METHOD AND CHEMICAL COMPOSITIONS TO IMPROVE EFFICIENCY OF CHEMICAL PULPING

Applicant: NALCO COMPANY, Naperville, IL (US)
Inventors: Prasad Y. Duggirala, Naperville, IL (US); Sergey M. Shevchenko, Naperville, IL (US)
Assignee: NALCO COMPANY, Naperville, IL (US)

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USPC 162/80

The invention provides methods and compositions for enhancing the digestion of pulp in a chemical pulping process. The method uses ultra-low, economically feasible dosages of BH applied right before the pulping process begins, in a stable alkaline solution fed into white liquor line, to improve the process by saving pulping chemicals, increasing pulp brightness and yield and reducing the kappa number.
FIG. 1

White liquor (WL) / Total liquor (TL), %

- WL/TL Data
- Average

Trial begins Trial ends

Time, days

0 2 4 6 8 10
% Alkali savings in a trial with 1.5 lb/t product; one day

Notice: if the data from digesters 4, 8 and 11 (cooking differently) are eliminated, the saving of white liquor is 6% = 744 gal

FIG. 2
METHOD AND CHEMICAL COMPOSITIONS TO IMPROVE EFFICIENCY OF CHEMICAL PULPING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation in part of co-pending U.S. patent application Ser. No. 13/839,091 filed on Mar. 15, 2013.

[0002] This application is also a continuation in part of co-pending U.S. patent application Ser. No. 12/400,326 filed on Mar. 9, 2009.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT


BACKGROUND OF THE INVENTION

[0004] The invention relates to compositions, methods, and apparatuses for improving the efficiency of chemical pulping. Chemical pulping with (kraft process) and without (alkaline or soda process) sodium sulfide can be enhanced by certain additives such as 9,10-anthraquinone (AQ) or sodium polysulfide. Such additives provide energy and chemical savings during the pulping process and chemical savings in subsequent bleaching stages. This is achieved, in particular, by delivering lower kappa numbers and higher yields that allow pulping at lower temperatures/shorter times and bleaching with lesser chemicals. However, the existing additives have serious shortcomings that warrant further development in this area. Thus, polysulfide is not quite efficient and applied in large quantities; AQ is currently restricted if not completely eliminated due to environmental and health regulations. As a result there is clear utility in a novel additive that can substitute in part or in full for AQ in chemical (soda and kraft) pulping.

[0005] The art described in this section is not intended to constitute an admission that any patent, publication or other information referred to herein is "prior art" with respect to this invention, unless specifically designated as such. In addition, this section should not be construed to mean that a search has been made or that no other pertinent information as defined in 37 CFR §1.56(a) exists.

BRIEF SUMMARY OF THE INVENTION

[0006] To satisfy the long-felt but unsolved needs identified above, at least one embodiment of the invention is directed towards a process for digesting pulp. The method comprising the addition of a composition to pulp undergoing a delignification process, the composition comprising a small dosage of borohydride (BH) (sodium borohydride preferred) relative to the oven dried mass of the pulp. The composition may be added to white liquor and fed to the digester with the liquor before the temperature ramping begins. The BH may be in the form of an alkaline solution in water. The amount of BH relative to oven dried pulp may be less than 0.1% on the active base. The BH solution that is the product added to the mill liquor may be sufficiently alkaline so it is stable under normal conditions and does not release hydrogen. The dosage of BH may be in an amount insufficient to be effective in bleaching the pulp.

[0007] At least one embodiment of the invention is directed towards a method for digesting wood chips. The method comprises the addition of a composition to a lignin bearing substrate in a pulping process and then applying to the substrate a subsequent bleaching step. The composition comprises a small dosage of BH relative to the oven dried mass of substrate. The BH is dosed at a point in the pulping process where there has been no black liquor in contact with the substrate, and where no more than at least 0.001%-10% or more of less than half of the hemicellulose originally present in the wood chip form of the substrate has been separated from the substrate. The dose is in an amount high enough to selectively reduce at least 0.001%-10% or more of less of the lignin alpha-carbonyl groups in substrate thereby making them more susceptible to subsequent easyquinone methide beta-O-4 bond splitting during pulping process, but not as high as it would substantially deactivate at least 0.001%-10% or more of less of the chromophores in the lignin by itself. The bleaching step involves adding a dosage of bleach no greater than an amount sufficient to cause the resulting paper stock to have been substantially whitened in the absence of AQ but for the presence of the low dose BH, and wherein the resulting paper stock is whitened.

