



(11) **EP 1 945 852 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
31.03.2010 Bulletin 2010/13

(51) Int Cl.:
D21C 9/08 (2006.01) D21H 21/02 (2006.01)

(21) Application number: **07803338.8**

(86) International application number:
PCT/EP2007/059398

(22) Date of filing: **07.09.2007**

(87) International publication number:
WO 2008/028960 (13.03.2008 Gazette 2008/11)

(54) **USE OF CARBONATE IONS FOR THE SOLUBILIZATION OF WOOD EXTRACTIVES IN A
PROCESS FOR DERESINATION OF PULP**

VERWENDUNG VON KARBONATIONEN FÜR DIE SOLUBILISIERUNG VON HARZ IN EINEM
VERFAHREN ZUR ENTHARZUNG EINES ZELLSTOFFS

UTILISATION D'IONS CARBONATE POUR SOLUBILISER LES MATIÈRE EXTRACTIBLES DANS
UN PROCEDE D'EXTRACTION DE LA RÉSINE DE UNE PATE À PAPIER

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**

(30) Priority: **08.09.2006 FI 20060805**
13.02.2007 FI 20070126

(43) Date of publication of application:
23.07.2008 Bulletin 2008/30

(73) Proprietor: **Linde AG**
80331 München (DE)

(72) Inventor: **TIGERSTRÖM, Anna**
S-116 21 Stockholm (SE)

(74) Representative: **Hjelt, Pia Dorrit Helene et al**
BORENIUS & Co Oy AB
Tallberginkatu 2 A
00180 Helsinki (FI)

(56) References cited:
WO-A-00/47813 WO-A-88/04706
US-A- 3 759 783 US-A- 4 016 029
US-A- 4 184 912 US-A- 4 444 621
US-A1- 2002 096 274

EP 1 945 852 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the use of carbonate ions for the solubilization of wood extractives in a process for the deresination of pulp as well as to the use of carbon dioxide or a (bi)carbonate compound for such solubilization in the deresination of pulp. More specifically, the invention relates to the removal of wood extractives or resin from an aqueous pulp suspension in an alkaline process stage of the pulping process.

BACKGROUND OF THE INVENTION

[0002] A problem associated with the production of pulp from wood either by chemical, mechanical or semi-mechanical processes is the liberation of wood extractives from the wood fibres into the aqueous phase of the pulp suspension. The wood extractives are solvent extractable organic materials and they are typically composed of a variety of more or less water-insoluble compounds, which form sticky particles and agglomerates (pitch) detrimental to the papermaking process and products. The compounds designated herein as wood extractives or resin include mainly fatty acids, resin acids, terpenes, sterols and phenols. Especially, the fatty and resin acids tend to form insoluble calcium salts, which are difficult to remove.

[0003] In chemical pulping, extractives cause problems by forming deposits on the equipment and on the fibers. Wires and screens may be clogged and dark specks are formed in the bleached pulp or paper. The problem is accentuated when chlorine free processes are developed and when the use of hardwood as a raw material increases. Pulp from hardwood contains even more extractives than softwood and this tends to increase the severity of the problems encountered in the handling of the pulp, especially in the bleaching and in the papermaking processes. Mechanical pulping also liberates extractives into the aqueous phase and, depending on the operating conditions, the processing of the pulp is disturbed to a greater or lesser degree by pitch.

[0004] In kraft processes using hardwood raw material, one way to alleviate the pitch problem is to add tall oil from softwood cooking into the hardwood cooking process. Other processes for reducing the pitch problem include adding soaps or other surfactants to the pulp to remove the detrimental substances. One such method is described in WO 2005/080672 (Kemira), which uses an organic stabilizing compound and a surfactant in a peroxide bleaching stage and then removes the extractives by dewatering or washing. WO 2004/101882 (Ciba) describes the use of water-soluble cationic polymers for controlling pitch deposits. CA 1162358 and US 4,444,621 (MoDo) uses a mild mechanical working in the bite of twin interdigitated rotating screws to deresinate a cellulose pulp. EP 1 205 598 (SCA) uses supercritical carbon dioxide for extracting wood extractives from dry pulp. The extract is then trapped in an organic solvent.

[0005] The book "Pitch control, Wood Resin and Deresination" edited by Ernst L. Back, et al., TAPPI Press Technology Park/Atlanta, 2000, pp 212-218, the contents of which are considered to be included by reference in the present specification, notes (p. 212) that the pH and the content of multivalent ions such as Ca and Mg in the washing water influences the resin content of pulps after the cooking. It is noted (p. 216) that the formation of calcium soaps late in the pulp washing operation may cause problems for deresination. However, these problems may be alleviated by blocking the free calcium by carbonate ions in the late stage of washing, or the washing may be improved by adjusting the pH in the wash water with carbon dioxide. The last mentioned washing process is described in EP 0 296 198 (AGA).

[0006] Thus, carbonates and carbon dioxide in the wash water are known to influence the extractives content of the washed pulp. However, there is no suggestion of using carbonates for deresination in the alkaline bleaching or extraction stages preceding such a washing procedure.

[0007] There are a number of alkaline reaction stages which are separate from said washing procedures and which are typically included in the processing of pulps in a pulp mill. Such alkaline processes include oxygen delignification stages, peroxide bleaching stages and extraction stages. In said stages, the pH is typically raised for the reaction in question to above pH 10 with the use of an alkali such as sodium hydroxide or oxidized white liquor. It is also known to use other alkaline agents such as sodium carbonate in this connection. Although sodium carbonate is not preferred as an alkaline agent, it is a much cheaper

[0008] WO 00/47813 (STFI) describes a process for oxygen delignification of a chemical pulp, wherein half of the alkali consists of carbonates and the pH is adjusted to exclude bicarbonates. The carbonates are used for their big buffering capacity, which gives an even alkali profile during the process. The Kappa number of the pulp is reduced by the process.

