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PROCESS FOR TREATING CELLULOSIC MATERIALS WITH ALKALI AND OXYGEN IN THE PRESENCE OF COMPLEX MAGNESIUM SALTS

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No Drawing. Continuation-in-part of applications Ser. No. 869,875, Oct. 27, 1969, now Patent No. 3,652,386, and Ser. No. 36,670, May 12, 1970, now Patent No. 3,652,385. This application Feb. 26, 1971, Ser. No. 119,369
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U.S. Cl. 162—65 **41 Claims**

ABSTRACT OF THE DISCLOSURE

A process is provided for treating cellulosic materials with alkali in the presence of oxygen, and particularly air, and in the presence of complex magnesium salts of aminopolycarboxylic acids or alkali metal salts thereof. The invention is of particular application to the reduction of lignin content in cellulose pulps and the digestion of wood cellulose without causing deleterious degradation of the cellulose, the complex magnesium salts reducing or entirely preventing attack of oxygen on hemicellulose and cellulose carbohydrates, without appreciably diminishing the oxidation of the lignin and its dissolution in the course of the process.

This application is a continuation-in-part of Ser. No. 869,875, now Pat. No. 3,652,386, filed Oct. 27, 1969 and Ser. No. 36,670 now Pat. No. 3,652,385, filed May 12, 1970.

It is known that chemical and semichemical cellulose pulps can be treated with oxygen in an alkaline medium in order to dissolve lignin. The oxygen treatment is carried out at an elevated temperature, of the order of 100° C., and does not normally require more than one hour. The amount of alkali required is of the order of 4 to 5% NaOH, based on the dry pulp. It is possible to obtain a good reduction in lignin content in this way, but unfortunately, at the same time hemicellulose is also dissolved, and a significant decomposition of the celluose takes place, as evidenced by a lower viscosity value. Also, the strength properties of paper manufactured from such treated pulp are poor.

It has been proposed (U.S. Pat. No. 3,384,533 to Robert et al., dated May 21, 1968) that the process be improved by carrying out the treatment in the presence of a metal carbonate, such as barium carbonate, calcium carbonate, magnesium carbonate or zinc carbonate, in an amount within the range from about 0.5 to 3% by weight of the pulp. Of these chemicals, magnesium carbonate gives the best results, when in an amount of approximately 1% by weight of the pulp. However, magnesium carbonate is quite expensive, and the treatment is costly. Calcium carbonate, which is cheaper, is much less effective. In the case of all of these salts, the difficulty is that a powdered water-insoluble material must be charged to and mixed with the aqueous cellulose pulp system, and it is accordingly hard to obtain and maintain a homogeneous mixture, with uniform effect.

It has also been proposed (South African Pat. No. 3771/68) that in addition to other water-insoluble magnesium compounds such as magnesium oxide and hydroxide, or magnesium silicate, water-soluble magnesium compounds such as magnesium chloride and acetate could be used. These, however, react with the alkali present in the treating liquor to form the water-insoluble hydroxide, and so do not actually resultin a solubilization of magnesium ion in the liquor.

In accordance with the present invention, a process is provided for treating cellulosic materials with alkali in the presence of oxygen, and in the presence of a complex magnesium salt of an aminopolycarboxylic acid or alkali metal salt thereof, or a mixture of a magnesium salt and an aminopolycarboxylic acid or alkali metal salt thereof. In this process, it has been found that it is possible in one stage to reduce the lignin content by more than 50% without causing deleterious degradation of the cellulose, or appreciable loss of hemicelluose. In fact, the dissolution of hemicellulose can be controlled so as to be insignificant or appreciable, as desired, so that the process is also applicable to hemicellulose dissolution. At the same time, these compounds are inexpensive, and since they are water-soluble, they can be added in solution form, and form a homogeneous aqueous alkaline system in which the cellulose pulp is suspended, and containing solubilized magnesium ion.

The process of the invention is particulary advantageous in the alkaline treatment of lignin-containing wood cellulose in the presence of oxygen gas or air, for the purpose of removing lignin. This process is referred to in the art as akaline oxygen gas bleaching. It is also applicable to the controlled dissolution of hemicellulose in cellulose pulps, either during or after delignification, as well as to the alkaline digestion or pulping of wood in the presence of oxygen gas or air.

The terms "treating" and "treatment" as used herein are inclusive of bleaching, digestion, and like processes, unless otherwise indicated.

The complex magnesium salts employed in the process of the invention have the important property of reducing or entirely preventing the attack of oxygen on the carbohydrates present in the cellulose and hemicellulose, without to any notably great extent affecting the oxidation of lignin and its dissolution. This protective effect is most noticeable with regard to the attack of oxygen on the cellulose molecule, and primarily the attack of oxygen along the anhydroglucose chain of the cellulose molecule, an attack which gives rise to a rapid lowering of pulp viscosity. Thus, in the presence of the complex magnesium compounds of the invention, the treated delignified pulp is found to have a higher viscosity than would be obtained in their absence.

The process of the invention is applicable to unbleached, partially bleached or bleached cellulose pulps, prepared from any cellulose source by any pulping process, for example, sulfate pulp, sulfite pulp and semichemical pulp. The invention is especially applicable to cellulose pulps derived from wood, such as spruce pulp, pine pulp, hemlock pulp, birch pulp, fir pulp, maple pulp. alder pulp, aspen pulp, eucalyptus pulp, cherry pulp, sycamore pulp, hickory pulp, ash pulp, beech pulp, poplar pulp, oak pulp, and chestnut pulp. The invention is particularly advantageous in the preparation of any pulp in which it is especially desired to avoid degradation of the cellulose during processing, such as most grades of paper pulp, and when it is desired to obtain a uniform controlled degradation, such as in the manufacture of viscose pulp of a desired viscosity.

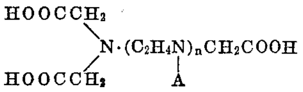
In most cases where the starting cellulose pulp is free of lignin, or where the lignin content is low, either naturally so, or because it has ben delignified, the process of the invention can be applied to remove hemicellulose, and/or cause oxidation of end groups of the cellulose, with a regulated diminution of the pulp viscosity. In these processes, the complex magnesium compounds have the property of protecting the cellulose and hemicellulose molecules against uncontrolled degradation.

