IMPREGNATION OF CELLULOSIC PULP UNDER SUPERATMOSPHERIC PRESSURE WITH WASTE ALKALINE OXYGEN GAS BLEACHING LIQUOR FOLLOWED BY OXYGEN-ALKALI BLEACHING

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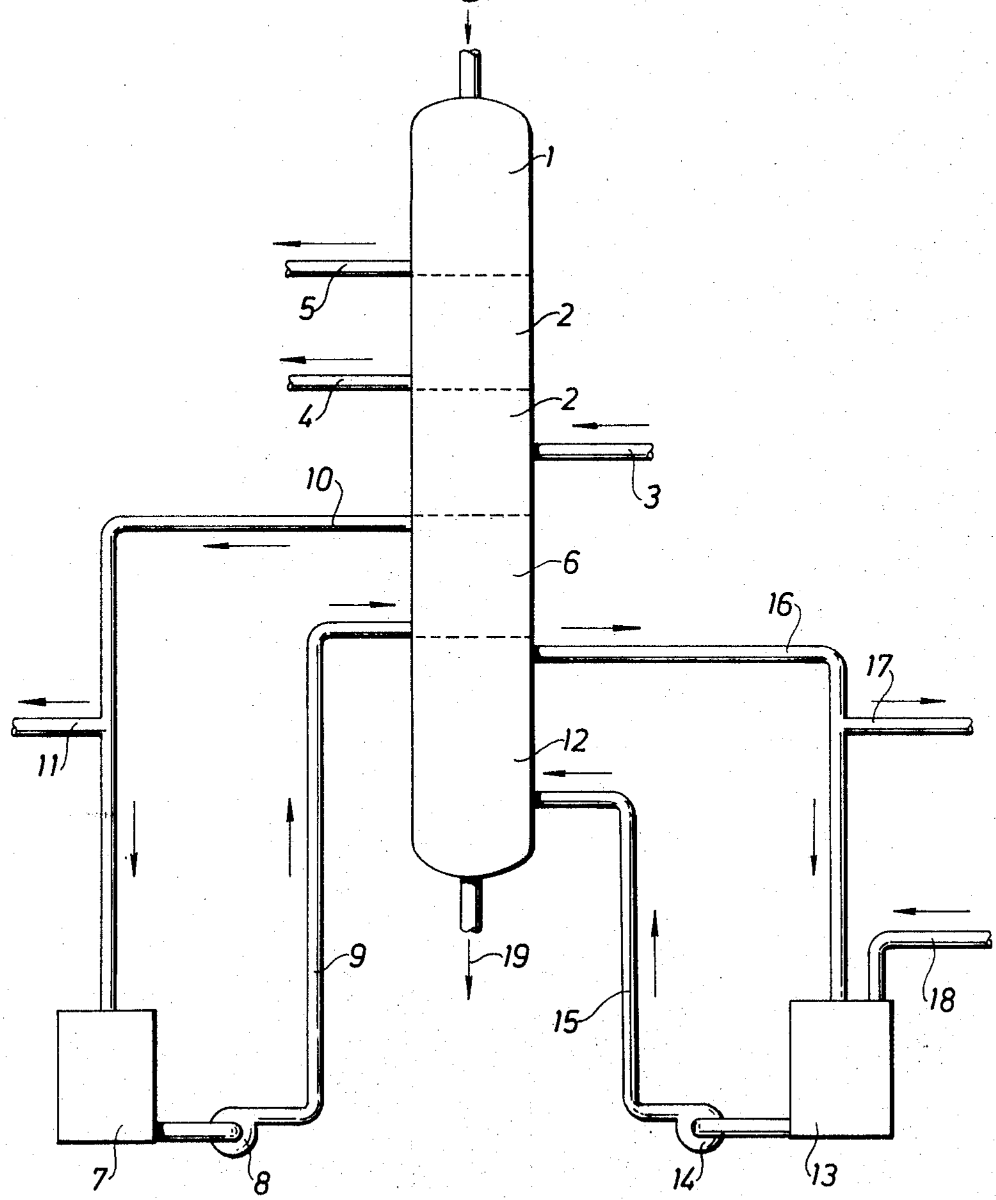
Fig.1



3,843,473

IMPREGNATION OF CELLULOSIC PULP UNDER SUPERATMOSPHERIC PRESSURE WITH WASTE ALKALINE OXYGEN GAS BLEACHING LIQUOR FOLLOWED BY OXYGEN-ALKALI BLEACHING