[0008] At least one embodiment of the invention may improve soda or kraft pulping. The method may comprise the step of adding a composition to pulp liquor comprising sodium borohydride in alkaline prior to pulping; the method provides fresh white liquor savings, decreased kappa number, increased brightness, lower rejects and higher yield of pulp. The composition may comprise 10-40% alkaline and 5-25% borohydride. The method may further comprise adding a surfactant to the pulp. The method may further comprise adding a polysulfide to the pulp.

[0009] The small dosage may be characterized as causing the BH to selectively attack functional groups in lignin in substructures critically important for accelerated further delignification in the pulping process and passivating hemicellulosic towards chemical degradation in the same process. The method may exclude using BH in a dosage sufficient to bleach the pulp.

[0010] Additional features and advantages are described herein, and will be apparent from, the following Detailed Description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] A detailed description of the invention is hereafter described with specific reference being made to the drawings in which:

[0012] FIG. 1. is a raw data graph of white liquor/total liquor ratio; a 3-day trial through 9-day period.

[0013] FIG. 2. is a graph of % alkaline savings in a trial with 1.5 lb/t product (0.07% as product, 0.008% as actives) through one day.

[0014] For the purposes of this disclosure, like reference numerals in the figures shall refer to like features unless otherwise indicated. The drawings are only an exemplification of the principles of the invention and are not intended to limit the invention to the particular embodiments illustrated.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The following definitions are provided to determine how terms used in this application, and in particular how the claims, are to be construed. The organization of the definitions is for convenience only and is not intended to limit any of the definitions to any particular category.
“AQ” means 9,10-anthraquinone.

“BH” means borohydride, it includes but is not limited to BH ions appended to any anion such as but not limited to alkali metals and alkali earth metals, it may be in the form of a solid and/or solution.

“Bulk Delignification Stage” means the phase of kraft cooking in which the major portion of the delignification occurs as a first order reaction and with a selectivity that is high compared to the initial delignification, it is further described in the textbook Handbook of Pulp & Paper Technology, by G. A. Smook, Angus Wilde, Vancouver, BC, (1990), generally and in particular pp. 75-85.

“Delignification” means one or more processes of removing lignin from wood at any point in a papermaking process.

“Bleaching” means one or more processes of removing color from pulp or paper by the removal and/or chemical alteration of chromophore groups from pulp or paper, bleaching may include but is not limited to the removal or alteration of at least some of the lignin originally present in the pulp or paper, bleaching may involve but is not limited to the addition of strong oxidizing and/or reducing agents such as chlorine dioxide.

“Whitening” means the process of removing most color in paper or pulp, representative methods of measuring whiteness include but are not limited to ASTM E313 and the description in Measurement and Control of the Optical Properties of Paper, by Technidyne Corporation, New Albany, In., (1996), generally and in particular pp. 16-18.

“Small Dose” or “Low Dose” means an amount of less than 0.25% actives relative to the oven dried mass of a pulp material, it includes but is not limited to a dosage of as low as (or lower than) 0.05-0.5% product (which may be 0.005-0.06% actives in a typical 10-12% alkaline solution) relative to oven dried pulp.

“Passivate” means to render a first material substantially, more, and/or essentially passive or non-reactive in relation to a second material prior to contact between the two materials, where but for the passivation the first and second materials would be reactive when in contact.

“Consisting Essentially of” means that the methods and compositions may include additional steps, components, ingredients or the like, but only if the additional steps, components and/or ingredients do not materially alter the basic and novel characteristics of the claimed methods and compositions.

“Paper Stock” means a substrate that has completed the pulping process and is or will be ready to be fed into a paper machine, it is described in more detail in Handbook for Pulp and Paper Technologists, 3rd Edition, by Gary A. Smook, Angus Wilde Publications Inc., (2002) in general and in particular pp. 190-204.

“Paper Product” means the end product of a papermaking process. It includes but is not limited to writing and/or graphic paper, printer paper, paper tissue, cardboard, paperboard, and packaging paper.