The oxygen digestion process of the invention is applicable to any kind of wood. In general, hardwood such as beech and oak can be pulped more easily than softwood, such as spruce and pine, but both types of wood can be pulped satisfactorily using this process. Exemplary hard woods which can be pulped include birch, beech, poplar, cherry, sycamore, hickory, ash, oak, chestnut, aspen, maple, alder and eucalyptus. Exemplary softwoods include spruce, fir, pine, cedar, juniper and hemlock.

In the case of softwood, the processing conditions, including the particle size of the wood fragments, the digestion temperature, the alkali concentration, and the oxygen pressure, should be carefully determined and controlled during the digestion.

The wood should be in particulate form. Wood chips having dimensions that are conventionally employed in the sulfate process can be used. However, appreciable advantages with respect to uniformity of the digestion process under all kinds of reaction conditions within the stated ranges can be obtained if the wood is in the form of nonuniform fragments of the type of wood shavings or chips having an average thickness of at most 3 mm., and preferably from about 0.2 to about 2 mm. Other dimensions are not critical. Sawdust, wood flour, slivers, splinters, wood granules and wood chucks and other types of food fragments can also be used. In the case of softwood, the particles should be thin.

The complex magnesium aminopolycarboxylic acid salts in accordance with the invention are formed from aminopolycarboxylic acids having the formula:



$$(\mathrm{HOOCCH_2})_2\mathrm{N\cdot(C_2H_4}\underset{\underset{\mathrm{A}}{|}}{\mathrm{N}})_n\mathrm{CH_2COOH}$$

or alkali metal salts thereof, in which A is the group —CH_2COOH or —CH_2CH_2OH, where *n* is an integer from zero to five. The mono, di, tri, tetra, penta and higher alkali metal salts are useful, according to the number of acid groups available and converted to alkali metal salt form.

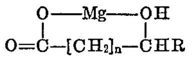
Examples of such aminopolycarboxylic acids are ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminopentaacetic acid, ethylenediaminetriacetic acid, tetraethylenepentaamineheptaacetic acid, and hydroxyethylethylenediamine triacetic acid, and their alkali metal salts, including the mono, di, tri, tetra and penta sodium, potassium and lithium salts thereof. Other types of aminocarboxylic acids which can be used to advantage are iminodiacetic acid, 2 - hydroxyethyliminodiacetic acid, cyclohexanediaminetetraacetic acid, anthranil - N,N - diacetic acid, and 2-picolylamine-N,N-diacetic acid.

These complexing acids can be present in rather large quantities, well in excess of the amount of magnesium present, and within the range from about two to about ten times the amount needed to complex with, solubilize, and thus prevent precipitation of magnesium hydroxide or other insoluble magnesium salts during the treatment.

The magnesium complexes with these acids by forming salts with the acid groups and by chelation with the nitrogen-containing groups or hydroxy groups, if present. Since the complexes are soluble in the alkaline treating liquor, the precipitation of insoluble magnesium compounds is effectively prevented.

It has been found that a particularly effective composition is a combination of the complex magnesium salts of the invention with other magnesium compounds, and especially other complex magnesium compounds.

U.S. Pat. No. 3,652,386 discloses a class of water-soluble complex magnesium compounds of magnesium and aliphatic alpha-hydroxycarboxylic acids of the type RCHOHCOOH and the corresponding beta-hydroxycarboxylic acids $RCHOHCH_2COOH$. These chelates are of the type:



In the above formula, *n* is zero or one. When *n* is zero, the acid is an alpha-hydroxy acid, and when *n* is one, the acid is a beta-hydroxy acid.

R is the above formula is hydrogen or an aliphatic radical, which may be a hydrocarbon radical having from one to about ten carbon atoms, or a hydroxy-substituted hydrocarbon radical having from one to nine hydroxyl groups, and from one to about ten carbon atoms.

Exemplary alpha- and beta-hydroxy carboxylic acids are glycolic acid, lactic acid, glyceric acid, α,β-dihydroxybutyric acid, α-hydroxy-butyric acid, α-hydroxy-isobutyric acid, α-hydroxy-n-valeric acid, α-hydroxy-isovaleric acid, β-hydroxy-butyric acid, β-hydroxy-isobutyric acid, β-hydroxy-n-valeric acid, β-hydroxy-isovaleric acid, erythronic acid, threonic acid, trihydroxy-isobutyric acid, and sugar acids and aldonic acids, such as gluconic acid, galactonic acid, talonic acid, mannonic acid, arabonic acid, ribonic acid, xylonic acid, lyxonic acid, gulonic acid, idonic acid, altronic acid, allonic acid, ethenyl glycolic acid, and β-hydroxy-isocrotonic acid.

Also useful are organic acids having two or more carboxylic groups, and no or from one to ten hydroxyl groups, such as oxalic acid, malonic acid, tartaric acid, malic acid, and citric acid, ethyl malonic acid, succinic acid, isosuccinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, maleic acid, fumaric acid, glutanconic acid, citramalic acid, trihydroxy glutaric acid, tetrahydroxy adipic acid, dihydroxy maleic acid, mucic acid, mannosaccharic acid, idosaccharic acid, talomucic acid, tricarballylic acid, aconitic acid, and dihydroxy tartaric acid.

The polyphosphoric acids are also good complexing agents for magnesium, and the magnesium salts of these acids are useful in combinations with the complex magnesium aminopolycarboxylic acid salts. Exemplary are disodium-magnesium pyrophosphate, trisodium-magnesium tripolyphosphate and magnesium polymetaphosphate.

Especially advantageous in such combinations from the standpoint of cost are the acids naturally present in waste liquors obtained from the alkaline treatment of cellulosic materials. These acids represent the alkali- or water-soluble degradation products of polysaccharides which are dissolved in such liquors, as well as alkali- or water-soluble degradation products of cellulose and hemicellulose. The chemical nature of these degradation products are complex, and they have not been fully identified. However, it is known that saccharinic and lactic acids are present in such liquors, and that other hydroxy acids are also present. The presence of C_6-isosaccharinic and C_6-metasaccharinic acids has been demonstrated, as well as C_4- and C_5-metasaccharinic acids. Glycolic acid and lactic acid are also probable degradation products derived from the hemicelluloses, together with beta-gamma-dihydroxy butyric acid.

Carbohydrate acid-containing cellulose waste liquors which can be used include the liquors obtained from the hot alkali treatment of cellulose, liquors from sulfite digestion processes, and liquors from sulfate digestion processes, i.e., kraft waste liquor. The waste liquors obtained in alkaline oxygen gas bleaching or digestion processes and alkaline peroxide bleaching processes can also be used. In this instance, the alkaline liquor can be taken out from the process subsequent to completing the oxygen gas treatment stage, or during the actual treatment process.