Hans Olof Samuelson, Goteborg, and Ingemar Liss-Albin Croon, Domsjoverken, Sweden, assignors to Mo Och Domsjo Aktiebolag, Ornskoldsvik, Sweden

Continuation-in-part of application Ser. No. 173,764, Aug. 23, 1971, now Patent No. 3,759,783. This application Mar. 23, 1973, Ser. No. 344,291
Claims priority, application Sweden, Mar. 30, 1972, 4,251/72
The portion of the term of the patent subsequent to Sept. 18, 1990, has been disclaimed
Int. Cl. D21c *9/10*
U.S. Cl. 162—40 19 Claims

ABSTRACT OF THE DISCLOSURE

Impregnating cellulosic pulp under superatmospheric pressure with waste alkaline oxygen gas bleaching liquor to displace pulping chemicals present in the cellulosic pulp, then impregnating the pulp under superatmospheric pressure with alkali and thereafter bleaching the pulp with oxygen in the presence of said alkali.

Specification

This application is a continuation-in-part of Ser. No. 173,764, filed Aug. 23, 1971, now U.S. Pat. No. 3,759,783, patented Sept. 18, 1973.

Processes for the alkaline oxygen gas bleaching of cellulose pulp have recently attracted considerable interest, as a way of avoiding the use of chlorine, with its accompanying pollution problems. However, although the alkaline oxygen gas bleaching process has been known for many years, it has not been applied commercially to any great extent, because of the problems that accompany it. A significant decomposition of the cellulose may take place, as evidenced by a lower viscosity value, and the strength properties of paper manufactured from alkaline oxygen gas bleached pulp may also be poor.

Attention has been devoted recently to overcoming these difficulties. Robert et al. U.S. Pat. No. 3,384,533, dated May 21, 1968, proposed that the process be improved by carrying out the treatment in the presence of a metal carbonate, but the materials described are water-insoluble, and are hard to maintain in a homogeneous mixture with the pulp.

Noreus and Samuelson, U.S. Pat. No. 3,652,368, patented Mar. 28, 1972, provided a process in which a soluble complex magnesium salt is used to avoid deleterious degradation of the cellulose or appreciable loss of hemicellulose during alkaline oxygen gas bleaching. In a modification of this process, Noreus and Samuelson, U.S. Pat. No. 3,652,385, also patented Mar. 28, 1972, proposed a pretreatment of the cellulose pulp, in which catalytically active metals and/or metal compounds are removed or deprived of their catalytic activity, and suggest that it may be desirable to add the alkaline liquid to the pretreated cellulosic material before the oxygen gas treatment is begun.

Nonetheless, despite the improvement in results obtained when these expedients are employed, it has proved difficult to obtain reproducible and acceptable bleaching results on a commercial scale, comparable to those obtained on a laboratory scale, without experiencing unacceptable losses of chemicals and heat, and the apparatus used in pretreating the cellulose pulp, subsequent to the pulping and prior to the alkaline oxygen bleaching, has become unnecessarily complicated and expensive.

In accordance with the instant invention, an alkaline

oxygen gas bleaching process is provided, which is capable of producing cellulose pulp of very good strength properties, while at the same time minimizing losses of bleaching and pulping chemicals and organic substances from both the pulping process and the bleaching process, as well as from the pulp. In the process of the invention, the bleaching system is combined with the pulping digestion system in a manner to conserve the chemicals of both, and minimize recycling of waste chemicals, together with the expensive processing of the waste pulping and bleaching liquors required to recover such chemicals. In the process of the instant invention, both alkaline oxygen gas bleaching liquor and waste pulping liquor are utilized to improve the cellulose pulp, prior to the alkaline oxygen gas bleaching.

In accordance with the invention, the cellulose pulp obtained from a continuous pulping or digestion process is pretreated under superatmospheric pressure, with waste alkaline oxygen gas bleaching liquor, in order to displace a major proportion of the pulping chemicals from the cellulose pulp but retain a minor proportion of such chemicals, and the resulting pulp then impregnated with alkali and optionally cellulose degradation inhibitors also under superatmospheric pressure, employed in the alkaline oxygen gas bleaching. The cellulose degradation inhibitors include in particular magnesium compounds, such as are described for instance in U.S. Pats. Nos. 3,652,386 and 3,652,385 referred to above.