“Papermaking process” means any portion of a method of making paper products from wood pulp comprising forming an aqueous cellulosic papermaking furnish, draining the furnish to form a sheet and drying the sheet. The steps of forming the papermaking furnish, draining and drying may be carried out in any conventional manner generally known to those skilled in the art. The papermaking process may also include a pulping stage, i.e. making pulp from a lignocellulosic raw material and bleaching stage, i.e. chemical treatment of the pulp for brightness improvement, papermaking is further described in the reference Handbook for Pulp and Paper Technologists, 3rd Edition, by Gary A. Smook, Angus Wilde Publications Inc., (2002) and The NALCO Water Handbook (3rd Edition), by Daniel Flynn, McGraw Hill (2009) in general and in particular pp. 32.1-32.44.

“Substrate” means a mass containing paper/cellulosic fibers going through or having gone through any point in a papermaking process, substrates includes wood, wood chips, pulp, paper stock, wet web, paper mat, slurry, paper sheet, and paper products.

“Surfactant” is a broad term which includes anionic, nonionic, cationic, and zwitterionic surfactants. Enabling descriptions of surfactants are stated in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, volume 8, pages 900-912, and in McCutcheon’s Emulsifiers and Detergents, both of which are incorporated herein by reference.

“Water Soluble” means materials that are soluble in water to at least 3%, by weight, at 25 degrees C.

In the event that the above definitions or a description stated elsewhere in this application is inconsistent with a meaning (explicit or implicit) which is commonly used, in a dictionary, or stated in a source incorporated by reference into this application, the application and the claim terms in particular are understood to be construed according to the definition or description in this application, and not according to the common definition, dictionary definition, or the definition that was incorporated by reference. In light of the above, in the event that a term can only be understood if it is construed by a dictionary, if the term is explained or defined in any of: Measurement and Control of the Optical Properties of Paper, by Technidyne Corporation, New Albany, Ind., (1996), Handbook for Pulp & Paper Technologists (3rd Edition), by Gary A. Smook, Angus Wilde Publications Inc., (2002), and the Kirk-Othmer Encyclopedia of Chemical Technology, 5th Edition, (2005), (Published by Wiley, John & Sons, Inc.) this definition (whose precedence is in order of their respective sequence) shall control how the term is to be defined in the claims.

In at least one embodiment a composition comprising a small quantity of reductive product is added to a substrate of a pulping process to save fresh white liquor, decrease kappa number and increase brightness and yield of pulp. The composition may be added before the alkaline pulping process, including kraft pulping process. The addition may result in substantial chemicals savings. The composition may comprise a borohydride composition. The borohydride composition may contain borohydride in a stabilized form (i.e. that is in a form that allows less than 10% activity loss after no less than 3 months under normal conditions). The borohydride composition may contain sodium borohydride. A representative example of the borohydride composition is the commercially available product Boral sold by Dow.

The composition may be fed into a substrate via white liquor at the very early stage of the pulping process. The effect is achieved through early lignin activation and hemicellulose stabilization at the stage of temperature ramping. Borohydride (BH) is a strong reductive agent that reacts with carbonyl groups in lignin and hemicelluloses before the bulk stage of pulping providing additional avenues for lignin depolymerization at the latter stages of pulping. It appears that contrary to how it performs at high dosages, at low dosages BH selectively attacks functional groups in pulp, thus acti-
vating e lignin and passivizing hemicelluloses relative to subsequent reactions before and through the bulk stage. This is why it is unexpectedly active at very small doses.

[0034] While BH has been known to be effective in the pulp and paper industry, its actual use has been limited to mechan- ical pulp bleaching, where it role normally was just to reduce the negative effect of oxidation of another component of the bleaching composition, air-sensitive sodium hypochlorite. For example, the prior art article: Brightness: "Premix I: A novel process for improved bleaching of mechanical pulps using a mixture of reductively active agents", by Wasshausen et al., Pulp and Paper Canada 107, 3, pp. 44-47 (2006) and European Patent Document EP 1418269 A1 describe how BH has been used in hypochlorite bleaching under neutral to slightly acidic conditions. In these prior art applications BH’s role is unlike that in this invention. In the prior art BH is used in reducing oxidized forms of sulfite such as bisulfite into hypochlorite; has no reaction with wood components thus providing no hint or suggestion of its benefit to pulping.

