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54 **Process for improved alkaline oxidative delignification of cellulose pulp.**

57 Treatment of the pulp with sufficient nitrosating agent to provide 0.1 to 1.2 weight percent active NO⁽⁺⁾ on a dry pulp basis at a pH of 1.7 to 4 and in oxygen environment under high intensity mixing conditions before an alkaline oxidative stage in a bleach sequence, the nitrosating agent being a compound that contributes predominantly nitrosonium ions.

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PROCESS FOR IMPROVED ALKALINE OXIDATIVE DELIGNIFICATION OF CELLULOSE PULP

Field of the Invention

The invention relates to an improved method for the alkaline oxidative delignification of lignocellulosic pulp. In particular, this invention relates to the treatment of the pulp with nitrosating agents in an acidic and oxygen environment under intense mixing conditions before the alkaline oxidative stage in a bleach sequence.

Background to the Invention

Pulping is the process by which lignocellulosic materials are converted to a fibrous mass. The process can be performed by mechanical, thermal or chemical means or a combination of these means. In chemical pulping, lignocellulosic materials such as wood chips are cooked with appropriate chemicals in an aqueous solution at elevated temperatures and pressures. Kraft (alkaline) pulping and sulfite (acidic) pulping are principal chemical methods employed. Others include soda, bisulfite and semichemical processes such as high yield Kraft, high yield sulfite and neutral sulfite (NSSC) processes.

The Kraft process, the most widely used process, can be used with a wide variety of species and tolerates bark whereas the sulfite, soda and NSSC processes are less tolerant. The Kraft process produces the highest strength pulp while the sulfite process produces a bright pulp that is easy to bleach to full brightness.

The pulping and bleach sequence chosen depend on the available lignocellulosic starting material and the end use envisioned for the pulp.

Lignocellulosic pulp from a pulping process is washed and subjected to subsequent treatment (bleach sequence) to remove residual lignin resulting in brighter pulp with improved optical and mechanical properties. Chemical pulping processes remove a major portion of the original lignin. Most of the subsequent process (bleach sequence) is directed towards removing the rest of the lignin, preferably under conditions that do not significantly degrade the cellulose and hemicellulose in the lignocellulosic material, to give the desired qualities in the end products.

Lignin is a complex biopolymer known to contain phenolic groups. Degrading or modifying these phenolic groups allows the lignin to be easily solubilized and removed. Preferably, the means used to modify the phenolic groups and remove the lignin should be ones that do not degrade the accompanying cellulose structures.

Lignin can be removed from chemically digested lignocellulosic pulps by treatment with strong oxidizing agents such as active chlorine chemicals (chlorine gas). But, with the addition of chlorine, noxious chloro-organics including chloroform, chlorophenols and chlorodioxins are formed. Since most chloro-organic wastes cannot be easily destroyed by biological means or by burning in the recovery boilers to recover energy because of their corrosivity and chloro-organic emission potential, they pose serious and increasing environmental concerns. Because of these concerns, paper mills desire to minimize the amount of chlorine used to reduce both toxic liquid wastes and air emissions.

Chlorine dioxide can replace chlorine gas as an oxidizing agent but the production of chlorine dioxide requires three times as much electrical energy per kilogram of active chlorine as chlorine gas.

Oxygen can be used instead of chlorine to partially delignify the pulp and thereby reduce or eliminate the amount of chlorine needed in the subsequent stages. With the reduction of chlorine, the formation of toxic and carcinogenic chloro-organics should be substantially reduced and the environmental problems associated with the bleaching process would be less severe. Also, the effluent from the oxygen delignification step can be incinerated for energy recovery.

Alkaline oxidative delignification, however, has required high pressures and results in severe cellulose degradation (lost selectivity) if the degree of delignification is carried to beyond about 50% of the remaining lignin from the pulping stage. Several processes have been taught to overcome these deficiencies. The purpose of these processes is to aid in a more efficient and selective alkaline oxidative stage by modification of the lignin so that it is more susceptible to oxidation.

Clarke in "The Action of Nitrogen Dioxide on Unbleached Pulp, Part I" Paper Trade Journal, Vol. 118, No. 8 (TAPPI Section), pp. 62 - 66 (1944) teaches using nitrogen dioxide (NO₂) as a direct lignocellulosic pulp delignifying agent to replace or reduce chlorine. He heats liquid NO₂ and the aqueous pulp at 90° C for 1 to 1.5 hours and then extracts the lignin with hot caustic. To avoid considerable damage to the

cellulose, Clarke advises only partially bleaching with NO_2 . Clarke theorizes that the bleaching occurs from the combined action of the nitrous and nitric acids formed when the NO_2 reacts with the water. He believes that the nitrous acid first modifies the lignin so that it can more easily be attacked by the nitric acid.

