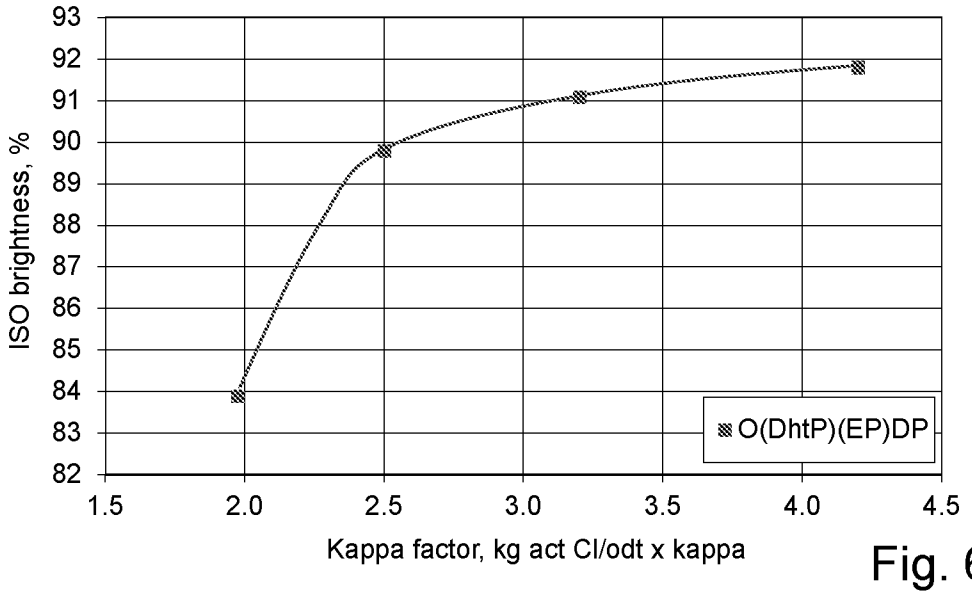
93
92
91
90
89
88
87
86
85
84
83
82
ISO brightness, %
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Kappa factor, kg act Cl/odt x kappa
O(DhtP)(EP)DP

Fig. 6

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/SE2016/051253

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08B, D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, COMPENDEX, alla NPL i Xfull

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 2015195030 A1 (VALMET OY), 23 December 2015 (2015-12-23); page 4, line 28 - line 32; claim 1 -- | 1-6 |
| A | JP 2013227705 A (OJI HOLDINGS CORP), 7 November 2013 (2013-11-07); (abstract) Retrieved from: EPODOC database; -- | 1-6 |
| A | US 6048437 A (FUKUSHIMA TAKAMASA ET AL), 11 April 2000 (2000-04-11); column 3, line 11 - line 17; column 4, line 28 - line 47; column 8, line 19 - line 33 -- | 1-6 |
| A | WO 2009139693 A1 (METSO PAPER INC ET AL), 19 November 2009 (2009-11-19); page 1, line 33 - page 2, line 19; page 3, line 15 - line 20; page 6, line 11 - line 13 -- | 1-6 |

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 20-02-2017 | 21-02-2017 |
| Name and mailing address of the ISA/SE<br>Patent- och registreringsverket<br>Box 5055<br>S-102 42 STOCKHOLM<br>Facsimile No. + 46 8 666 02 86 | Authorized officer<br>Jens Waltin<br>Telephone No. + 46 8 782 28 00 |

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/SE2016/051253

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| | --- | |

International application No.
PCT/SE2016/051253

**Continuation of:** second sheet

**International Patent Classification (IPC)**

***D21C 9/14*** (2006.01)
*D21C 1/04* (2006.01)
*D21C 3/02* (2006.01)

| | | | | | | |
|---|---|---|---|---|---|---|
| WO | 2015195030 | A1 | 23/12/2015 | SE | 538064 | C2 | 23/02/2016 |
| | | | | SE | 1450753 | A1 | 18/12/2015 |
| JP | 2013227705 | A | 07/11/2013 | JP | 5953909 | B2 | 20/07/2016 |
| US | 6048437 | A | 11/04/2000 | CA | 2186066 | C | 26/04/2005 |
| | | | | JP | 09143891 | A | 03/06/1997 |
| | | | | JP | 3698178 | B2 | 21/09/2005 |
| | | | | US | 6432266 | B1 | 13/08/2002 |
| WO | 2009139693 | A1 | 19/11/2009 | CN | 102027167 | A | 20/04/2011 |
| | | | | EP | 2276883 | A1 | 26/01/2011 |
| | | | | JP | 5478610 | B2 | 23/04/2014 |
| | | | | JP | 2011521116 | A | 21/07/2011 |
| | | | | SE | 532470 | C2 | 02/02/2010 |
| | | | | SE | 0801074 | L | 14/11/2009 |