[0035] As described in the article: “DBI” bleaching of recycled fibers for the production of towel and napkin grades, by Rangamannar et al., TAPPI Engineering, Pulping and Environmental Conference, Philadelphia, Pa., United States, Aug. 28-31, 2005 (2005), BH has also been added as a bleaching agent to pulp and as an activator in oxygen delignification (an oxidative process). All these applications, however, require relatively large doses of BH to achieve any measurable bleaching effect. Because BH’s thermodynamic stoichiometry is different at low dosages (in pulp, activation of selected groups towards following reactions) than it is at these higher dosages (direct change in the color of the materials through lignin removal and reduction of maximum, possible chromophore groups as a sole agent, regardless of any following processes) it preferentially reacts with different materials at low dosages than it is known to react in these prior art references.

[0036] The ability of BH to replace, to some extent, the functionality of AQ in kraft and soda pulping is quite unexpected. BH, unlike AQ, is not a catalyst involved in a perpetual cycle but an immediately consumed pulp activator. This led to universal but incorrect assumption that a high dose of BH is always required to achieve a measurable effect. Considering the cost of the treatment, this deemed the technology opposite that of U.S. Pat. No. 3,617,431. In at least one embodiment the method excludes using the material in black liquor and at high temperatures at the feeding stage (over 60° F.).

[0037] In at least one embodiment, a soda or kraft pulping process is improved by feeding a composition comprising BH in alkaline (including but not limited to Borol, Venpure or any other commercial or ad hoc liquid containing 10-25% (or higher or lower) NaOH in 20-40% (or higher or lower) NaOH as a potential range for the compositions) into white liquor prior to pulping that eventually provides decreased kappa number, increased brightness, lower rejects and higher yield of pulp, also saving process chemicals (white liquor) as compared to the conventional technology. Feeding the composition in a liquid form provides convenience in delivery, safety, and, most important, fast homogenization in white liquor thus ensuring even and efficient delivery to wood chips and fast if not immediate reaction that is required for the efficiency of the process.

[0038] In at least one embodiment the method includes also adding one or more surfactants to the pulp. The surfactant(s) may be mixed into (be within) the composition and/or may be fed separately to the pulp. The latter method is preferred due to the salting effect of relatively concentrated alkali in the liquid BH formulation. The surfactant may be ionic, anionic, polyvalent, amphoteric, cationic, anionic, and any combination thereof. It was found in a separate stability test (keeping a solution of the two components at elevated temperature and measuring residual active BH by the means of acidification and comparing the volume of evolved hydrogen with the one in a control sample) that both components are compatible.