In U.S. Patent 4,076,579, Brink reveals prior treatment of the pulp with aqueous nitric acid or nitric acid made in situ from nitric oxide, oxygen and water. The aqueous nitric acid solutions can include an array of compounds, ions and radicals such as nitrogen trioxide, nitrogen tetroxide, nitric oxide, nitrate ions, nitrite ions, nitronium ions and nitrosonium ions. Water content is critical to avoid cellulose degradation but not inhibit penetration of nitric acid into the lignin.

In U.S. Patent No. 4,406,735, Samuelson discloses delignifying chemically digested pulp with oxygen gas in the presence of an alkali after activation of the pulp by bringing it into intimate contact with gaseous NO_2 at 20° - 100°C and washing the activated pulp. NO_2 and oxygen is taught as reacting with the lignocellulosic pulp as opposed to the reactions with nitric acid that Brink refers to.

In U.S. Patent No. 4,439,271, Samuelson discloses pretreating chemical pulp with NO_2 and then delignifying with alkaline oxygen. The NO_2 is added to the chemical pulp in an amount so that the nitrogen monoxide (NO) formed in the reaction is consumed and essentially none of the NO_2 and NO remains at the conclusion of the activation stage. The pretreatment step is followed by oxygen treatment of the modified pulp and extraction in the presence of an alkali.

In U.S. Patent No. 4,445,969, Samuelson discloses a process for delignifying and bleaching the lignocellulosic pulp in three stages - (1) an activation step where the water-containing pulp is mixed with gaseous NO and/or NO_2 and oxygen and, optionally, with nitric acid; (2) a wash step and extraction with an alkali such as a carbonate; and (3) a second alkaline step.

In U.S. Patent No. 4,602,982, Samuelson improves upon U.S. 4,445,969 with the introduction of at least 5 weight (wt.%) sodium nitrate with gaseous NO_2 , water and oxygen along with, optionally, nitric acid. The pulp is then washed and treated with an alkaline solution in the presence of oxygen. Samuelson suggests that nitrolignins are formed in the pretreatment stage which reacts preferentially with the reactive oxygen species which would otherwise degrade the cellulose.

Chemical Abstracts 52:14158e (Kuniak et al., "Delignification of Wood with Nitric Acid" Papir a Celulosa 12, 6 - 11 (1957)) states that use of 1 or less weight percent to 3 weight percent nitric acid can be used to delignify the pulp without cellulose degradation.

Summary of the Invention

A process has recently been discovered that improves delignification and bleaching by intimately contacting lignocellulosic pulp, particularly chemically digested lignocellulosic pulp, under high intensity mixing conditions with sufficient liquid-phase nitrosating agents in an acidic and oxygen environment prior to an alkaline oxidative stage in a bleach sequence.

The nitrosating agent is liquid-phase, that is, a solution or a pure liquid at ambient temperature and pressure, and includes any compound that will freely contribute predominantly active nitrosonium ions ($\text{NO}^{(+)}$) under reaction conditions. For the purposes of this invention, nitroacidium ions ($\text{H}_2\text{NO}_2^{(+)}$) are included in the definition of nitrosonium ions in that they are hydrated nitrosonium ions. By predominantly, it is meant that greater than 60 % of the nitrogen in the nitrosating compound is contributed as $\text{NO}^{(+)}$. Thus, it comprises NO-X wherein X is a halogen, OH, O- SO_3H , O- SO_2H , or other inorganic groups such as hexafluorobromate, pyrosulfate, phosphate, hexafluoroplatinate, hexafluorostanate, trisulfate, tetrachloroferrate(III), tetrachloroborate, chlorosulfate, difluorochlorate, fluorosulfate, tetrachloraluminum and tetrafluoroborate, or organic compounds in which the NO is bound to an oxygen or sulfur in the organic molecule. Liquid nitrosating agents such as solutions of nitrosylsulfuric acid (NSA), of nitrosyl chloride (NOCl) and of nitrosyl tetrafluoroborate (NOBF_4) are particularly useful.

Alternatively, under appropriate conditions, the nitrosating agent may be made in situ by adding a high enough concentration of acid to the pulp before or concurrently with a water-soluble inorganic nitrite such as sodium nitrite to acidify the pulp to a pH of less than 4. Also, the water-soluble inorganic nitrite may be reacted with sufficient acid to yield an acidic solution of nitrous acid, which then can be added to the pulp as a nitrosating agent. The acidity of the nitrous acid solution should be such that the resultant pH upon addition to the pulp is in the range of about 1.7 to 4, preferably 1.8 to 3.4. Preferably, the pulp should be preacidified before addition of the nitrous acid solution to a pH of less than 4.

The nitrosating agent is present in a sufficient amount to provide about 0.1 to 1.2 wt.%, preferably 0.1 to 1.0 wt.% active nitrosonium ion $\text{NO}^{(+)}$ on a oven-dried (OD) pulp basis.