The complex magnesium salts can be formed first, and then added to the cellulose pulp. They can also be formed in situ from a water-soluble or water-insoluble magnesium salt, oxide or hydroxide, in admixture with the complexing acid, the aminopolycarboxylic acid, hydroxycarboxylic acid, or polyphosphoric acid, or salt thereof, and this mixture can be added to the pulp. For instance, a waste liquor employed as a source of complexing acid or anhydride or salt thereof can be mixed with a magnesium salt, oxide or hydroxide, before being introduced to the process, or the magnesium salt, oxide or hydroxide can be added to the pulp, and then the pulp brought into contact with the complexing acid or anhydride or salt thereof. It is also possible to combine the complexing acid or anhydride or salt thereof with the pulp, and then add the magnesium salt, oxide or hydroxide, but this method may be less advantageous in practice.

In whatever form the magnesium is added, whether as salt, oxide, hydroxide, or complex salt, the amount of magnesium is calculated as MgO.

A noticeable improvement in the treating process is obtained when as little magnesium as 0.005% MgO, calculated on the dry weight of the pulp, is added. A high proportion of magnesium, up to 1% MgO, calculated on the dry weight of the pulp, has been employed without disadvantageous effect. However, for economic reasons, it is usually desirable to use as little magnesium as possible, and normally an amount within the range from about 0.01 to about 0.5% MgO, calculated on the dry weight of the pulp, is employed.

Upon conclusion of the alkaline oxygen gas treatment, it is possible to separate the magnesium-containing waste liquor and recycle it for reuse. The consumption of magnesium salts is negligible, and usually it is not even necessary to replenish the magnesium content before recycling. However, additional magnesium compound can be added before recycling, if necessary, to restore the magnesium content, as MgO, and maintain a high enough level, for instance, to prevent oxidative degradation of the cellulose or hemicellulose. The consumption of magnesium salt has been noted to be particularly low when waste liquor from a part of the alkaline oxygen gas treatment process is employed as the source of complexing acid, and recycled for continued treatment of new batches of pulp.

Some wood pulps are particularly high in magnesium ion because of the nature of the pulp or of the pulping process. For example, unbleached pulps produced by digestion of wood with magnesium bisulfite or magnesium sulfite usually contain enough magnesium ion so that no addition of magnesium compound need be made. Waste liquors from these processes can be used per se, in the process of the invention, inasmuch as they already contain the complexing acids, and a sufficient proportion of magnesium ion as well.

As a source of magnesium, one may add any magnesium salts, oxide or hydroxide, either to regenerate a spent treatment liquor, or to prepare a waste liquor or other material for use in the process. Any water-soluble or -insoluble magnesium compound can be used, such as, for example, magnesium sulfate, magnesium chloride, magnesium bromide, magnesium chlorate, magnesium potassium chloride, magnesium formate, magnesium acetate, magnesium oxide, magnesium hydroxide, and magnesium nitrate. If it is desired to recover the liquor after the treatment, then it is usually preferable to employ magnesium sulfate, so as to avoid the introduction of foreign anions into the system. Magnesium compounds which have no deleterious anion or which have an anion which is destroyed in the course of the process, such as magnesium oxide, magnesium hydroxide, and magnesium carbonate, are also advantageous. Since these are water-insoluble, it is desirable, however, to combine these with the complexing agent in the presence of water, and await their dissolution, indicating that the complex has been formed, before combining with the pulp, or before commencing the alkaline oxygen gas reaction. Any other water-insoluble magnesium compounds can be used in this way, for instance, magnesium oxide or hydroxide, magnesium phosphate, magnesium silicate and magnesium sulfide.

The alkaline treatment of the pulp in the presence of oxygen is carried out in the normal way. Since the processes differ somewhat in the steps and conditions, bleaching (with delignification) and digestion (with delignification) are considered separately, in that order.

In bleaching, in order to obtain a rapid reaction between the cellulosic material and the oxygen gas or air supplied to the system, the partial pressure of oxygen at the beginning of the bleaching should be at least one atmosphere. However, lower pressures can be used, when a slower reaction is acceptable. When using pure oxygen gas, the process can be carried out at pressures approximating atmospheric pressure, while if air is used, because of the lower proportion of oxygen, higher pressures, usually superatmospheric pressures, are employed. If oxygen is used, a practical upper limit is 20 atmospheres, while if air is used, a practical upper limit is 60 atmospheres. The higher the pressure, the more rapid the reaction. Usually, an oxygen gas pressure within the range from about 2 to about 12 atmospheres is preferred.

It is frequently expedient to supply the oxygen gas or air during the process, and to release air enriched with regard to inert gas during the process.

The reaction will proceed at low temperatures, of the order of 25 to 50° C., but then the reaction is slow, and a large reaction vessel is necessary. Consequently, in order to reduce reaction time to a practical range, and keep the equipment small, the bleaching is usually carried out at a temperature within the range from about 80 to about 150° C. If it is desired to reduce the viscosity of the pulp, the higher temperatures can be used, of the order of 130 to 140° C. When treating sulfate paper pulps, a lower temperature is used, if a significant reduction of the hemicellulose content is not desired. If a significant reduction of the hemicellulose is desired, however, then it is desirable to employ a rather high temperature. Usually, in the case of sulfate paper pulps, the treatment is carried out advantageously at from 90 to 100° C.

The temperature can be varied upwardly or downwardly, progressively or continuously, during the process. It is in many cases desirable to begin the reaction at a low temperature, and then to gradually increase the temperature during the reaction. This is particularly true in the case of pulps containing hemicellulose which in an unoxidized condition is attacked by alkali, for example, sulfite pulps, and semichemical pulps. Thus, the reaction temperature is low while the hemicellulose remains unoxidized, but as it becomes oxidized, in the course of the reaction, the temperature can be increased, thus reducing the total reaction time.

The concentration of cellulosic material in the reaction mixture can be varied within wide limits, and is in no way critical. Concentrations within the range from about 3 to about 45% are employed. It is, however, preferable to effect the treatment at a concentration in excess of 10%, and preferably within the range from about 15 to about 35%. When high pulp concentrations are treated, the pulp should be shredded mechanically after or at the same time as the reagent chemicals are added to the reaction mixture.