[0009] SE 219 677 (Watanabe) describes a process for the purification of pulp by oxidation of a pulp with oxygen or air. The purification is started by soaking the pulp in a solution of sodium hydroxide or sodium carbonate. Thereafter the pulp is compressed, disintegrated and placed in water. Air or oxygen is applied at an elevated temperature and then the oxidized pulp is washed with water. The oxidation removes resins and provides a light pulp which is easy to bleach.

[0010] US 3,055,794 describes a method for the deresination of a sulfite pulp in connection with the removal of the

cooking lye and the washing of the pulp. The acidic pulp is washed with one or two alkaline washing mediums including sodium hydroxide and/or soda, and finally with water to extract resins without mechanical action. The resin extracted pulp may be acidified directly after the washing operation.

[0011] SE 522 161 (Kvaerner) discloses an oxygen delignification process wherein sodium hydroxide is added to the reactor in connection with the generation of carbon dioxide therein. The subsequent formation of carbonate and bicarbonate ions provide a buffering action. An improved selective Kappa reduction is obtained.

[0012] US 4,445,969 (Samuelson) describes a three stage bleaching stage wherein alkali is supplied in the form of carbonate and liberated carbon dioxide gas is removed.

[0013] Manoucheri and Samuelson, Oxygen bleaching of kraft pulp, Svensk papperstidning, 12, 1975, p 451 to 454, describe experiments using carbonates and bicarbonates as the added alkali. An increased carbon dioxide concentration is said to retard the delignification.

[0014] EP 1 266 994 (Weyerhaeuser) describes bleaching of mechanical pulps with hydrogen peroxide and using magnesium hydroxide and sodium carbonate as alkali. The brightness of the pulp is increased by the process.

[0015] Thus, the prior art includes the use of carbonates in the alkaline bleaching of pulps and notes its influence on the brightness and the Kappa number. The Kappa number is a widely used measure of the lignin content of a pulp. There is no suggestion in the prior art, however, that the carbonates in the alkaline stages might improve the deresination of the pulp. The presence of carbon dioxide in an oxygen delignification stage is rather considered to impair the reaction.

BRIEF DESCRIPTION OF THE INVENTION

[0016] It is an object of the present invention to provide a process for improving the deresination of a pulp. The objects of the invention are achieved by a process and use, which are characterized by what is stated in the independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

[0017] The invention is based on the realization that carbonate ions can be actively utilized for improving the deresination of resinous pulps when the pulp is being treated in a strongly alkaline process stage, preferably at an elevated temperature. It has been realized that in an alkaline process stage the conditions are more favourable for the solubilization of the wood extractives than in a washing stage. Provided that the pulp is dewatered after the alkaline process stage under conditions, which maintain the solubilized extractives in solution, improved deresination of the pulp is obtained.

[0018] Accordingly, the present invention in a first aspect provides the use of carbonate ions for the solubilization of wood extractives in a process for the deresination of pulp, which comprises providing an aqueous pulp suspension, which contains wood extractives in water-insoluble form; subjecting said pulp suspension to an alkaline process stage at a pH above 10; providing carbonate ions in said pulp suspension; in said alkaline stage, subjecting said pulp suspension to the action of said carbonate ions for solubilizing a significant part of said wood extractives; said carbonate ions being provided by adding a sufficient amount of a substance selected from carbonate compounds and carbonate-forming substances for solubilization; and dewatering the resulting carbonate-treated pulp suspension without lowering the pH below 10 for removing solubilized extractives from said pulp and for providing a deresinated pulp.

[0019] In the preferred embodiment of the invention, the carbonate ions are provided by a carbonate forming substance, which comprises carbon dioxide. Most preferably the carbonate forming substance is provided in the form of gaseous carbon dioxide or a gas, wherein the major component is carbon dioxide. The carbon dioxide is added to the pulp so that carbonate ions are present in the alkaline process. The carbon dioxide is preferably added into the alkaline process stage itself or to a pipe line leading to the alkaline process stage. The carbon dioxide may also be combined with a gaseous or vapour phase component which is used for the alkaline process stage.

[0020] When carbon dioxide is used to provide the carbonate ions, the amount of carbon dioxide added may be such that it has a pH lowering effect on the aqueous pulp suspension. In such a case, it may be necessary to counter the pH-lowering effect by adding extra alkali to the alkaline process stage to maintain the pH at a desired level above pH 10.

[0021] In another embodiment the carbonate compound comprises an aqueous solution of an alkali metal (bi)carbonate.

[0022] In one embodiment of the invention, the carbonate compounds are provided by liquors from other parts of the mill which contain carbonate and/or bicarbonate compounds, e.g. bicarbonate brine from a tall oil recovery process or liquors from black liquor gasification or gas scrubbing liquors.

[0023] In a further embodiment of the invention, a (bi)carbonate solution containing a desired level of (bi)carbonates and a desired pH may be produced by reaction of suitable acids and bases outside the main process. An apparatus suitable for such a reaction is described in EP 1 461 499 (Linde).. pulp suspension. In such a case, it may be necessary to counter the pH-lowering effect by adding extra alkali to the alkaline process stage to maintain the pH at a desired level above pH 10.

[0024] The pulp suspension in the alkaline process stage in question may already contain some carbonate ions deriving from other operations in the mill. The carbonates may, for instance be a result of the use of sodium carbonate as an alkali or the carbonates may derive from carbon dioxide used for improving the washing of the pulp in a preceding or subsequent process stage. Some carbonate may also derive from the cooking of the wood fibres. In order for the

carbonate ions to perform their deresinating action according to the invention, the carbonate content should be controlled to between 30 and 200 mmol/l of the aqueous phase of the pulp. According to an embodiment of the invention, the pulp to be treated has an initial carbonate ion content and the carbonate ion concentration in the pulp increased by the addition of carbon dioxide to said pulp.

[0025] One aspect of the invention relates to the use of carbon dioxide or to the use of a liquid containing carbonate and/or to the use of bicarbonate brine for providing carbonate ions for the solubilization of wood extractives the deresination of an aqueous pulp suspension in an alkaline process stage operating at a pH above 10.5. The deresinated pulp so obtained is preferably further processed into a dried product selected from paper, board, paperboard and dry pulp in a manner known *per se*.