[0039] In at least one embodiment the method excludes using the material in black liquor and at high temperatures at the feeding stage (over 60° F.).
the claims, it is believed that the invention operates by applying a strong reductive chemical or combination of chemicals in white liquor at an early stage of the pulping process. This affects the alkaline pulping process, including a Kraft pulping process through lignin activation and carbohydrate stabilization; as a result, less white liquor chemicals are required. [0046] Moreover, an important finding that illustrates the difference between this invention and prior art is that the actual application of low doses of BH results in well documented chemicals savings comparable to those achieved with AQ, and at a commercially viable (comparable) cost. This is neither discovered nor in any way anticipated in prior art for a simple reason of the technology never applied at a mill. This effect was demonstrated in real-life applications and was confirmed in several runs. The invention uses a very small, economical quantity of the product. The effect is achieved at a very early stage of the pulping process. BH is a strong reductive agent that immediately reacts with functional groups in lignin and hemicelluloses providing additional avenues for lignin depolymerization at further stages of the pulping process and reducing carbohydrate degradation thus increasing yield and reducing amount of alkalii required to neutralize degradation products. [0047] The invention leads in a number of unexpected results. It provides safety and efficiency that was never achieved before because the mechanism for the operation of BH in pulp was not properly understood in the prior art. It was a common misconception in regards to the mechanism and application of BH that resulted in all the studies limited by high doses of borohydride (>0.5% actives to oven dried pulp). For example, in U.S. Pat. No. 3,042,575 its Example 3, it shows that for solid BH, there is no difference between the use of 0% BH and 0.2% and only when up to and in excess of 0.4% any effect measured. However, by using a BH solution as proposed in the Invention even much smaller dosages are effective. [0048] In addition, the small dosages of BH impart a pronounced positive effect on the actual pulping process at doses that, unexpectedly, differ from those suggested in the prior art based on the laboratory experiments, by the order of magnitude. This makes the difference that allows commercial application of the technology. As additional benefits, the proposed technology assures safety and convenience of the operation. Moreover, in low boron presence lignin system that eliminates potential regulatory and recovery issues (boron content as element in 17.3% pulp after the oxygen delignification (Eo) stage in a trial with the additive pulp after a mill trial at 1.7 lb/100 c.d. as described below was found at 457 ppb). [0049] At least one embodiment of the invention imparts a benefit that becomes apparent after cooking. Typically, most of the lignin is removed during cooking and the residual lignin is removed/alteried by one or more bleaching steps. In at least one embodiment the low dose BH so selectively modifies the lignin that a dosage of bleaching agent that would otherwise be too low to effectively whiten the pulp does indeed whiten the pulp when the pulp has been treated by low dose BH. [0050] In at least one embodiment the low dose BH selectively reduces a few alpha-carbonyls in native lignin that makes them susceptible to subsequent easy quinone methide beta-O-4 bond splitting. But for this selective reduction such structures would remain intact and deter lignin depolymerization. But for this selective reaction with low dose BH, the carbonyl groups would have become more chemically stable would have contributed significantly to the presence of residual lignin in pulp. [0051] In at least one embodiment particular care is taken in the procedure of BH addition to effect superior results. The scientific article Kraft Pulping with Addition of Sodium Borohydride, by Gugnin et al., Izvestiya Vysshikh Uchebnykh Zavedenii, Lesnoi Zhurnal, 7 (5), 160-6 (1964) teaches that under cooking conditions BH reacts with wood at 110° and that when the temperature reaches 135° a large fraction of the additive is already consumed,” “in the absence of wood, NaBH₄ was completely decomposed by heating with white liquor to 135°.” In fact, the reaction is expected and as can be seen in the Examples Section of this Application, there is unlikely any borohydride left at the beginning of the bulk stage. What was missed by the prior art however is that there is a higher rate of reduction of dissolved wood components as compared to the solid fraction and therefore a need of consistent effort to deliver BH to wood at as low temperature as possible and with the least possible quantity of dissolved organics in the liquor. At the very least, it means feeding BH with white liquor to chips at the lowest temperature available. Similarly the article Sulfite Cooking with the Addition of Reducing Agents, III. The Effect of Added Sodium Borohydride, by Anrell et al., Tappi Journal, 46, 209-15 (1963) teaches that for cooking at 1% or greater dosage optimum conditions is at 80° and 30-min. treatment time. This is in contrast to the highly effective low dosages used in the Invention. Examples [0052] The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the invention. In particular, the examples demonstrate representative examples of principles innate to the invention and these principles are not strictly limited to the specific condition recited in these examples. As a result it should be understood that the invention encompasses various changes and modifications to the examples described herein and such changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims. [0053] Laboratory testing was conducted with the digester screening of pulping additives. Material: [0054] Hardwood chips (sorted, from a mill in Wisconsin), conditioned in a constant temperature and humidity (CTH) room for >4 days, consistency 92%. Liquor/Wood: [0055] 8:1 ratio, with 16% alkali and 33% sulfidity charge. The doses were based on actives unless stated otherwise. Cooking Protocol: [0056] Rotating 250 ml stainless steel digesters, 85°C. for 20 min., then ramping to 170° C. in 50 min. and keeping the samples at 170° C. for additional 20 min. (variations in the protocol are indicated in the tables). After cooking, the digesters were cooled with running water, the pulp disinte-
grated in a blender and washed. The pulp samples were equili-
brated in the CTH room and kappa numbers measured
according to TAPPI test method T 236. Handsheets were
made, and brightness measured on air-dried sheets using a
Technodyne instrument. BH was added to the white liquor as
Borol (Rohn & Haas, 12% sodium borohydride; 40% sodium
hydroxide) with pH adjustment.

Positive trends were observed in a series of tests on
chips (Tables 1-3). The experiments revealed that presence
of large quantities of black liquor in a model pulping system
from the very beginning decreases the effect consistently
observed in experiments with white liquor alone (Table 4);
this is why feeding the product into white liquor is preferred.
This method was actually implemented during a mill trial.