In a preferred embodiment of the invention, which gives a particularly uniform bleaching and a pulp whose properties can be controlled within the narrow limits, the cellulosic material is first impregnated with an aqueous solution of the complex magnesium salt, or an aqueous solution of the components which in admixture give rise to the complex magnesium salt, before being treated with air or oxygen. The excess of the impregnating solution can then be removed, for example, by filtering and/or by pressing, before the treatment is begun. The solution that is removed can, of course, be used for impregnating additional cellulosic material.

The amount of alkali required in the bleaching depends on the quantity of lignin and/or hemicellulose which it is desired to remove. Normally, the alkali charge (calculated as NaOH) is within the range from about 0.5 to about 12% NaOH, based on the weight of the cellulosic material present. Other alkalis can be used, such as potassium hydroxide or lithium hydroxide, and sodium carbonate, in which event the amounts are changed proportionately. If it is desired to dissolve large quantities of lignin and/or hemicellulose during the process, an alkaline charge within the range of about 7 to about 12% can be used. When bleaching a pulp having a low lignin content, in which case a smaller amount of lignin and/or hemicellulose is to be dissolved, the charge can be within the range from about 0.5 to about 7%.

The proportion of hemicellulose dissolved decreases as the amount of alkali is reduced, and accordingly, the amount of both the lignin and the hemicellulose dissolved can be regulated by control of the amount of alkali added.

It may be advantageous to add only a portion of the total quantity of alkali at the beginning of the process, and then add additional alkali as the reaction proceeds. The alkali attacks the lignin preferentially, and by limiting the amount of alkali present at any given time, it is possible to remove the lignin with a minimum of attack upon the cellulose and hemicellulose in the course of the reaction. The desired grade of pulp can thus be controlled by the manner and rate at which the alkali is charged to the system, and the size of the alkali charge, and the reaction time.

The alkali can be combined with the pulp either before, during, or after combination with the complex magnesium salt, and it can be introduced in whole or in part in this way. The mixing with alkali can be effected at the desired reaction temperature, or at a lower temperature, after which the temperature is increased to reaction temperature.

The reaction time required depends upon the oxygen gas pressure and the reaction temperature. If the oxygen gas pressure is high, and the reaction temperature is high, the reaction can be complete in rather a short time, for example, five minutes. When oxygen gas is employed at atmospheric pressure, reaction times of ten hours and more can be used. Normally, however, in a commercial process, where a high rate of production per hour is desirable, the reaction times will be within the range from about 10 to about 120 minutes. The reaction time is easy to control, since the reaction halts when the alkali is consumed, and thus the reaction time can be increased or shortened, depending upon the amount of alkali added at any given time, for a given gas pressure and temperature of reaction.

The bleached and delignified pulp can be further processed in accordance with known methods, as desired. It can, for example, be bleached with chlorine and/or sodium chlorate and/or chlorine dioxide, and it may also be subjected to continued refinements, in accordance with known procedures.

The digestion process of the invention under controlled conditions and moderate oxygen pressures digests wood with a mixture of alkali and oxygen and obtains in high yield a cellulose pulp having a high brightness and a low lignin content. What is essential in order to obtain these results is to limit the amount of alkali at the beginning of the digestion to at most 75%, and preferably from about 5 to about 20%, of the total molar quantity of alkali required for the digestion, and to add the alkali progressively, either continuously or in increments, during the digestion, while maintaining the pH of the digestion liquor in the course of the digestion within the range from about 9.2 to about 13, and preferably from about 9.5 to about 11.5.

The total amount of alkali that is required for the digestion is determined by the quality and type of the pulp to be produced, and is within the range from about 1 to about 10 kilomoles per 1000 kg. of dry wood. It is well known that certain types of pulp are more digested than others. This is entirely conventional, and does not form a part of the instant invention. Cellulose pulps intended to be used in the production of regenerated cellulose fibers, such as viscose, acetate and cuprammonium pulps, are quite fully digested, and should have a low content of lignin and hemicellulose. In the production of such pulps, in accordance with the process of the invention, the amount of alkali can be within the range from about 6 to about 8 kilomoles per 1000 kg. of dry wood. Semichemical pulps are given an intensive mechanical treatment following their digestion, in order to liberate the cellulose fibers, and in the production of such pulps, using the process of the invention, the amount of alkali can be much less, within the range from about 1 to about 2 kilomoles per 1000 kg. of dry wood. For the production of bright paper pulp, which is readily defibered when the digester is blown, the amount of alkali used in the process of the invention can be within the range from about 2.5 to about 5 kilomoles. Generally, for most of the types of pulps given an intermediate degree of digestion, such as pulps for fine paper, plastic fillers, and soft paper or tissue paper, the amount of alkali in the process of the invention is within the range from about 2 to about 6 kilomoles per 1000 kg. of dry wood.

Any alkali metal hydroxide or alkali metal carbonate can be employed, such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate and lithium carbonate. The sodium carbonate obtained in the burning of cellulose digestion waste liquors can be used for this purpose. The use of alkali metal carbonates may be more advantageous than the use of alkali metal hydroxides in maintaining the pH of the digestion liquor within the stated range, because of the buffering properties of the carbonate or bicarbonate present or formed in situ. Consequently, mixtures of alkali metal hydroxides and alkali metal carbonates are particularly satisfactory, to obtain the advantages of each, and dilute their disadvantages.

It is also possible to use mixtures with alkali metal hydroxides or carbonates with alkali metal bicarbonates, such as sodium bicarbonate and potassium bicarbonate. The alkali metal bicarbonate in this case serves as a buffer. Other buffering agents of alkali metals with nondeleterious acidic anions can be employed, such as alkali metal acid phosphates, and alkali metal acid or bisulfites, such as potassium dihydrogen phosphate, potassium monohydrogen phosphate, sodium dihydrogen phosphate, sodium monohydrogen phosphate, sodium acid sulfite, and potassium acid sulfite, as well as the lithium salts of these anions.

The amount of buffering agent such as alkali metal bicarbonate is usually within the range from about 1 to about 5 kilomoles per 1000 kg. of dry wood. The alkali metal bicarbonate or other buffering agent should be added to the digestion liquor either initially or at an early stage of the digestion. The addition of the bicarbonate or other buffering agent increases the buffer capacity of the digestion liquor, thereby assisting in avoiding variations in pH outside the prescribed range during the digestion. The buffering agent, particularly a bicarbonate, is especially desirable when it is desired to operate at a relatively low pH, for example, from about 9.2 to about 9.5. In this case, bicarbonate or other buffering agent can be added to advantage even if alkali metal carbonate is present.