DESCRIPTION OF THE INVENTION

[0026] According to the invention an aqueous pulp suspension is deresinated with the aid of carbonate ions. The pulp suspension contains wood extractives in water-insoluble form and the extractives are solubilized by the action of the carbonate ions. The carbonate ions are caused to act on the pulp in a strongly alkaline environment so that insoluble compounds are solubilized and can be removed in the subsequent dewatering stage.

[0027] In the present specification and claims, the term "deresination" means the removal of wood extractives from the aqueous pulp suspension which is being treated. The deresination obtained by the present invention should be significant in the sense that it should bring about a clearly noticeable improvement in the process in the form of reduced clogging, reduced dirt specks in the product and less problems related to the presence of a clearly noticeable improvement in the process in the form of reduced clogging, reduced dirt specks in the product and less problems related to the presence of extractives such as bad smell and taste. The improvement should be understood as referring to a comparison to an otherwise similar process but lacking the carbonate levels of the present invention. The content of certain extractives is reduced by at least 25 % and preferably at least 30 % by the process of the invention. This specific reduction refers primarily to the unsaturated fatty acids included as part of the extractives.

[0028] In the present specification and claims, the terms "solubilizing" or "solubilized" is used to indicate that extractive components which are insoluble or sparingly soluble in the aqueous phase of the pulp suspension is made to enter the aqueous phase in a form which facilitates the removal of extractives with the removal of said the aqueous phase. Especially, the unsaturated fatty acids are components which may be dissolved or dissociated and they preferably form micelles.

[0029] In the present specification and claims, the term "carbonate ion" refers to ions having the chemical formula CO_3^{2-} . In the specification and claims, the term "carbonate" is sometimes used to denote the carbonate ion, such as in the terms "carbonate action" or "carbonate treatment". The carbonate ion is an anion, which is more or less closely associated with a cation such as sodium Na^+ or calcium Ca^{2+} . The term "carbonate compound" refers to a chemical compound such as sodium carbonate, sodium bicarbonate, calcium carbonate, etc. The carbonate compounds of the invention are capable of dissociating in an aqueous medium and of providing carbonate ions therein.

[0030] In the present specification and claims, the term "carbonate-forming substance" refers to a compound or mixture, which is capable of creating carbonate ions in the conditions of the process in question. The preferred carbonate-forming substance is carbon dioxide, which forms carbonate ions in water according the equation



[0031] The present invention is suitable for the deresination of both chemical and mechanical pulps. Both chemically and mechanically produced pulps include wood extractives which may cause problems at some point of the process. During the handling of the fibres from the wooden raw material to the end product, the fibres undergo various treatments, wherein wood extractives are liberated and may be either solubilized or desolubilized depending on the prevailing conditions. For instance, resin acids and fatty acids are relatively soluble when they are in the form of sodium soaps while the corresponding calcium soaps are fairly insoluble and will stick to fibres and equipment. Under favourable conditions the solubilized soaps, especially the soaps of the unsaturated fatty acids, form micelles, which in turn are capable of picking up and solubilizing also such species, which are not in themselves soluble. The micelles are broken and the solubilized compounds are deposited on solid surfaces such as inner walls of pumps and pipes, in washers, and on fibers, if the conditions for micelle formation are disturbed.

[0032] It has been found that the solubility of the wood extractives, and especially the solubility of the unsaturated fatty acid soaps of the extractives is significantly increased by the presence of carbonate ions in a strongly alkaline environment. This phenomenon is utilized in the present invention by providing a sufficient carbonate ion content in an alkaline process step to solubilize extractives. By removing the solubilized components under conditions, which favour the maintaining of the micelles in intact form, a significant improvement in the deresination is obtained.

[0033] Since the greatest problems with extractives are encountered when the pulp is of hardwood origin or contains

hardwood pulp, the greatest benefits of the invention are provided in a process, wherein the wood extractives comprise extractives from hardwood. Under favourable conditions, also betulinal, which is an especially problematic component of birch extractives, can be removed.

[0034] The pulp, which is to be subjected to the deresination process of the invention may be a chemical pulp, a mechanical pulp, a semi-mechanical pulp, a totally or partly recycled pulp or a mixture of such pulps. The pulp to be treated may, for instance, be a kraft pulp, sulfite pulp, groundwood pulp, thermomechanical pulp, chemithermomechanical pulp, high-yield pulp, deinked recovered paper pulp, stone groundwood, refiner mechanical pulp. In a preferred embodiment, the pulp contains kraft pulp of hardwood, softwood or mixtures thereof.

[0035] The influence of carbonate ions on the solubility of the extractives has previously been utilized in the washing of pulps, especially after the oxygen delignification or hydrogen peroxide bleaching stages. However, in the present invention, carbonate ions are made to act on the pulp in the alkaline stage itself. In this manner, the conditions for solubilization can be adjusted so as to greatly improve the deresination compared to performing a washing operation with carbonate-rich water.

[0036] The alkaline process stage of the invention should provide a sufficiently high pH, i.e. one above pH 10. The pH is preferably 10.5 or higher, especially between pH 11 and 14. The alkaline process step is preferably operated at a pH of 11 to 13.5. The pH value in the specification and claims refers to a value measured at room temperature (about 25 °C). Suitable alkaline process stages comprise oxygen delignification stages, peroxide bleaching stages and extraction stages. Such stages are typically designated O, P and E, respectively, in chemical pulping.

[0037] In a preferred embodiment of the invention, the alkaline process stage comprises an oxygen delignification stage and the pH of the aqueous pulp suspension during the oxygen delignification stage is maintained at a value above 10, preferably pH 11 to 13.5, by an alkali. The alkali used in the oxygen delignification stage is typically sodium hydroxide or oxidized white liquor, the main component of which is sodium hydroxide. If desired, the alkali may also include sodium carbonate or bicarbonate. Mixtures of alkalis may also be used. Various other chemicals known to those skilled in the art may also be added to the oxygen delignification stage provided that they do not impair the action of the carbonate ions on the deresination.