TABLE 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>18.36</td>
</tr>
<tr>
<td>0.0125% NaBH4</td>
<td>17.98</td>
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<tr>
<td>0.025% NaBH4</td>
<td>17.84</td>
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</tbody>
</table>

TABLE 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>17.19</td>
</tr>
<tr>
<td>0.0125% NaBH4</td>
<td>16.26</td>
</tr>
</tbody>
</table>

TABLE 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa #</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>17.04</td>
<td>29.77</td>
</tr>
<tr>
<td>0.0125% NaBH4</td>
<td>16.69</td>
<td>30.43</td>
</tr>
<tr>
<td>0.025% NaBH4</td>
<td>16.05</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4

Effect of added black liquor (BL) on performance (Borol added to white liquor; water of BL added; alkalinity 32%, sulfidity 33%,
ramping 50-170° C. for 1 hr., 170° C. for 1 hr.).

<table>
<thead>
<tr>
<th>Sample</th>
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</thead>
<tbody>
<tr>
<td>Control - water</td>
<td>18.47</td>
</tr>
<tr>
<td>Control - BL</td>
<td>18.40</td>
</tr>
</tbody>
</table>

TABLE 4-continued

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa #</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05% NaBH4 - water</td>
<td>17.09</td>
</tr>
<tr>
<td>0.05% NaBH4 - BL</td>
<td>18.54</td>
</tr>
</tbody>
</table>

Mill trials conducted at an unbleached pulp mill in
kraft digester brought positive results in terms of the kappa
number and economy of pulping chemicals (white liquor
savings up to 70% of those achieved with AQ) at the dose
1.5-2 lb/t trial product per t o.d. pulp (12% active sodium
borohydride solution that corresponds to 0.008-0.011% actives on pulp).

Each trial lasted several days to observe benefits of
lower white liquor demand in hardwood digesters at the mill
and possible reduced recovery loading. The trial alkali
concentration was monitored using the multiplier factor for the
digester chemical to wood ratio (C/W), the actual C/W ratio
for each digester, and lb. of alkali per charge.

In the first trial, during the initial trial period, a
reduction of 4.14% was monitored in C/W ratio by observing
the Metso Kappa Analyzer Multiplier. The reduction across
all digesters was fairly even. The reduction would average out
to a reduction of 340 lb. of alkali per digester. During the next
trial period data was collected for each day in the trial compared
to the starting point of the trial. Initially, a reduction of
2.76% was observed in C/W ratio and 63 percent reduction in
HW Kappa to 16.98. Later, a reduction of 4.01% was
observed in C/W ratio and the kappa had increased to 17.56
allowing for possibly more reduction. The reduction would
average out to a reduction of 267 lb. alkali per digester.
Generally, at the introduction of the product during both trial
periods the results were repeatable, reducing alkali by about
4% and several hundred pounds per digester charge. No
downstream problems were reported. The results were con-
firmed in the second (FIG. 1) and third (FIG. 2, Table 5) trials.
In the third trial, the average compensation factor for the past
day was reduced by 5.64% or, if the data from digester 4, 8
and 11 are disregarded, 5.98%. The elimination of data from
digesters 4, 8 and 11 is realistic since these three digesters
cook differently than the others. In reality, all it comes down
to the pounds of alkali it takes to cook the hardwood chips to
the target kappa number. For comparison, the typical alkali
reduction from AQ is 800 gallons or 568 #EA per cook at 7% reduction in compensation factor. If you include all hardwood
digesters, 5.64% reduction equates to 458 #EA reduction per
cook or 654 gallons per cook. If you exclude the data from the 3 questionable digesters, 5.98% reduction equates to 692
#EA per cook or 733 gallons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa #</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05% NaBH4 - water</td>
<td>17.09</td>
</tr>
<tr>
<td>0.05% NaBH4 - BL</td>
<td>18.54</td>
</tr>
</tbody>
</table>

Compensation factor for additive addition: alkali/wood (A/W) ratio.
Compensation factor for additive addition
% change is in comparison to run 1 baseline