Large amounts of buffering agents, and particularly bicarbonates, should be avoided, however, since the presence of large amounts of additional foreign anions can be undesirable. In the case of bicarbonates, carbon dioxide may be produced in the course of the digestion as the buffer is consumed. The carbon dioxide dilutes the oxygen, and adds an extra load to the chemical recovery system, and is therefore undesirable in large amounts. However, the addition of minor amounts of the buffering agent within the stated range contributes to pulp uniformity because of its assistance in maintaining pH.

It is also important to restrict the amount of bicarbonate or other buffering agents to an amount which is soluble in the digestion liquor, so as to avoid precipitation thereof within the wood being digested.

Also useful as a buffer are the base liquors from previous digestions and/or the waste liquors from oxygen bleaching processes, such as those described in U.S. Pats. Nos. 3,652,385 and 3,652,386 referred to above. In this way, better economy is obtained in chemical recovery, which can be effected after evaporating and burning the waste digestion liquor, using known methods.

For economic reasons, the sodium compounds are preferred as the alkali metal hydroxide, alkali metal carbonate and alkali metal bicarbonate.

It is also possible to add the additional chemicals normally present in digestion liquors, such as sodium sulfate, as well as small amounts of sodium sulfide or other alkali metal sulfide. At most, such chemicals are added in an amount of about 1 kilomole per 1000 kg. of dry wood.

Limiting the amount of alkali metal hydroxide and/or alkali metal carbonate in the initial stages of the process is quite important in obtaining a cellulose pulp of the desired quality. At most, 75% of the total molar quantity required of the alkali can be added ab initio, and even this high percentage is only desirable if the pulp to be manufactured is a semichemical pulp, or if the wood has been pretreated with sulfur dioxide in aqueous solution. For most pulps, including even the semichemical pulps, a better cellulose pulp is obtained if the initial charge of alkali is within the range from about 2 to about 50% of the total molar quantity required for the digestion. The remainder of the alkali is added progressively, either incrementally or continuously, as the digestion continues. When producing bright pulps having a low lignin content, it is satisfactory to charge not more than 20% and suitably from about 5 to about 20% of the alkali at the beginning of the digestion process.

If a mixture of alkali metal hydroxide and alkali metal carbonate is used, it is particularly suitable if the initial charge comprises sodium carbonate optionally with an addition of sodium bicarbonate as described above, the remainder of the alkali added as the digestion proceeds being sodium hydroxide. If the alkali charge initially is alkali metal hydroxide, it is usually important in producing pulps having a low lignin content that the initial charge be low, within the range from about 2 to about 10%, of the total molar quantity of alkali.

Whether or not the digestion process is carried out continuously or as a batch process, the alkali metal hydroxide and/or alkali metal carbonate can be charged continuously or in increments to the digestion liquor. In a continuous digestion, the wood is caused to move through the digester from one end to the other which thereby constitutes a reaction zone. In a batch process, the wood usually in the form of chips is retained in the reaction vessel throughout the digestion.

Since the oxygen that is employed as an essential component in the digestion process of the invention is a gas, the so-called gas phase digestion procedure can be used to advantage. In this case, the wood and the film of digestion liquor present on the wood are kept in continuous contact with the oxygen-containing gas. If the wood is completely or substantially immersed in the digestion liquor, it is important to agitate the wood and/or the gas and/or atomize the gas or the liquor. The oxygen should be dissolved or dispersed in the digestion liquor to the greatest extent possible. Dissolution or dispersion of the oxygen in the liquor can take place within the digestion vessel and/or externally of the same, such as in nozzles, containers or other known devices used for dissolving or dispersing gases in liquids.

Transfer of oxygen to the wood material impregnated with digestion liquor is important in the process, and is controlled by adjusting the oxygen pressure, the digestion temperature and/or the proportion of gas-liquid contact surfaces, including the wood impregnated with digestion liquor.

The oxygen is preferably employed as pure oxygen, but mixtures of oxygen with other inert gases can be used, such as, for example, mixtures of oxygen with nitrogen and with carbon dioxide and with both, as well as air. Compressed air can also be used, although this complicates the devices for dissolving or dispersing the oxygen in the reaction mixture.

Prior to contact with the oxygen, the wood suitably in the form of chips can be impregnated with an aqueous digestion liquor containing the desired chemicals. The chips are impregnated under vacuum, or under atmospheric pressure or superatmospheric pressure, or by other methods conventional in wood digestion processes. The wood may also be treated with steam before being brought to the digestion zone.

The temperature employed during the impregnation can be within the range from about 20 to about 120° C., although temperatures within the range from 90 to 120° C. would not normally be used except under special circumstances. In the latter case, the highest temperature during the digestion may be the same as the impregnating temperature, as well as the initial digestion temperature. Generally, however, it is to advantage if the digestion temperature is allowed to rise during the digestion process, so that normally the temperature during impregnation would not exceed about 60° C.

The digestion can be carried out at a temperature within the range from about 60 to about 175° C. Usually, it is advantageous if the digestion temperature is permitted to rise during the digestion process from an initial temperature of the order of from 60 to 90° C. to the maximum digestion temperature of the order of from 110 to 150° or 175° C.

At a maximum temperature of 90° C., the digestion process proceeds slowly, but on the other hand, moderate oxygen pressure and simple technical apparatus can be used. A digestion temperature of from 90 to 110° C. can be used to advantage when producing semi-chemical pulps, the fibers of which are not fully liberated until after subjection to a mechanical treatment process, such as in a refiner, after the digestion process. These are high yield pulps.

If a maximum digestion temperature of from 150 to 175° C. is used, the digestion will proceed rapidly. On the other hand, in this case an exceedingly effective transfer of oxygen to the wood from the gas phase is required. This requires intimate contact and high oxygen pressure. By effective control methods, however, all of which are conventional, it is possible to control the digestion within this temperature range, particularly when producing cellulose pulp of moderate yield.

Normally, a maximum digestion temperature within the range from 110 to 150° C. is preferred at which temperature the digestion can take place in a reasonable time using relatively simple apparatus and under moderate oxygen pressure, with good control of pulp quality, irrespective of whether semichemical pulps are being produced or cellulose pulps whose fibers can be liberated without intensive mechanical treatment, or are simply liberated when the cooker or digestion vessel is blown.