[0038] In a preferred embodiment of the invention the carbonate forming substance comprises carbon dioxide. The carbon dioxide is preferably gaseous carbon dioxide or a gas containing carbon dioxide. It is, possible e.g. in an oxygen delignification stage to mix the carbon dioxide with the oxygen gas prior to feeding it into the reaction chamber. The carbon dioxide may also be added to steam which is used for heating the pulp prior to the alkaline process stage. However, it is preferable to add the carbon dioxide separately and controllably to provide a desired concentration of carbonate ions. The carbonate concentration may be analysed by conventional means. When the carbon dioxide is fed into the pulp, it is preferably fed into the pulp in the alkaline process stage itself or prior to said stage, such as into a pipe leading into the process stage. When gaseous carbon dioxide or a gas containing carbon dioxide is fed into a pipe line, it is preferably fed to the pressure side of a pump. The carbon dioxide may also be mixed into water used for diluting the pulp suspension in or before the alkaline process stage. Carbon dioxide may be fed also to alkaline storage stages or alkaline transport stages such as storage towers and stand pipes.

[0039] When the carbonate ions are provided by carbon dioxide, which has a pH lowering effect on the aqueous pulp suspension, this pH-lowering effect is preferably countered by adding extra alkali to the process stage to maintain the pH at a desired level above pH 10. Also bicarbonates have a tendency to lower the pH of the alkaline pulp suspension and the pH may need to be adjusted by using more alkali if bicarbonate is used to provide the carbonate ions.

[0040] In another embodiment of the invention, the carbonate compounds of the invention are provided by liquor of the mill. Such liquors comprise recover liquids comprising carbonate and/or bicarbonate compounds, e.g. brine from tall oil recovery processes, wherein carbon dioxide has been used for acidulation or liquors from black liquor gasification or gas scrubbing liquors. It is possible to feed the recover liquid into the pulp in the alkaline process stage itself or prior to said stage such as into a pipe leading into the process stage. The recover liquids may also be mixed into water used for diluting the pulp suspension in or before the alkaline process stage.

[0041] The pulp suspension entering the alkaline stage may initially include carbonate ions deriving from some other process step. In the preferred embodiment of the invention, carbon dioxide is added to the pulp suspension for increasing the carbonate ion concentration in the aqueous phase of the pulp suspension. According to the invention, a carbonate compound or carbonate-forming compound is added to the pulp in an amount sufficient for providing a carbonate ion concentration of 30 to 200 mmol/l, preferably 40 to 140 mmol/l and most preferably 60 to 120 mmol/l in the aqueous phase of the pulp suspension.

[0042] Adding solid carbonate compounds such as sodium carbonate or sodium bicarbonate into a continuous industrial process, such as a pulping process, is technically possible but it is also rather cumbersome and messy. The solid compound needs to be weighed and dissolved in water before the addition and this requires a lot of handling and manual work. Moreover, when carbonates are added into the process in the form of sodium carbonate or sodium bicarbonate, the chemical at the same time adds extra sodium. That disturbs the sodium/sulphur balance in the closed part of the mill.

[0043] In accordance with the preferred embodiment of the present invention the carbonate ions are provided by

carbon dioxide which is easy to handle in the mill and which does not add sodium or any other component to the process. The carbon dioxide reacts with the water and provides the desired carbonates in a simple and elegant manner.

[0044] In the prior art, there has been suggested that carbon dioxide in an alkaline reaction stage such as the oxygen delignification stage, might be harmful for the delignification. However, in accordance with the present invention, the carbon dioxide fed into the pulp suspension has not been found to cause any harm. The carbon dioxide is quickly dissolved in the alkaline aqueous phase of the suspension and any pH-lowering effect is countered by additional alkali. The amount of carbon dioxide fed into the pulp is typically from 0.5 to 10 kg per ton bone dry cellulose, preferably from 1 to 7 kg per ton and most preferably from 2 to 4 kg per ton. The amount of carbon dioxide needed may be calculated by measuring the carbonate concentration or by measuring the surface tension of the pulp suspension.

[0045] By adding 10 kg of carbon dioxide to a pulp stream for an oxygen delignification stage, the carbonate content will be immediately increased by about 31 mmol/l. When the recirculation of filtrate has reached equilibrium, the carbonate content will have increased by 68 mmol/l from the initial carbonate level of the pulp.

[0046] When a (bi)carbonate solution or a liquor from other parts of the mill is used, the amounts of carbonate ions can be easily analysed and/or calculated to provide a corresponding increase in carbonate content.

[0047] A sodium bicarbonate brine from a carbon dioxide based tall oil recovery process will typically contain carbon dioxide about 5-30 kg/m³. The amount of bicarbonate brine liquid fed into the pulp is typically from 0.01 m³ to 1 m³ per ton bone dry cellulose, preferably 0.05 to 0.80 m³ per ton and most preferably from 0.15 m³ to 0.60 m³ per ton.

[0048] The tall oil recovery brine includes in addition to carbon dioxide and (bi)carbonate, also water soluble extractives, which may assist in the deresination.

[0049] In addition to pH, temperature is a factor which influences the solubilization of the wood extractives and an elevated temperature is preferred. The alkaline process stage is preferably operated at a temperature between 60 and 130 °C, more preferably at 75 to 110 °C.

[0050] A prolonged exposure to the action of the carbonate ions improves the micelle formation and hence enhances the deresination of the pulp suspension. In the traditional washing of bleached pulp with carbonate-rich water, the exposure time is very short, typically a matter of seconds. In the preferred embodiment of the present invention, the pulp suspension is subjected to the carbonate action for a longer time. The exposure time should be at least 5 minutes and preferably 10 minutes, or more. The exposure time is preferably between 0.5 and 3 hours, more preferably between 1 and 2 hours.