The mixing conditions are such that the nitrosating agent and the oxygen are intimately, uniformly and

rapidly contacted with the pulp fiber so that desired reactions occur with the lignin before the $\text{NO}^{(+)}$ becomes inactive, that is, equilibrates to NO_2^- in the water with the pulp. Mixing is preferably done in a high-shear mixer at a pulp consistency of at least 5 weight percent in water, more preferably at medium to high consistency, so as to distribute the agents uniformly and rapidly in the pulp matrix. Mixing intensity must be high enough that the reaction mixture becomes fluidized or fluid-like in behavior in the mixing zone, the nitrosating agent and pulp being contacted in the mixing zone.

The pH at which the pretreatment takes place is 1.7 to 4, preferably 1.8 to 3.4.

The oxygen, which may be added as molecular oxygen, as an oxygen-containing gas such as air or as hydrogen peroxide, must be present at least in a stoichiometric amount. By stoichiometric, it is meant one gram atom of oxygen per gram mole of $\text{NO}^{(+)}$ that is theoretically added to the system. The theoretical amount of $\text{NO}^{(+)}$ added is the amount of $\text{NO}^{(+)}$ moiety in the chemical structure of the nitrosating agent. Thus, undissociated nitrous acid (NO-OH) will have 100% of its nitrogen in the form of $\text{NO}^{(+)}$ and 63.8 wt.% $\text{NO}^{(+)}$ in the molecule.

After the pretreatment with sufficient liquid-phase nitrosating agents under the consistency, acidic, oxygen and mixing conditions of this invention, the treated pulp is optionally washed before treatment with an alkali and oxidative compound according to known alkaline oxidative stage conditions.

The present invention has several advantages, the main advantage being that greater delignification of the pulp can be accomplished with lower cellulose degradation than when the pretreatment is not made. Also, as compared to the use of nitrogen dioxide and nitrogen monoxide which are gases under reaction conditions, improvements in safety and environmental protection associated with not having to handle gases are made with the present invention. Further, the present invention, which requires mixing only liquids and solids, presents fewer complications associated with distribution of reagents and handling equipment than the processes of the prior art which require mixing gases with liquids and solids. Liquid-phase agents are more reactive and selective since there is more efficient mass transfer across the aqueous layer on the pulp fibers.

It is thought that use of nitric acid forming chemicals such as NO_2 , NO_x and nitrate ions of the prior art creates an oxidizing environment that results in cellulose attack by nitric acid oxidation. Thus, both nitration of lignin and degradation of cellulose occur simultaneously because of the occurrence of both nitrating and oxidizing chemical reactions.

It is thought that, since the present process avoids the use of nitric acid forming chemicals and assures reaction of the active $\text{NO}^{(+)}$ before the $\text{NO}^{(+)}$ becomes inactive by equilibrating to NO_2^- in the water with the pulp, the nitrosating chemicals do not cause as much cellulose degradation. The nitrosating chemicals are felt to rapidly nitrosate the lignin structure by introducing NO groups in the lignin to form nitrosolignins without the concurrent formation of nitric acid. The nitrosolignins, in the presence of at least a stoichiometric amount of oxygen, are oxidized to nitrolignins. The nitrolignins, not removed in the optional wash step which can follow, are then efficiently oxidized, hydrolyzed and solubilized in the alkaline oxidation stage.

Details of the Invention

A wide range of pulps can be treated by the methods described in the invention. The lignocellulosic pulp treated by the process of this invention is preferably from a Kraft process but may be from other chemical, semichemical, chemi-mechanical processes, particularly sulfite, soda, high yield Kraft, high yield sulfite or NSSC processes. The pulp may also be from a mechanical or thermomechanical process. Particularly in the case of chemically digested pulp, the pulp generally is washed prior to being fed to subsequent processing (a delignification and bleach sequence) that includes one or more alkaline oxidative stages as well as stages using chlorine, chlorine dioxide, hydrogen peroxide and other bleaching agents.

The pretreatment stage of this invention is inserted in the bleach sequence prior to any of the alkaline oxidative stages, preferably before the first such stage. The pulp that is to be treated in this stage is herein also referred to as "untreated pulp" and the pulp that has been treated in this stage is herein also referred to as "treated pulp".

The consistency of the untreated pulp can vary over a wide range but should be greater than about 5 wt.%. Preferably, the consistency should be in the range of 5 to 30 wt.%, more preferably 8 to 15 wt.%.

The nitrosating agent is liquid-phase, that is, a solution or a pure liquid at ambient temperature and pressure, and is defined as any compound that will freely contribute predominantly active nitrosonium ions ($\text{NO}^{(+)}$) under reaction conditions. For the purposes of this invention, nitroacidium ions ($\text{H}_2\text{NO}_2^{(+)}$) are included in the definition of nitrosonium ions in that they are hydrated nitrosonium ions. By predominantly, it is meant that greater than 60 % of the nitrogen in the nitrosating compound is contributed as $\text{NO}^{(+)}$. Thus, it

comprises NO-X wherein X is a halogen, OH, O-SO₃H, O-SO₂H, or other inorganic groups such as hexafluorobromate, pyrosulfate, phosphate, hexafluoroplatinate, hexafluorostanate, trisulfate, tetrachloroferrate(III), tetrachloroborate, chlorosulfate, difluorochlorate, fluorosulfate, tetrachloraluminum and tetrafluoroborate, or organic compounds in which the NO is bound to an oxygen or sulfur in the organic molecule.