The partial pressure of oxygen during the digestion process should be within the range from about 1 to about 20 atmospheres, preferably from about 3 to about 20 atmospheres. Higher pressures should not be used, from the standpoint of safety, and are definitely unnecessary. At lower pressures, the digestion proceeds more slowly, and such pressures are not economically practical. Normally, a pressure within the range from about 3 to about 12 atmospheres is preferred.

Because of the consumption of oxygen in the course of the digestion, and the higher rate at which the digestion proceeds at high reaction temperatures, it follows that the higher the reaction temperature, the higher the pressure that should be applied during the reaction. The optimum temperature and pressure conditions for a given pulp can be determined by digestion sampling procedures, as is well known. Such trial-and-error experimentation is conventional, and is not a part of this invention.

It is often suitable during the digestion to withdraw a portion of the digestion liquor, such as by draining, pressing, displacement or filtering. This liquor can be returned to the digestion process at a later stage, or to a subsequent batch, and in this event it is advantageous to heat the liquid or a part thereof under pressure to an elevated temperature of the order of from 110 to about 200° C. in intimate contact with an oxygen-containing gas such as air in order to oxidize organic substances in the liquor. The liquor can be fortified by adding additional alkali metal hydroxide and/or alkali metal carbonate and/or inhibitor before or after pressure-heating.

In the manufacture of many types of cellulose pulp, particularly viscose pulp, cuprammonium pulp, and paper pulp having a high degree of opacity, it has been found advantageous to pretreat the wood before the digestion with water or an aqueous acidic, neutral, or alkaline solution, optionally in several stages. In the case of such pulps, this pretreatment is preferably effected at a high temperature, within the range from about 90 to about 150° C., whereupon a marked dissolution of from about 2 to about 15% of the wood material takes place. Waste liquor from wood cellulose alkaline treatment processes or alkaline digestion processes can be used as the alkaline medium, and the treatment may be continued until the pH of the solution drops and the solution becomes acidic. It has been found particularly suitable to use in this pretreatment the alkaline waste liquor removed subsequent to or during the oxygen digestion process of the instant invention.

When producing high strength paper pulps, the pretreatment can be carried out with such solutions at lower temperatures, from about 30 to about 100° C., preferably using an acid solution such as a 0.1 to 1% aqueous solution of sulfuric acid, nitric acid, or phosphoric acid. These acids can also be used in high temperature pretreatment.

Before carrying out the oxygen digestion process of the present invention, it is particularly suitable to pretreat the wood with an aqueous solution containing sulfur dioxide, sodium bisulfite and/or sodium sulfite or other alkali metal sulfite such as potassium bisulfite or sulfite. The treatment causes some dissolution and modification of the wood material, which has been found to be favorable during the oxygen digestion, particularly in the case of wood material which is difficult to pulp without any form of pretreatment, such as softwood. By pretreating the wood in this manner with water or aqueous solutions, the pulp can be modified to any desired degree, and by suitably selecting the conditions according to trial-and-error experimentation (which can be carried out on a small sample) to suit the wood used, the treating conditions can be optimized for different fields of use of the pulp product. Generally speaking, the pretreatment causes a reduction in the consumption of alkali during the oxygen digestion process of the invention.

When producing many types of pulps which should be metal-free, or substantially so, such as viscose and cuprammonium pulps and pulps for high strength papers, the pretreatment stage or part thereof is preferably carried out in the presence of a complexing agent for bivalent and/or polyvalent metal ions, such as copper, iron, manganese, cobalt and vanadium. In this way, it is possible to remove and/or render harmless ions of the so-called transition metals, which catalyze an oxidative degradation of the carbohydrates during the subsequent digestion process. Examples of suitable complexing agents are chelating salts of nitrogen-containing polycarboxylic acids of the class set forth above in conjunction with the magnesium complex as well as polyphosphates and ethylenediamine and ethylenediamine derivatives, although other complexing agents of an inorganic or organic nature can also be used to advantage. The effect can be increased if mixtures of different complexing agents are used, since certain complexing agents have more of an affinity for certain polyvalent metal ions than others, and a blend is better capable of chelating a mixture of polyvalent metal ions for this reason. The use of complexing agents in connection with the pretreatment has been found to promote uniformity of the pulp during digestion.

It may be desirable to wash the wood with water between the pretreatment stage and the oxygen digestion process. This washing step may be desirable in the case of any of the pretreatment processes described above. The washing, however, increases the cost of the processing, and also increases the risk of water contamination of the pulp with metal ions and metal compounds, and consequently it may often be more practical to omit the washing step, unless it can be carried out with deionized water, at low cost. Omission of the washing is usually disadvantageous.

It has also been found advantageous to have complexing agents for bivalent and/or polyvalent metal ions present during the oxygen digestion process. Any complexing agents which are stable and not deleteriously affected by the digestion liquor can be used. Suitable complexing agents include those mentioned above.

After the oxygen digestion process has been completed, the pulped wood may optionally be subjected to a mechanical treatment in order to liberate the fibers. If the pulping is brief or moderate, a defibrator, or disintegrator, or shredder, may be appropriate. After an extensive or more complete pulping or digestion, the wood can be defibrated in the same manner as in other conventional cellulose cooking processes, such as sulfate pulping, by blowing off the material from the digester, or by pumping.

The pulped wood cellulose that is obtained in accordance with the process of the invention is of such whiteness that it can be used to advantage directly for producing tissue paper, light cardboard and magazine paper. When a higher degree of brightness is desired as for fine paper, rayon and cellulose derivatives, the pulp can easily be bleached in accordance with known methods by treatment with chlorine, chlorine dioxide, chlorite, hypochlorite, peroxide, peracetate, oxygen or any combinations of these bleaching agents in one or more bleaching sequences as described in for example U.S. Pat. No. 3,652,388. Chlorine dioxide has been found to be a particularly suitable bleaching agent for the oxygen digested cellulose pulp obtained in accordance with this invention. The consumption of bleaching chemicals is generally markedly lower in bleaching oxygen digested pulps of the invention than when bleaching sulfate cellulose.

The chemicals used for the digestion process can be recovered after the waste liquor is burned and subsequent to optionally causticizing all or part of the carbonate obtained when burning the liquor.

Preferred embodiments of the digestion process of the invention and of the cellulose pulps of the invention are shown in the following examples:

EXAMPLE 1

Unbleached pine sulfite pulp having a kappa number of 33.9 and a viscosity of 1181 cm.^{3}/g. according to SCAN (170 cp. according to TAPPI) was bleached and delignified in the manner described under (a) to (e) below. The following general procedure was used in all runs.