[0051] Without wishing to be bound by any theory, it is believed that the beneficial action of the carbonate ions is at least partly dependent on the action of the carbonate ions on sparingly soluble calcium soaps of unsaturated fatty acids such as oleic acid, linoleic acid and linolenic acid. At a high pH (above pH 10 and especially above pH 10.5) the carbonate ions cause said soaps to form solubilized free anions and these, in turn, form micelles capable of capturing undissolved extractive components. This facilitates the removal of both solubilized soaps and insoluble extractive components in a subsequent dewatering step. If the pH is lowered below about 10, the micelles start to disintegrate and the extractives are again deposited on the fibres or the equipment.

[0052] In a traditional pulping process there are certain steps such as one or more chlorine dioxide bleaching steps, which affect the unsaturated fatty acids and tend to saturate them. The saturated fatty acids do not seem to have the same capacity to form micelles as the unsaturated ones. Therefore, the pulp suspension should preferably be subjected to the carbonate action in the alkaline process stage prior to being subjected to any stage capable of significantly saturating the unsaturated fatty acids of the wood extractives.

[0053] When the pulp suspension in the alkaline process step contains a sufficient amount of free unsaturated fatty acids, the surface tension of the aqueous phase is at a substantially constant level. This level is preferably below 35 mN/m and more preferably below 30 mN/m measured at 70 °C according to the well known Du Noüy Ring method.

[0054] When the micelles start to disintegrate, the surface tension rises. Therefore, the dewatering stage should not only retain a high pH but it should preferably also retain a substantially constant surface tension, preferably below 35 mN/m. When the filtrate of the pulp is analysed, the surface tension should preferably not change more than 5 % when the pulp is diluted with equal amounts of deionized water (1:1). When the pulp suspension in the alkaline process stage has been treated with carbonate ions in the desired amount, the system becomes robust and can be diluted as much as 1:1 without reaching the critical micelle concentration at which the micelles disintegrate. The surface tension is an important factor since it indicates the amount of washing water that can safely be introduced into the pulp for the dewatering stage without destroying the micelles.

[0055] The dewatering of the carbonate treated alkaline pulp may be performed in any standard manner providing that the pulp is not diluted with such an amount of water that the pH falls below the critical value of 10. Preferably the pulp has a pH of at least 10.5 and more preferably pH 11 or higher, when being dewatered.

[0056] The dewatering of the carbonate-treated pulp provides a deresinated pulp, which may be used in a well known manner. The deresinated pulp is preferably further processed into an end product. The end product is typically a dried product selected from paper, board, paperboard and dry pulp. The procedures for processing a dewatered and deresinated pulp into such end products are well known to those skilled in the art and such procedures are therefore not

described in detail herein.

[0057] In a preferred embodiment of the invention, a kraft pulp suspension containing pulp selected from softwood pulp, hardwood pulp and mixtures thereof is subjected to an oxygen delignification stage at a pH of 11 to 13 provided by the introduction of oxidized white liquor into said pulp, and gaseous carbon dioxide is injected into said pulp suspension in an amount of 0.5 to 10 kg per ton bone dry cellulose to increase the carbonate ion content of the suspension and improve the solubilization of the wood extractives, whereafter the delignified pulp suspension is dewatered at a pH of no less than 11.

[0058] The above description illustrates the use of carbonate compounds and carbonate-forming substances for the deresination of an aqueous pulp suspension in an alkaline process stage operating at a pH above 10. In the preferred embodiment, the carbonate ions are provided by gaseous carbon dioxide.

[0059] The following example illustrates the invention.

EXAMPLE

Reference process

[0060] A kraft pulp suspension made of hardwood pulp is subjected to oxygen delignification. The carbonate content of the pulp is analysed and is found to be about 25 mmol/l. The pulp is first mixed with oxidized white liquor to raise the pH for the oxygen delignification. Then oxygen is added to the pulp and it is fed into the delignification reactor. The temperature of the reactor is raised to about 95 °C and the reaction is allowed to proceed for about 70 minutes.

[0061] The pH at the end of the oxygen delignification reaction is about 11.5. The pulp is diluted with filtrate from a washer and dewatered. The pulp so obtained is washed, treated further in a bleaching line, washed again, stored and is then fed to a paper machine to produce paper.

[0062] The dewatering apparatus after the oxygen delignification stage is badly clogged by extractives coming from the delignified pulp. Also the later washing stages suffer from sticky deposits. The paper produced in the paper machine contains a significant amount of darks specks due to the extractives in the pulp.

Process of the invention

[0063] The same delignification operation as above is repeated with the difference that carbon dioxide is fed into the pulp after the alkali feed and before the oxygen feed. The amount of carbon dioxide is 8 kg per bone dry ton of pulp, which raises the carbonate content of the aqueous phase of the pulp to 79 mmol/l. The alkali feed is increased to compensate for the pH-lowering effect of the carbon dioxide.

[0064] At the end of the delignification reaction the pH is 11.5 and in the dewatering the pH remains at a value above 11. The dewatered pulp is treated as above and used to make paper.

[0065] Due to the action of carbonate ions on the extractives in the highly alkaline reaction stage, a significant portion of the extractives are removed with the washing waters. There is significantly less clogging of the dewatering equipment after the oxygen delignification stage and the paper produced has an improved quality and fewer dark specks.

Claims

1. Use of carbonate ions for the solubilization of wood extractives in a process for the deresination of pulp, **characterized in**

- providing an aqueous pulp suspension, which contains wood extractives in water-insoluble form;
- subjecting said pulp suspension to an alkaline process stage at a pH above 10;
- providing carbonate ions in said pulp suspension;
- in said alkaline stage, subjecting said pulp suspension to the action of said carbonate ions for solubilizing a significant part of said wood extractives;
- said carbonate ions being provided by adding a sufficient amount of a substance selected from carbonate compounds and carbonate-forming substances for causing said solubilization; and
- dewatering the resulting carbonate-treated pulp suspension without lowering the pH below 10 for removing solubilized extractives from said pulp and for providing a deresinated pulp.

2. A use according to claim 1, wherein said pulp is selected from chemical pulps, mechanical pulps, semi-mechanical pulps, recycled pulps and mixtures thereof.