Liquid nitrosating agents such as solutions of nitrosylsulfuric acid (NSA), of nitrosyl chloride (NOCl) and of nitrosyl tetrafluoroborate (NOBF₄) are particularly useful with NSA being the most preferred. Preferably, sulfuric acid is used to dissolve the nitrosating agent.

The pH of the pretreatment must be acidic for the process to be successful. Preferably, the pH is in the range of 1.7 to 4, more preferably 1.8 to 3.4 and most preferably the pH is 1.9 to 3.0. If the pH is too low, cellulose degradation will increase; if too high, pretreatment effectiveness will decrease.

Alternatively, under appropriate conditions, the nitrosating agent may be made in situ by adding a high enough concentration of acid to acidify the pulp to a pH of less than 4, preferably 1.8 to 3.4 and more preferably 1.9 to 3.0, before or concurrently with adding a water-soluble inorganic nitrite such as sodium nitrite. Also, the water-soluble inorganic nitrite may be reacted with sufficient acid to yield an acidic solution of nitrous acid, which then can be added to the pulp as a nitrosating agent. The acidity of the nitrous acid solution should be such that the resultant pH upon addition to the pulp is less than 4, preferably in the range of about 1.8 to 3.4, more preferably 1.9 to 3.0. Preferably, the pulp should be preacidified before addition of the nitrous acid solution to a pH of less than 4.

Preferably, the acid used to dissolve the nitrosating agent or to acidify the pulp or react with the inorganic nitrite should be a strong mineral acid, more preferably a non-oxidizing mineral acid, particularly sulfuric acid.

Preferably, if the pulp is preacidified, the preacidification should be shortly before the nitrosating agent or inorganic nitrite is added under the intense mixing and other limitations of the invention so as to minimize attack of the cellulose by free acid.

The temperature of the pretreatment can be adapted to mill conditions but should be at a temperature that is low, since high temperatures contribute to cellulose degradation, but not so low that the reaction of the active NO⁽⁺⁾ with the lignin is hampered. Preferably the temperature should be in the range of 5° to 80° C. More preferably, the temperature should be 20° to 55° C.

The concentration of NO⁽⁺⁾, the active ingredient in the process, should be 0.1 to 1.2 wt.%, preferably 0.1 to 1.0 wt.% on an OD pulp basis. The upper limit is dictated by the economics of the process. That is to say, when nearly all of the nitrosonium ion receptor moieties in the pulp have reacted with the nitrosating agent, adding more nitrosating agent does not serve a useful purpose. If the concentration is too low, pretreatment effectiveness will be reduced.

The pretreatment must be done under such high-intensity mixing conditions that intimate, uniform and rapid contact is achieved between the nitrosating agent and the lignocellulosic material. Preferably the equipment used should be a high-shear mixer, although any other device known in the art to provide intense enough mixing may be used. A high-shear mixer provides the best way known to the inventors for assuring that the nitrosating agent intimately, uniformly and rapidly contacts the fiber so that it can then react with the lignin that is to be removed before the agent equilibrates to NO₂⁻ species in the water present with the pulp.

When using the high-shear mixer employed in the experiments set forth herein, a tip speed of the mixer blades of 5 to 50 feet/second (ft./sec.) assured intense enough mixing. Actual mixing parameters will vary with the mixer employed, but one skilled in the art will be able to define the parameters for the particular mixer and the pulp type and consistency based on the following. The mixer must provide sufficient shear rate that the reaction mixture becomes fluid-like in behavior so that the chemicals are added uniformly and as rapidly as the reaction itself. The chemicals should be introduced so as to assure uniform distribution of the chemicals in the reactor and preferably at the point of high shear.

The time of mixing can vary over a wide range according to the pulp properties. The time is normally 1 to 900 seconds. Best results occur when conditions are such that the nitrosating agent intimately and uniformly contacts the fiber in the pulp essentially instantaneously (within less than about 15 seconds) upon addition. Additional time to allow full diffusion in the fiber may be used. The diffusion stage may be at lower intensity or tip speed than the initial contacting of the fiber with the nitrosating agent. High intensity mixing may be prolonged to include both the reagent distribution and diffusion phases of the reaction.

Oxygen must be added to the pretreatment vessel for the lignin reactions to occur. Oxygen may be added as molecular oxygen or as an oxygen-containing gas such as air or as a compound such as hydrogen peroxide. While oxygen-containing compounds such as NO_x can be used, they are not preferred since they can cause undesired degradation of the cellulose. The amount of oxygen to be added should be

at least equal to one gram atom per gram mole of $\text{NO}^{(+)}$ present in the nitrosating agent (stoichiometric amount).