The pulp was finely divided in a peg shredder at a dry content of 30%. Water and sodium hydroxide were added in amounts to give a 3% pulp concentration. The pulp suspension was then vigorously stirred with a propeller agitator, and the additives mentioned below were blended in. The pulp was then separated by filtration, and squeezed to a dry solids content of 27%, after which the pulp was shredded in a peg shredder. The oxygen gas bleaching was carried out under an oxygen gas pressure of 8 kg./cm.^{2}

at 100° C. for 15 minutes. The pulp was then removed and washed with water.

(a) This pulp was bleached as a control, with no other additives than water and NaOH, and contained 3.2% NaOH based on the dry pulp during the oxygen gas treatment stage.

(b) This pulp was bleached using complex magnesium salts as an additive, obtained by mixing magnesium sulfate in waste liquor pressed from pulp treated with oxygen gas according to (a), the hydroxy carboxylic acids in the waste liquor serving as complexing agents. The waste liquor was pressed from the pulp before the pulp was washed. The waste liquor containing magnesium complexes replaced $1/50$ of the added water in (a), and was mixed together with water and sodium hydroxide into the pulp, after which the bleaching was carried out in the same manner as that of (a). The pulp contained 3.7% sodium hydroxide during the oxygen gas treatment stage.

(c) This pulp was bleached in the same manner as (a), but the additive (at 3% pulp concentration) was an aqueous solution containing a complex compound of magnesium and ethylenediamine tetraacetic acid (EDTA). The pulp contained 3.3% sodium hydroxide during the oxygen gas treatment stage.

(d) This pulp was bleached in the same manner as (b) with the exception that EDTA was added to the extracted waste liquor prior to adding to the pulp. The pulp contained 3.3% sodium hydroxide during the oxygen gas treatment stage.

(e) This pulp was bleached in the same manner as (c), with the exception that diethylenetriamine pentaacetic acid was used instead of EDTA. The pulp contained 3.3% sodium hydroxide during the oxygen gas treatment stage.

The pulps were analyzed, and the following results were obtained:

Pulp	Kappa No.	Viscosity, cm.³/g. (SCAN)	Cp. (TAPPI)	MgO, percent based on pulp	EDTA, percent based on pulp
a	15.8	898	57	----------	----------
b	16.7	1,010	84	0.3	----------
c	16.4	1,010	84	0.1	0.8
d	16.2	1,017	86	0.1	0.2
e	16.6	1,000	81	0.1	[1] 0.8

[1] DETPA, not EDTA.

The results for (a) show that the addition of a magnesium complex (b) to (e) greatly improves the viscosity of the pulp, when bleaching with oxygen gas. When using only diluted waste liquor as the complexing agent, as in (b), however, there is a risk that magnesium hydroxide will form, a large portion of which accompanies the pulp. This causes an increased consumption of magnesium compound and sodium hydroxide. The precipitation of magnesium compounds can be totally avoided, however, by adding additional complexing agents of the type referred to (for example, EDTA or DETPA) as in (c) to (e). Very good results are also obtained solely by employing complexing agents according to the invention (c) and (e) without using waste liquor from the process as complexing agent. As is evident from the foregoing the invention also makes possible a reduction in the amount of magnesium compound by as much as 66%, which is of great economic significance.

EXAMPLE 2

Birch chips about 1 mm. thick and having a lignin content of 21.1% were digested in a series of four runs. In the last run, a magnesium complex prepared from $MgSO_4$ and ethylenediaminetetraacetic acid (EDTA) was added.

The magnesium complex was added prior to the heating. The quantity of magnesium (as MgO) corresponded to 0.1% based on the dry wood. The amount of EDTA was 0.5% based on the dry wood.

(a) As a reference control, the chips were treated in an alkaline aqueous solution under the following conditions:

Oxygen partial pressure, atmospheres	8
Initial temperature, ° C.	80
Initial pH	13.4
Time for temperature rise from 80° to 120° C., minutes	45
Wood-to-liquid ratio, kg./l.	1:4
Alkali charge, NaOH kmol/1000 kg. dry wood, all added at the start, before heating was begun	5
Liquor was withdrawn to obtain a wood-to-liquid ratio of 1:2.	
pH after 45 minutes	11.5
Time digested at 120° C. after liquid withdrawal, minutes	360
pH after 405 minutes	10.8
Total digestion time, minutes	405

The digestion was conducted in an autoclave rotating in a heated glycol bath. After the digestion, the chips were washed. A 63.4% yield was obtained. The chips were dark brown in color, and the lignin content after the digestion was 20.4%.

(b) In a second digestion, the alkali addition was conducted in four stages. 1.25 kmol of NaOH based on 1000 kg. of dry wood was charged in the first stage, and in each of the three following stages, 0.75 kmol of NaOH was charged. The digestion was otherwise carried out as before, with the exception that the alkali charge was reduced in accordance with the aforegoing. The digestion time at each stage was 240 minutes. The cellulose material was washed with water between each treatment stages. Subsequent to impregnating the wood with cooking liquor, the pH was 13, but fell to 10 in the liquor which was withdrawn the first time at 120° C. The pH of the liquor withdrawn in the later stages was within the range from 10 to 11.

The lignin content of the pulp after the digestion was 1.5%, the pulp yield was 51.5%, and pulp brightness 75% SCAN.

(c) In another digestion, the wood was digested as in (b), but not under oxygen pressure. Burnt chips, dark brown in color, were obtained, but no pulp.

The results in (a), (b) and (c), show that if the desired delignification effect is to be achieved at a pH of approximately 9 to approximately 13, it is necessary that:

(i) the digestion be effected under oxygen pressure (b) v. (c).

(ii) the alkali charge be added in several stages and not all ab initio (b) v. (a).

The plup obtained in (b) had a particularly high brightness.

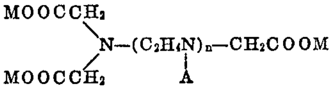
(d) (b) was repeated, but with the addition of a magnesium complex prepared from $MgSO_4$ and ethylenediaminetetraacetic acid (EDTA). The magnesium complex was added prior to the heating. The quantity of magnesium (as MgO) corresponded to 0.1% based on the dry wood. The amount of EDTA was 0.5% based on the dry wood. In this instance, the pH values during the oxygen digestion were approximately 0.5 unit higher than in Example 2b. This is related to the fact that the yield of carbohydrates was higher, due to the presence of the magnesium complex. The lignin content of the pulp was 2%, pulp yield was 57.5%, and the brightness of the pulp was the same as that in Example 2b.