3. A use according to claim 1, wherein said alkaline process stage is selected from an oxygen delignification stage, a peroxide bleaching stage and an extraction stage.
- 5 4. A use according to claim 1, wherein said alkaline process stage comprises an oxygen delignification stage and the pH of said aqueous pulp suspension during said process stage is maintained at a value above 10 by an alkali selected from sodium hydroxide, sodium carbonate, oxidized white liquor and mixtures thereof.
- 10 5. A use according to claim 1, wherein said carbonate forming substance comprises carbon dioxide or a liquid containing carbonate and/or bicarbonate ions.
6. A use according to claim 5, wherein said substance is gaseous carbon dioxide.
- 15 7. A use according to claim 5, wherein said liquid containing carbonate and/or bicarbonate ions is produced by reaction of suitable acids and bases.
- 20 8. A use according to claim 5 wherein gaseous carbon dioxide is combined with a gaseous or vapour phase component used for said process stage.
- 25 9. A use according to claim 5, wherein gaseous carbon dioxide is added to said alkaline process stage or to a pipe line leading to said process stage in an amount which has a pH-lowering effect on the aqueous pulp suspension and said pH-lowering effect is countered by adding extra alkali to said process stage to maintain the pH at a desired level above pH 10.
- 30 10. A use according to claim 5, wherein said carbonate forming substance comprises sodium bicarbonate brine from a tall oil recovery process.
- 35 11. A use according to claim 1, wherein said carbonate compound or carbonate-forming compound is added in an amount sufficient for providing a carbonate ion concentration of 30 to 200 mmol/l in the aqueous phase of said pulp suspension.
- 40 12. A use according to claim 1, wherein said alkaline process stage is operated at a temperature between 60 and 130 °C.
- 45 13. A use according to claim 1, wherein the surface tension of the aqueous phase of said pulp suspension in said alkaline process stage is below 35 mN/n measured at 70 °C according to the Du Noüy Ring method in said process stage and in said dewatering.
- 50 14. A use according to claim 13, wherein said surface tension is changed no more than 5% when the pulp is diluted with equal amounts of deionized water (1:1).
- 55 15. A use according to claim 1, wherein a kraft pulp suspension containing pulp selected from softwood pulp, hardwood pulp and mixtures thereof is subjected to an oxygen delignification stage at a pH of 11 to 13 provided by the introduction of oxidized white liquor into said pulp, and gaseous carbon dioxide is injected into said pulp suspension in an amount of 0.5 to 10 kg per ton bone dry cellulose to increase the carbonate ion content of the suspension and improve the solubilization of the wood extractives, whereafter said delignified pulp suspension is dewatered at a pH of no less than 11.
16. A use to claim 1, wherein a kraft pulp suspension containing pulp selected from softwood pulp, hardwood pulp and mixtures thereof is subjected to an oxygen delignification stage at a pH of 11 to 13 provided by the introduction of oxidized white liquor into said pulp, and sodium bicarbonate brine is injected into said pulp suspension in an amount of 0.01 m³ to 1 m³ per ton bone dry cellulose to increase the carbonate ion content of the suspension and improve the solubilization of the wood extractives, whereafter said delignified pulp suspension is dewatered at a pH of no less than 11.
17. A use according to any one of the preceding claims, wherein said deresinated pulp is further processed into a dried product selected from paper, board, paperboard and dry pulp.
18. Use of carbon dioxide for providing carbonate ions for the solubilization of wood extractives in the deresination of an aqueous pulp suspension in an alkaline process stage operating at a pH above 10.

19. Use of a liquid containing carbonate and/or bicarbonate ions for the solubilization of wood extractives in the deresination of an aqueous pulp suspension in an alkaline process stage operating at a pH above 10.

5 Patentansprüche

1. Verwendung von Carbonationen zur Solubilisierung von Holzextraktstoffen bei einem Verfahren zur Entharzung von Halbstoff, **dadurch gekennzeichnet, daß** man
 - eine wäßrige Halbstoffsuspension, die Holzextraktstoffe in wasserunlöslicher Form enthält, bereitstellt;
 - die Halbstoffsuspension einer alkalischen Verfahrensstufe bei einem pH-Wert über 10 unterwirft;
 - in der Halbstoffsuspension Carbonationen bereitstellt;
 - in der alkalischen Stufe die Halbstoffsuspension der Einwirkung der Carbonationen unterwirft, um einen erheblichen Teil der Holzextraktstoffe zu solubilisieren;
 - wobei die Carbonationen durch Zugabe einer ausreichenden Menge einer unter Carbonatverbindungen und carbonatbildenden Substanzen ausgewählten Substanz zur Verursachung der Solubilisierung bereitgestellt werden; und
 - die resultierende carbonatbehandelte Halbstoffsuspension ohne Senkung des pH-Werts unter 10 zur Entfernung von solubilisierten Extraktstoffen aus dem Halbstoff und zur Bereitstellung eines entharzten Halbstoffs entwässert.
2. Verwendung nach Anspruch 1, bei der der Halbstoff unter Zellstoffen, mechanischen Halbstoffen, halbmechanischen Halbstoffen, rezyklierten Halbstoffen und Mischungen davon ausgewählt wird.
3. Verwendung nach Anspruch 1, bei der die alkalische Verfahrensstufe aus einer Sauerstoffdelignifizierungsstufe, einer Peroxidbleichstufe und einer Extraktionsstufe ausgewählt wird.
4. Verwendung nach Anspruch 1, bei der die alkalische Verfahrensstufe eine Sauerstoffdelignifizierungsstufe umfaßt und der pH-Wert der wäßrigen Halbstoffsuspension während der Verfahrensstufe durch ein unter Natriumhydroxid, Natriumcarbonat, oxidierte Weißlaugung und Mischungen davon ausgewähltes Alkali bei einem Wert über 10 gehalten wird.
5. Verwendung nach Anspruch 1, bei der die carbonatbildende Substanz Kohlendioxid oder eine Carbonat- und/oder Hydrogencarbonationen enthaltende Flüssigkeit umfaßt.
6. Verwendung nach Anspruch 5, bei der es sich bei der Substanz um gasförmiges Kohlendioxid handelt.
7. Verwendung nach Anspruch 5, bei der die Carbonat- und/oder Hydrogencarbonationen enthaltende Flüssigkeit durch Umsetzung von geeigneten Säuren und Basen hergestellt wird.
8. Verwendung nach Anspruch 5, bei der gasförmiges Kohlendioxid mit einer für die Verfahrensstufe verwendeten Gas- oder Dampfphasenkomponente kombiniert wird.
9. Verwendung nach Anspruch 5, bei der gasförmiges Kohlendioxid in einer Menge, die eine pH-senkende Wirkung auf die wäßrige Halbstoffsuspension hat, zu der alkalischen Verfahrensstufe oder einer zu der Verfahrensstufe führenden Rohrleitung gegeben wird und der pH-senkenden Wirkung durch Zugabe von zusätzlichem Alkali zu der Verfahrensstufe entgegengewirkt wird, um den pH-Wert bei einem gewünschten Niveau über pH 10 zu halten.
10. Verwendung nach Anspruch 5, bei der die carbonatbildende Substanz Natriumhydrogencarbonatlauge aus einem Tallölgewinnungsverfahren umfaßt.
11. Verwendung nach Anspruch 1, bei der die Carbonatverbindung oder carbonatbildende Verbindung in einer Menge zugegeben wird, die zur Bereitstellung einer Carbonationenkonzentration von 30 bis 200 mmol/l in der wäßrigen Phase der Halbstoffsuspension ausreicht.
12. Verwendung nach Anspruch 1, bei der die alkalische Verfahrensstufe bei einer Temperatur zwischen 60 und 130°C betrieben wird.