Pressure is not critical to the success of the pretreatment process. But, the oxygen pressure must be high enough to assure intimate contact of the oxygen with the pulp during treatment. For example, if the oxygen source is air, then the pressure preferably should be atmospheric pressure to 100 pounds per square inch gauge (psig.). If molecular oxygen is used, a pressure of atmospheric pressure to 40 psig. should be used. In the case of hydrogen peroxide, pressure is not a consideration. The concentration of hydrogen peroxide (100% basis) should be about 0.2 to 5 wt.% based on the OD weight of pulp.

After the pulp has been pretreated with nitrosating agents, the modified pulp preferably is washed with water to remove free acid and soluble metal ions and then is extracted with any oxidative delignification process known in the art. Magnesium compounds may be added after the pretreatment to inhibit the degradation of the cellulose in the oxidative delignification stage. In a typical oxidative delignification that can follow the pretreatment, the pulp can be treated with oxygen at 70° to 120° C for 15 to 60 minutes in the presence of an alkali, the alkali content based on sodium hydroxide being about 2 to 8% on an OD pulp basis and the oxygen pressure being between 50 and 100 psig. The oxygen stage can then be followed by a peroxide stage, a second oxygen stage or a dioxide stage to complete delignification and various washes.

EXAMPLES

The reactor in which the following examples were run was a high-shear, baffled, laboratory mixer. The reactor has four mixing blades (impellers) having the dimensions of 140 millimeters (mm) in width, 21 mm in height and 6 mm in thickness. This makes the diameter of the shaft plus blades about 76 mm (about 3 inches). There are three hollow baffles positioned around the reactor facing the center axis of the reactor. There are 9 holes (1/64 inch diameter) in each baffle. The inlet to the mixer is connected to the holes in the baffles through check valves to permit introduction of liquids and gases through the holes to facilitate uniform distribution of chemicals at the point of high shear (where the blade tips come in close proximity to the baffles) while the mixer is running. The tip speed of the blades is as follows:

Revolutions Per Minute	Tip Speed (m./sec.)
200	0.8 (2.6 ft./sec.)
300	1.2 (3.9 ft./sec.)
1000	4.0 (13.1 ft./sec.)
2000	8.0 (26.2 ft./sec.)
3000	12.0 (39.3 ft./sec.)

All percentages, unless otherwise stated, are based on the oven-dried (OD) weight of the pulp.

All washings with tap water were repeated until the bleach liquor was clear. About 2 washings were required in each case.

Example 1

A. Oxygen Delignification

Unbleached Southern pine softwood pulp (kappa number of 22.1, viscosity of 24 centipoise (cp)) at a 10 wt.% consistency was placed into the reactor and 0.2 wt.% MgSO_4 (0.04% Mg^{++}) was introduced into the reactor. They were mixed at 300 revolutions per minute (rpm). The temperature of the reactor was maintained at 100° C. NaOH (4wt.%) was introduced into the reactor along with oxygen at 100 psig. The delignification took place for 30 minutes. The pH of the bleach liquor was 12 at the end of the delignification. The delignified pulp was washed and air dried. The kappa number of the resulting pulp was determined to be 12.0 and the viscosity was 16.4 cp, which amounts to reductions of 45.7% and 31.7%, respectively.

B. NSA Treatment + Oxygen Delignification

The unbleached pulp of Example 1-A at 10 wt.% consistency was placed in the reactor at 40 ° C. While mixing the pulp at 1000 rpm, 1 wt.% NSA (100% weight basis) was introduced into the reactor along with oxygen gas at 40 psig. The NSA used was 40 wt.% NSA (NOHSO₄), 52.2 wt.% H₂SO₄ and 7.8 wt.% water. After 5 minutes at these conditions, the oxygen was released and the activated pulp was washed. This treated pulp at 10 wt.% consistency was then subjected to the oxygen delignification conditions used in Example 1-A. The kappa number of the resulting pulp was 9.3 and the viscosity was 19.0 cp, which amounts to reductions of 57.9% and 20.8%, respectively.

Example 2A. Oxygen Delignification

Unbleached Southern pine pulp (kappa number of 26.5 and viscosity of 29.0 cp) at a 10 wt.% consistency was subjected to oxygen delignification in a manner similar to Example 1-A. In this case the Mg⁺⁺ concentration was 0.2% and NaOH concentration was 4%. The temperature and the oxygen pressure in the reactor were maintained at 100 ° C and 100 psig oxygen pressure, respectively. The pulp was mixed at 300 rpm and the delignification took place for 30 minutes. The pulp was washed and air dried. The kappa number and the viscosity of the delignified pulp were 14.0 and 24.0 cp, respectively. The reductions in kappa number and viscosity as compared to the unbleached pulp were 47.2% and 17.2%, respectively.