<table>
<thead>
<tr>
<th>1.7#ton I</th>
<th>1.7#ton II</th>
<th>% change</th>
<th>2.0#ton III</th>
<th>% change</th>
<th>1.7#ton IV</th>
<th>% change</th>
<th>1.5#ton V</th>
<th>% change</th>
</tr>
</thead>
<tbody>
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<td>1.16</td>
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<td>0.96</td>
<td>-8.87</td>
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</table>
While this invention may be embodied in many different forms, there are described in detail herein specific preferred embodiments of the invention. The present disclosure is an exemplification of the principles of the invention and is not intended to limit the invention to the particular embodiments illustrated. All patents, patent applications, scientific papers, and any other referenced materials mentioned herein are incorporated by reference in their entirety. Furthermore, the invention encompasses any possible combination of some or all of the various embodiments mentioned herein, described herein and/or incorporated herein. In addition the invention encompasses any possible combination that also specifically excludes any one or some of the various embodiments mentioned herein, described herein and/or incorporated herein.

The above disclosure is intended to be illustrative and not exhaustive. This description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the claims where the term “comprising” means “including, but not limited to”. Those familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims.

All ranges and parameters disclosed herein are understood to encompass any and all subranges subsumed therein, and every number between the endpoints. For example, a stated range of “1 to 10” should be considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more, (e.g. 1 to 6.1), and ending with a maximum value of 10 or less, (e.g. 2.3 to 9.4, 3 to 8, 4 to 7), and finally to each number 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 contained within the range. All percentages, ratios and proportions herein are by weight unless otherwise specified.

This completes the description of the preferred and alternate embodiments of the invention. Those skilled in the art may recognize other equivalents to the specific embodiment described herein which equivalents are intended to be encompassed by the claims attached hereto.

1. A method for digesting wood chips, the method comprising the addition of a composition to a lignin bearing substrate in a pulping process and then applying to the substrate a subsequent bleaching step, the composition comprising a small dosage of BH relative to the oven dried mass of substrate,

wherein the BH is dosed at a point in the pulping process where there has been no black liquor in contact with the substrate, and where no more than 1% of hemicellulose originally present in the wood chip form of the substrate has been separated from the substrate, and optionally when the substrate is in contact with white liquor, the dose is in an amount high enough to selectively reduce at least 1% of the lignin alpha-carbonyl groups in substrate thereby making them more susceptible to subsequent easy quinone methide beta-O-4 bond splitting during pulping process, but not as high as it would substantially denature the chromophores in the lignin by itself,

wherein the bleaching step involves adding a dosage of bleach no greater than an amount insufficient to cause the resulting paper stock to have been substantially whitened in the absence of AQ but for the presence of the low dose BH, and

wherein the resulting paper stock is whitened.

2. A method for digesting pulp, the method comprising the addition of a composition to pulp undergoing a delignification process, the composition comprising a small dosage of BH relative to the oven dried mass of the pulp.

3. The method of claim 2 wherein the composition is added to white liquor and fed to the digester with the liquor before the temperature ramping begins.

4. The method of claim 2 wherein the BH is in the form of an alkaline solution in water.

5. The method of claim 2 wherein the amount of BH relative to oven dried pulp is less than 0.1% on the active base.

6. The method of claim 2 in which the BH is sufficiently alkaline so it is stable under normal conditions and does not release hydrogen.

7. The method of claim 2 wherein the dosage of BH in an amount insufficient to be effective in bleaching the pulp.

8. A method to improve soda or kraft pulping, the method comprises the step of adding a composition to pulp liquor comprising sodium borohydride in alkali prior to pulping, the method provides white liquor chemicals saving, decreased kappa number, lower rejects and higher yield of pulp.

9. The method of claim 8 in which the composition comprises 10-40% alkali and 5-25% borohydride.
10. The method of claim 8 further comprising adding a surfactant to the pulp.

11. The method of claim 8 further comprising adding a polysulfide to the pulp.

12. The method of claim 2 in which the small dosage is characterized as causing the BH to preferentially attack functional groups in lignin and passivate hemicelluloses.

13. The method of claim 12 in which the method excludes using BH in a dosage sufficient to bleach the pulp.

14. The method of claim 2 in which the dosage of BH is small enough for the process to be economically and regulatory viable, on the other hand providing sufficient economic benefits via saving of pulping chemicals.

15. The method of claim 2 excluding the use of a non-delignification pulp treatment process.

16. The method of claim 1 wherein the delignification process including a cooking step followed by a bleaching step, the bleaching step addressing residual lignin not removed or not having its chromophores deactivated by the delignification step.

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