13. Verwendung nach Anspruch 1, bei der die Oberflächenspannung der wäßrigen Phase der Halbstoffsuspension in der alkalischen Verfahrensstufe unter 35 mN/n, gemessen bei 70°C nach der Du-Noüy-Ring-Methode, in der Verfahrensstufe und bei der Entwässerung beträgt.

14. Verwendung nach Anspruch 13, bei der die Oberflächenspannung sich bei Verdünnung des Halbstoffs mit gleichen Mengen von entionisiertem Wasser (1:1) um nicht mehr als 5% ändert.

15. Verwendung nach Anspruch 1, bei der eine unter Nadelholzhalbstoff, Laubholzhalbstoff und Mischungen davon ausgewählten Halbstoff enthaltende Kraftzellstoffsuspension einer Sauerstoffdelignifizierungsstufe bei einem pH-Wert von 11 bis 13, der durch Eintragen von oxidierte Weißlauge in den Halbstoff bereitgestellt wird, unterworfen wird und in die Halbstoffsuspension gasförmiges Kohlendioxid in einer Menge von 0,5 bis 10 kg pro Tonne absolut trockener Cellulose zur Erhöhung des Carbonationengehalts der Suspension und zur Verbesserung der Solubilisierung der Holzextraktstoffe eingeleitet wird, wonach die delignifizierte Halbstoffsuspension bei einem pH-Wert von nicht weniger als 11 entwässert wird.

16. Verwendung nach Anspruch 1, bei der eine unter Nadelholzhalbstoff, Laubholzhalbstoff und Mischungen davon ausgewählten Halbstoff enthaltende Kraftzellstoffsuspension einer Sauerstoffdelignifizierungsstufe bei einem pH-Wert von 11 bis 13, der durch Eintragen von oxidierte Weißlauge in den Halbstoff bereitgestellt wird, unterworfen wird und in die Halbstoffsuspension Natriumhydrogencarbonatlauge in einer Menge von 0,01 m³ bis 1 m³ pro Tonne absolut trockener Cellulose zur Erhöhung des Carbonationengehalts der Suspension und zur Verbesserung der Solubilisierung der Holzextraktstoffe eingeleitet wird, wonach die delignifizierte Halbstoffsuspension bei einem pH-Wert von nicht weniger als 11 entwässert wird.

17. Verwendung nach einem der vorhergehenden Ansprüche, bei der der entharzte Halbstoff zu einem aus Papier, Pappe, Karton und trockenem Halbstoff ausgewählten getrockneten Produkt weiterverarbeitet wird.

18. Verwendung von Kohlendioxid zur Bereitstellung von Carbonationen zur Solubilisierung von Holzextraktstoffen bei einem Verfahren zur Entharzung einer wäßrigen Halbstoffsuspension in einer bei einem pH-Wert über 10 arbeitenden alkalischen Verfahrensstufe.

19. Verwendung einer Carbonat- und/oder Hydrogencarbonationen enthaltenden Flüssigkeit zur Solubilisierung von Holzextraktstoffen bei einem Verfahren zur Entharzung einer wäßrigen Halbstoffsuspension in einer bei einem pH-Wert über 10 arbeitenden alkalischen Verfahrensstufe.

Revendications

1. Utilisation d'ions carbonate pour la solubilisation de produits d'extraction du bois dans un procédé d'extraction de la résine de la pâte,
caractérisée par

- l'obtention d'une suspension aqueuse de pâte, laquelle contient des produits d'extraction du bois sous une forme insoluble dans l'eau ;
- la soumission de ladite suspension de pâte à un stade de processus alcalin avec un pH supérieur à 10 ;
- la fourniture d'ions carbonate dans ladite suspension de pâte ;
- la soumission de ladite suspension de pâte, dans ledit stade alcalin, à l'action desdits ions carbonate pour solubiliser une partie importante desdits produits d'extraction du bois ;
- lesdits ions carbonate étant utilisés en ajoutant une quantité suffisante d'une substance choisie à partir de composés de carbonate et de substances formant du carbonate pour obtenir ladite solubilisation ; et
- la déshydratation de la suspension de pâte traitée au carbonate résultante sans réduire le pH sous 10 pour retirer les produits d'extraction solubilisés de ladite pâte et pour obtenir une pâte dépourvue de résine.