B. NSA Pretreatment + Oxygen Delignification

The unbleached pulp of Example 2-A at 10 wt.% consistency was pretreated with 2.3 wt.% NSA at 40 ° C and 40 psig. oxygen pressure in the reactor for 5 minutes in the manner indicated in Example 1-B. The pulp was then washed with tap water and subjected to oxygen delignification at conditions identical to Example 2-A. The kappa number of the delignified pulp was 11.8 and its viscosity was 28.0 cp, which amounts to reductions of 52.5% and 3.4%, respectively.

C. NO₂ Pretreatment + Oxygen Delignification

Pretreatment of pulp used in Example 2-A was conducted in the reactor with 2.3% NO₂ gas at 40 ° C and atmospheric pressure in the manner indicated in Example 2-B. No oxygen was present in the pretreatment stage. The activated pulp was washed with tap water and then delignified with oxygen at conditions indicated in Example 2-A. The kappa number of the delignified pulp was 15.5 and the viscosity was 27.3 cp, a reduction of 27.3% and 5.9%, respectively.

Example 3Effect of NSA Concentration

Southern pine brownstock pulp (kappa number of 24.0 and viscosity of 27.8 cp) at 10% consistency was delignified with oxygen in a manner similar to Example 1-A. The conditions of the oxygen stage were as follows:

Temperature = 100 ° C

Pressure = 100 psig oxygen pressure

Impeller speed = 200 rpm

time = 30 minutes

NaOH concentration = 5.5 wt.%

Mg⁺⁺ (in the form of MgSO₄) = 0.16 wt.%

The delignified pulp was washed and air dried. The kappa number at the end of this stage was 12.9 and

the viscosity was 21.5 cp, a 46.3% and a 22.7% reduction, respectively. The selectivity (change in viscosity per unit change in kappa number) was 0.57.

Experiments in which the untreated pulp indicated above was pretreated using 0.5%, 1.5% and 2% NSA were then run. In each case, Oxygen at 40 psig. was used, the temperature was 40 °C and impeller speed 3000 rpm for 5 sec. and 200 rpm for 15 minutes. Each pretreatment was followed by washing followed by an identical oxygen delignification stage as indicated above. The results are summarized in Table 1.

Table 1

Effect of NSA Concentration							
NSA Conc. %	Kappa No.	% Red	Visc. cp	% Red	Select. cp	pH at End of	
						Pretreat.	Oxygen
Brownstock	24.0	-	27.8	-	-	-	-
0	12.9	46.3	21.5	22.7	0.57	-	11.8
0.5	13.5	43.8	22.1	20.5	0.54	5.7	12.0
1	11.3	52.9	24.5	11.9	0.26	2.1	12.0
2	10.4	56.7	24.9	10.4	0.21	1.9	11.7

Example 4

Pretreatments were done on Southern pine brownstock pulp (kappa number of 26.5 and viscosity of 29.0 cp) at 10% consistency with 1 wt.% NSA the reactor at conditions similar to that indicated in Example 1B (1000 rpm for 5 minutes). Two identical pretreatments were carried out and each was subjected to an identical oxygen stage to determine the reproducibility of the results. The conditions of the oxygen stage are summarized below.

Temperature = 100 °C

Pressure = 100 psig oxygen pressure

time = 30 minutes

NaOH concentration = 4 wt. %

Mg⁺⁺ = 0.16 wt. %

impeller speed = 200 rpm

consistency = 10 wt. %

The results are summarized in Table 2.

Table 2

Reproducibility					
Exper.	Kappa No.	% Red	Viscosity cp	% Red	Selectivity (cp)
Brownstock	26.5	-	29.0	-	-
1	13.1	50.6	27.1	6.6	0.14
2	13.8	47.9	26.0	10.3	0.24

Example 5

Effect of Mixing

In the NSA pretreatment stage, three different mixing conditions were used to determine the effect of mixing intensity. Mixing conditions were as follows:

5 Experiment 1 - Mixing at 1000 rpm for 5 mins.

Experiment 2 - Mixing at 3000 rpm for 5 secs. and then at 200 rpm for 15 mins.

Experiment 3 - Mixing at 200 rpm for 5 mins.

10 In each of the above experiments, 1 wt.% NSA was used in the pretreatment stage along with oxygen at 40 psig pressure at a temperature of 40 °C. Each pretreatment was followed by washing followed by an identical oxygen delignification stage. Results were compared with the results from Experiment 4 in which the same oxygen-stage conditions were used but without pretreatment. The results are summarized in Table 3.