The results show that the yield is greatly improved by the addition of the magnesium complex.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. In the process for treating cellulosic materials with alkali in the presence of oxygen, and particularly air, the improvement which comprises treating the cellulose material with alkali in the presence of oxygen and in the presence of a complex magnesium salt of an aminopolycarboxylic acid or alkali metal salt thereof, the complex magnesium salt reducing or entirely preventing attack of oxygen on the hemicellulose and cellulose in the course of the process.

2. A process according to claim **1**, in which the aminopolycarboxylic acid has the formula:



$$(MOOCCH_2)_2N-(C_2H_4N(A))_n-CH_2COOM$$

wherein A is selected from the group consisting of —CH_2COOM and —CH_2CH_2OH, M is hydrogen or an alkali metal, and *n* is a number within the range from zero to five.

3. A process according to claim **2**, wherein the complex magnesium salt is a chelate of magnesium and a nitrilotriacetic acid.

4. A process according to claim **2**, wherein the complex magnesium salt is a chelate of magnesium and an ethylenediaminetetraacetic acid.

5. A process according to claim **1**, wherein the treatment is carried out on lignin-bearing wood cellulose to remove lignin at least in part.

6. A process according to claim **1**, including a complex magnesium salt of a magnesium-complexing organic acid contained in waste liquor from a process in which cellulosic material is treated with alkali.

7. A process according to claim **6**, wherein a magnesium salt is added to the waste liquor to form the complex magnesium salt in situ in the liquor.

8. A process according to claim **1** in which the quantity of aminopolycarboxylic acid is sufficient to solubilize substantially all of the magnesium present as complex magnesium salt.

9. A process according to claim **1** in which the amount of magnesium complex is within the range from about 0.005 to about 0.5%, calculated as MgO and based on the weight of the cellulosic material.

10. A process according to claim **1** in which the mole ratio of aminopolycarboxylic acid per mole of magnesium is within the range from about 0.01:1 to about 15:1.

11. A process according to claim **1**, wherein the cellulosic material is an unbleached, partially bleached or bleached cellulose sulfate pulp, sufite pulp or semichemical pulp derived from wood.

12. A process according to claim **1** wherein the cellulosic material is cellulose pulp and the partial pressure of the oxygen at the beginning of the treatment is at least about 1 atm.

13. A process according to claim **1** wherein the cellulosic material is cellulose pulp and the treatment is carried out at a temperature within the range from about 80° C. to about 130° C.

14. A process according to claim **1** wherein the cellulosic material is cellulose pulp and the treatment is carried out at a concentration of cellulosic material in excess of 10% up to about 35%

15. A process according to claim **1** wherein the cellulosic material is cellulose pulp and the cellulosic pulp prior to being treated is impregnated with an aqueous solution of the complex magnesium salt or components which in the solution form a complex magnesium salt.

16. A process according to claim **15**, wherein a portion of the solution is removed from the pulp prior to the treatment.

17. A process according to claim **1** wherein the cellulosic material is cellulose pulp and the quantity of alkali calculated as NaOH is within the range from about 0.5 to about 10% based on the dry weight of the cellulosic material.

18. A process according to claim **1**, wherein the source of magnesium is $MgSO_4$, MgO, $MgCl_2$, $Mg(OH)_2$, $MgCO_3$ or $Mg(NO_3)_2$.

19. A process according to claim **1**, wherein the complex magnesium salt includes in addition a complex magnesium salt of an aliphatic α- or β-hydroxycarboxylic acid.

20. A process according to claim **19**, wherein the hydroxycarboxylic acid is an aliphatic hydroxy acid having from two to about twelve carbon atoms and from one to about ten hydroxyl groups.

21. A process according to claim **1** in which the cellulosic material is wood.

22. A process according to claim **21** in which the wood is hardwood.

23. A process according to claim **21** in which the wood is softwood.

24. A process according to claim **21** in which the wood is in particulate form.

25. A process according to claim **21** in which the amount of alkali at the beginning of the digestion is limited to at most 75% of the total molar quantity of alkali required for the digestion, and the remainder of the required alkali is added progressively during the digestion, while maintaining the pH of the digestion liquor in the course of the digestion within the range from about 9.2 to about 13 during the first stages and the major portion of the digestion process.

26. The process of claim **25**, in which the amount of alkali is within the range from about 5 to about 20% of the total molar quantity of alkali required.

27. The process of claim **25**, in which the alkali is added continuously during the digestion.

28. The process of claim **25**, in which the alkali is added in increments during the digestion.

29. The process of claim **25** in which the pH is within the range from about 9.5 to about 11.5.

30. The process of claim **25**, in which the pH is permitted to drop below 9, down to about 8, during the final stages of the process without seriously affecting the quality of the pulp.

31. The process of claim **25** in which the total amount of alkali is within the range from about 1 to about 10 kilomoles per 1000 kg. of dry wood.

32. The process of claim **31** in which the cellulose pulp produced is a viscose, acetate or cuprammonium pulp, and the amount of alkali is within the range from about 6 to about 8 kilomoles per 1000 kg. of dry wood.

33. The process of claim **31** in which the cellulose pulp produced is a semichemical pulp, and the amount of alkali is within the range from about 1 to about 2 kilomoles per 1000 kg. of dry wood.

34. The process of claim **31** in which the cellulose pulp produced is a paper pulp and the amount of alkali is within the range from about 2.5 to about 5 kilomoles per 1000 kg. of dry wood.

35. The process of claim **31** in which the cellulose pulp produced is a pulp for use in making fine paper, plastic fillers, and soft paper or tissue paper, and the amount of alkali is within the range from about 2 to about 6 kilomoles per 1000 kg. of dry wood.

36. The process of claim **1** in which the alkali is any alkali metal hydroxide or alkali metal carbonate.

37. The process of claim **36** in which the alkali metal hydroxide is sodium hydroxide.

38. The process of claim **36** in which the alkali metal carbonate is sodium carbonate.

39. The process of claim **36** in which the alkali is a mixture of alkali metal hydroxide or alkali metal carbonate with an alkali metal bicarbonate.

40. The process of claim **39** in which the alkali metal bicarbonate is sodium bicarbonate which serves as a buffer.

41. The process of claim **39** in which the amount of alkali metal bicarbonate is within the range from about 1 to about 5 kilomoles per 1000 kg. of dry wood.

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