2. Utilisation selon la revendication 1, dans laquelle ladite pâte est choisie parmi des pâtes chimiques, des pâtes mécaniques, des pâtes semi-mécaniques, des pâtes recyclées et des mélanges de celles-ci.

3. Utilisation selon la revendication 1, dans laquelle ledit stade de processus alcalin est choisi parmi une étape de délignification à l'oxygène, une étape de blanchiment au peroxyde et une étape d'extraction.

4. Utilisation selon la revendication 1, dans laquelle ledit stade de processus alcalin comprend une étape de délignification à l'oxygène et le pH de ladite suspension aqueuse de pâte pendant ledit stade de processus est maintenu à une valeur supérieure à 10 par un alcali choisi parmi l'hydroxyde de sodium, le carbonate de sodium, une liqueur blanche oxydée et des mélanges de ceux-ci.
5. Utilisation selon la revendication 1, dans laquelle ladite substance formant du carbonate comprend du dioxyde de carbone ou un liquide contenant des ions carbonate et/ou bicarbonate.
6. Utilisation selon la revendication 5, dans laquelle ladite substance est du dioxyde de carbone gazeux.
7. Utilisation selon la revendication 5, dans laquelle ledit liquide contenant des ions carbonate et/ou bicarbonate est produit par réaction d'acides et de bases appropriés.
8. Utilisation selon la revendication 5, dans laquelle le dioxyde de carbone gazeux est combiné avec un composant en phase gazeuse ou en phase vapeur utilisé pour ledit stade de processus.
9. Utilisation selon la revendication 5, dans laquelle le dioxyde de carbone gazeux est ajouté audit stade de processus alcalin ou à une canalisation qui mène audit stade de processus en une quantité qui possède un effet d'abaissement du pH sur la suspension aqueuse de pâte et ledit effet d'abaissement du pH est contrôlé en ajoutant un alcali supplémentaire audit stade de processus pour maintenir le pH à un niveau souhaité supérieur à 10.
10. Utilisation selon la revendication 5, dans laquelle ladite substance formant du carbonate comprend de la saumure de bicarbonate de sodium obtenue d'un procédé de récupération de l'huile de pin.
11. Utilisation selon la revendication 1, dans laquelle ledit composé de carbonate ou composé formant du carbonate est ajouté en une quantité suffisante pour obtenir une concentration en ions carbonate de 30 à 200 mmoles/l dans la phase aqueuse de ladite suspension de pâte.
12. Utilisation selon la revendication 1, dans laquelle ledit stade de processus alcalin fonctionne à une température située entre 60 et 130 °C.
13. Utilisation selon la revendication 1, dans laquelle la tension superficielle de la phase aqueuse de ladite suspension de pâte dans ledit stade de processus alcalin est inférieure à 35 mN/n, mesurée à 70 °C selon la méthode Du Noüy Ring dans ledit stade de processus et dans ledit épaississement.
14. Utilisation selon la revendication 13, dans laquelle ladite tension superficielle est modifiée à pas plus de 5 % lorsque la pâte est diluée avec des quantités égales d'eau déionisée (1:1).
15. Utilisation selon la revendication 1, dans laquelle une suspension de pâte Kraft contenant une pâte choisie parmi une pâte de résineux, une pâte de feuillus et des mélanges de celles-ci est soumise à une étape de délignification à l'oxygène à un pH de 11 à 13 obtenu par l'introduction d'une liqueur blanche oxydée dans ladite pâte, et du dioxyde de carbone gazeux est injecté dans ladite suspension de pâte en une quantité de 0,5 à 10 kg par tonne de cellulose anhydre pour augmenter la teneur en ions carbonate de la suspension et pour améliorer la solubilisation des produits d'extraction du bois, après quoi ladite suspension de pâte délignifiée est épaissie à un pH d'au moins 11.
16. Utilisation selon la revendication 1, dans laquelle une suspension de pâte Kraft contenant une pâte choisie parmi une pâte de résineux, une pâte de feuillus et des mélanges de celles-ci est soumise à une étape de délignification à l'oxygène à un pH de 11 à 13 obtenu par l'introduction d'une liqueur blanche oxydée dans ladite pâte, et de la saumure de bicarbonate de sodium est injectée dans ladite suspension de pâte en une quantité de 0,01 m³ à 1 m³ par tonne de cellulose anhydre pour augmenter la teneur en ions carbonate de la suspension et pour améliorer la solubilisation des produits d'extraction du bois, après quoi ladite suspension de pâte délignifiée est épaissie à un pH d'au moins 11.
17. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle ladite pâte dépourvue de résine est en outre transformée en un produit sec choisi parmi un papier, un carton blanchi, un carton et une pâte sèche.
18. Utilisation de dioxyde de carbone pour obtenir des ions carbonate pour la solubilisation des produits d'extraction du bois dans l'extraction de la résine d'une suspension aqueuse de pâte dans un stade de processus alcalin qui

fonctionne à un pH supérieur à 10.

19. Utilisation d'un liquide contenant des ions carbonate et/ou bicarbonate pour la solubilisation des produits d'extraction du bois dans l'extraction de la résine d'une suspension aqueuse de pâte dans un stade de processus alcalin qui fonctionne à un pH supérieur à 10.

5

10

15

20

25

30

35

40

45

50

55

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 2005080672 A [0004]
- WO 2004101882 A [0004]
- CA 1162358 [0004]
- US 4444621 A [0004]
- EP 1205598 A [0004]
- EP 0296198 A [0005]
- WO 0047813 A [0008]
- SE 219677, Watanabe [0009]
- US 3055794 A [0010]
- SE 522161, Kvaerner [0011]
- US 4445969 A, Samuelson [0012]
- EP 1266994 A, Weyerhaeuser [0014]
- EP 1461499 A, Linde [0023]

Non-patent literature cited in the description

- Pitch control, Wood Resin and Deresination. TAPPI Press, 2000, 212-218 [0005]
- **Manoucheri ; Samuelson.** Oxygen bleaching of kraft pulp. *Svensk papperstidning*, 1975, vol. 12, 451-454 [0013]