Table 3

Exp. #	Kappa #	% Red	Visc. cp	% Red	Select. cp	pH at End of	
						Pretreat.	Oxygen
Brownstock	27.9	-	29.4	-	-	-	-
1	13.7	50.9	26.5	9.9	0.20	2.0	10.6
2	13.7	50.9	26.6	9.5	0.20	2.1	10.5
3	15.3	45.2	24.6	16.3	0.38	2.1	10.9
4 *	15.2	45.5	22.6	23.1	0.54	-	11.8

*no pretreatment

Example 6Variation of Viscosity With Kappa Number With and Without Pretreatment

35 NaOH concentrations of 4%, 6% and 8% were used in the oxygen delignification stage. With the exception of the alkaline concentration all other conditions were similar to those used in Example 3. Three identical pretreatments were done with 1 wt.% NSA on Southern Pine pulp as indicated in Experiment 2 of Example 5. The pretreatments were followed by washing followed by an oxygen delignification stage with
 40 NaOH concentrations of 4%, 6% and 8% as done above. The results are presented in Table 4.

Table 4

Variation of Viscosity With Kappa Number						
					pH at End of	
NaOH Conc.	Kappa No.	% Red	Viscosity (cp)	% Red	Pre-stage	Oxygen
Brownstock	27.9	-	29.4	-	-	-
Oxygen Delignification						
4%	15.2	45.5	22.6	23.1	-	11.8
6%	14.5	48.0	20.7	29.6	-	12.2
8%	13.5	51.6	16.9	42.5	-	12.5
NSA Pretreatment/Oxygen Delignification						
4%	13.7	50.9	26.6	9.5	2.1	10.5
6%	11.0	60.6	24.0	18.4	2.1	12.0
8%	10.8	61.3	21.5	26.9	2.1	12.3

Example 7Pretreatment with Nitrosation Chemicals

The following pretreatments were conducted with $\text{NaNO}_2/\text{HNO}_3$, NSA and $\text{NaNO}_2/\text{H}_2\text{SO}_4$. Each pretreatment was followed by washing followed by an identical oxygen delignification stage, according to conditions indicated in Example 4.

The pretreatments were done according to conditions indicated in Experiment 2 of Example 5 (mixing at 3000 rpm for 5 seconds and then at 200 rpm for 15 minutes. In Experiment 3, the pH after the pretreatment with NSA was 2.1, and the pH after the oxygen delignification was 10.5. In Experiment 4, 5, 6 and 8, the pulp was first acidified and then the sodium nitrite was added. In Experiment 7 the sodium nitrite was premixed with sufficient nitric acid and then added to the pulp. In Experiment 4, the pH after pretreatment was 1.9, and the pH after oxygen delignification was 11.9. In Experiment 5, the pH's, respectively, were 2.1 and 11.7. In Experiment 6, the pH's, respectively, were 1.8 and 10.3. In Experiment 7, the pH's, respectively, were 1.9 and 11.5. In Experiment 8, the pH's, respectively, were 1.9 and 11.4. The results are summarized in Table 5.

Table 5

Nitrosation Followed by Oxygen Delignification						
No.	Type	Kappa #	Red	Visc. (cp)	% Red	Select.
1	Brownstock	27.9	-	29.4	-	-
2	Oxygen	15.2	45.5	22.6	23.1	0.54
3	1% NSA/Oxygen	13.7	50.9	26.6	9.5	0.20
4	NaNO ₂ /HNO ₃ *	16.4	41.2	23.9	18.7	0.48
	(equivalent to NSA in 3)					
5	NaNO ₂ /H ₂ SO ₄ **	17.7	36.6	25.6	12.9	0.37
	(equivalent to NSA in 3)					
6	1% NaNO ₂ /3% HNO ₃	14.7	47.3	25.5	13.3	0.30
7	1% NaNO ₂ /3% HNO ₃	14.3	48.7	24.6	16.3	0.35
	(premixed)					
8	1% NaNO ₂ /2.3% H ₂ SO ₄	14.3	48.7	24.2	17.7	0.38

* 0.544 wt.% NaNO₂/2.17 wt.% HNO₃ is equivalent to 1 wt.% NSA in reactive species and normality.

** 0.544 wt.% NaNO₂/1.69 wt.% H₂SO₄ is equivalent to 1 wt.% NSA in reactive species and normality.

Example 8

Effect of Temperature in the Pretreatment Stage

Pretreatments were conducted with 1 wt.% NSA at 25 °C, 40 °C and 48 °C at the conditions indicated in Experiment 2 of Example 5, except for the temperature. Each pretreatment was followed by washing followed by an oxygen stage at the conditions indicated in Example 4. The results are summarized in Table 6.

Table 6

Effect of Temperature in the Pretreatment Stage							
Pretreat (Temp. °C)	Kappa #	% Red	Visc. (cp)	% Red	Select. (cp)	pH at End of	
						Pre	Oxygen
Brownstock	27.9	-	29.4	-	-	-	-
25	14.9	46.6	27.2	7.5	0.17	2.0	10.4
40	13.7	50.9	26.6	9.5	0.20	2.1	10.5
48	16.0	42.7	24.9	15.3	0.38	2.1	10.8
Oxygen	15.2	45.5	22.6	23.1	0.54	-	-

Claims

1. A process for delignifying and bleaching lignocellulosic pulp having a consistency in water of at least 5 weight percent and containing residual lignin, the process having one or more alkaline oxidative stages in a bleach sequence and being characterised by the inclusion of a pretreatment stage prior to the one or more alkaline oxidative stages, the pretreatment stage comprising contacting the pulp under appropriate mixing conditions for a sufficient time with a nitrosating agent and at least a stoichiometric amount of oxygen at a pH of 1.7 to 4 wherein the nitrosating agent is a liquid-phase composition that freely contributes predominantly nitrosonium ions ($\text{NO}^{(+)}$) and is in sufficient amount to contribute about 0.1 to 1.2 weight percent active $\text{NO}^{(+)}$ on an oven-dried pulp basis under reaction conditions, the mixing conditions being such that the nitrosating agent and oxygen are intimately, uniformly and rapidly contacted with the pulp fiber so that they can react with the lignin before the $\text{NO}^{(+)}$ becomes inactive.

2. A process according to claim 1 wherein the nitrosating agent is NO-X wherein X is a halogen, OH, $\text{O-SO}_3\text{H}$, $\text{O-SO}_2\text{H}$, or other inorganic groups such as hexafluorobromate, pyrosulfate, phosphate, hexafluoroplatinate, hexafluorostanate, trisulfate, tetrachloroferrate(III), tetrachloroborate, chlorosulfate, difluorochlorate, fluorosulfate, tetrachloroaluminate and tetrafluoroborate, or organic compounds in which the NO is bound to an oxygen or sulfur in the organic molecule.

3. A process according to claim 2 wherein the nitrosating agent is nitrosylsulfuric acid, nitrosyl chloride or nitrosyl tetrafluoroborate.

4. A process according to any one of the preceding claims wherein the pH is 1.8 to 3.4.

5. A process according to any one of the preceding claims wherein the pretreatment stage is operated at a temperature of 5° to 80° C.

6. A process according to any one of the preceding claims wherein the mixing is performed in a high-shear mixer operated so as to create fluid-like conditions at points of high-shear and the chemicals are added at the points of high-shear.

7. A process according to any one of claims 1 to 6 wherein the oxygen is introduced as molecular oxygen and the pretreatment is operated at a pressure of about atmospheric pressure to 40 pounds per square inch gauge.

8. A process according to any one of claims 1 to 6 wherein the oxygen is introduced as air and the pressure is about atmospheric pressure to 100 pounds per square inch gauge.

9. A process according to any one of claims 1 to 6 wherein the oxygen is introduced as hydrogen peroxide at a concentration of about 0.2 to 5 weight percent hydrogen peroxide (100 percent basis) based on the oven-dried weight of pulp.

10. A process according to any one of the preceding claims wherein the pulp consistency is about 5 to 30 weight percent.

11. A process for delignifying and bleaching lignocellulosic pulp having a consistency in water of at least 5 weight percent and containing residual lignin, the process having one or more alkaline oxidative stages in a bleach sequence and being characterised by the inclusion of a pretreatment stage prior to the one or more alkaline oxidative stages, the pretreatment stage comprising contacting the pulp under appropriate mixing conditions for a sufficient time with a nitrosating agent and at least a stoichiometric amount of oxygen wherein the nitrosating agent is made in situ by acidifying the pulp to a pH of 1.7 to 4 before or concurrently with the addition of sufficient water soluble inorganic nitrite to provide about 0.1 to 1.2 weight percent active $\text{NO}^{(+)}$ on an oven-dried pulp basis, the mixing conditions being such that the nitrosating agent produced and the oxygen are intimately, uniformly and rapidly contacted with the pulp fiber so that they can react with the lignin before the $\text{NO}^{(+)}$ becomes inactive.

12. A process for delignifying and bleaching lignocellulosic pulp having a consistency in water of at least 5 weight percent and containing residual lignin, the process having one or more alkaline oxidative stages in a bleach sequence and being characterised by the inclusion of a pretreatment stage prior to the one or more alkaline oxidative stages, the pretreatment stage comprising contacting the pulp under appropriate mixing conditions for a sufficient time with a nitrosating agent and at least a stoichiometric amount of oxygen wherein the nitrosating agent is first made by reacting sufficient acid with water soluble inorganic nitrite so that when the nitrosating agent is added to the pulp the resultant pH will be 1.7 to 4 and the nitrosating agent is added in sufficient amount to the pulp to provide about 0.1 to 1.2 weight percent active $\text{NO}^{(+)}$ on a dry pulp basis, the mixing conditions being such that the nitrosating agent produced and the oxygen are intimately, uniformly and rapidly contacted with the pulp fiber so that they can react with the lignin before the $\text{NO}^{(+)}$ becomes inactive.