In a preferred embodiment of the process of the present invention, cellulose pulp obtained by digestion of wood under superatmospheric pressure in a continuously operating digester is freed from a major proportion of the pulping liquor contained therein by passing the pulp while still under superatmospheric pressure through a washing zone, in which pulping liquor in the pulp is displaced with waste alkaline oxygen gas bleaching liquor, and the resulting pulp while still under superatmospheric pressure is passed through one or more impregnating zones, in which the cellulose pulp is impregnated with the alkali required for the alkaline oxygen gas bleaching, and also with any additional chemicals desired in such bleaching, particularly cellulose degradation inhibitors.

The process of the invention uses apparatus in combination as an intermediate pretreatment system between a continuous digester for preparing cellulose pulp from wood or other source and a reactor for alkaline oxygen gas bleaching of cellulose pulp. Both may be of known type. The apparatus can be a component part of the continuous digester, and/or of the alkaline oxygen gas reactor. The apparatus comprises, in combination, a washing zone for washing cellulose pulp from the digester under superatmospheric pressure, including means for introducing waste alkaline oxygen gas bleaching liquor into the washing zone to displace pulping liquod from the cellulose pulp by bleaching liquor; means for removing as effluent spent pulping liquor displaced from the washed cellulose pulp; means for impregnating the washed cellulose pulp under superatmospheric pressure with alkali for the alkaline oxygen gas bleaching; and, optionally, means for introducing cellulose degradation inhibitors into the cellulose pulp for the alkaline oxygen gas bleaching. At least one and optionally several such impregnation zones are provided, for introduction of the necessary chemicals one at a time or in various combinations, but all such impregnation zones are also adapted for operation under superatmospheric pressure. Means are also optionally included for conveying the impregnated cellulose pulp from the last impregnation zone to the alkaline oxygen gas bleaching reactor.

FIG. 1 shows apparatus for carrying out the process of the invention, including a continuous sulphate-process digester, with two washing zones and two impregnation zones, with a line connection to an alkaline oxygen gas bleaching reactor.

The process of the invention is applicable to cellulose pulp prepared from any kind of wood by any digestion process, including the alkaline, neutral and acidic cellulose digestion processes, preferably using pulping liquors containing sodium compounds and/or magnesium compounds as the digestion chemicals, such as sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium sulfite, sodium polysulfide, magnesium carbonate, magnesium sulfite, and magnesium bicarbonate. Thus, the process of the invention is applicable to acid sulfite cellulose pulp, bisulfite cellulose pulp, neutral sulfite cellulose pulp, alkaline sulfite cellulose pulp, multistage sulfite cellulose pulp, sulfate, cellulose pulp, polysulfide cellulose pulp, hydrogen sulfide-alkali cellulose pulp, sodium hydroxide or soda cellulose pulp, oxygen gas-alkali cellulose pulp, and oxygen gas-bicarbonate cellulose pulp, derived from such woods as spruce, pine, hemlock, birch, fir, cherry, sycamore, hickory, ash, beech, popular, oak, and chestnut.

Since the process of the invention is operated under superatmospheric pressure, there is no loss of chemicals from the cellulose pulp to the atmosphere in the course thereof. The release of poisonous and foul-smelling gases is inhibited, thus minimizing pollution of the surrounding atmosphere, as well as retaining these chemicals for use in the alkaline oxygen gas bleaching process. Since the washing and impregnation can be carried out while the pulp is still under the superatmospheric pressure of the pulping or digestion process, heat is conserved, as well as pressure, and these both are utilized to enhance the washing and impregnation. The only chemicals separated from the cellulose pulp are those in the pulping or digestion liquor as washing effluent from the washing process, and since this liquor is only a portion of the total pulping liquor content, it does not contain the normal content of waste chemicals from the digestion. A minor proportion of these chemicals remain with the cellulose pulp, and so the amount of digestion and bleaching chemicals that needs to be recovered is reduced. At the same time, any cellulose degradation inhibitors in the waste alkaline oxygen gas bleaching liquor are also conserved and reutilized. The result is that less alkali and less cellulose degradation inhibitors need to be added to cellulose pulp for the alakaline oxygen gas bleaching, in the process and apparatus of the invention.

Since the process is carried out in apparatus that can be integrated with conventional cellulose pulping and alkaline oxygen gas bleaching apparatus, the invention also provides an efficient and simplified recovery of waste pulping liquor and waste alkaline oxygen gas bleaching liquor in apparatus of uncomplicated and inexpensive construction.

An unexpected result of the process and apparatus of the invention is that the strength properties of the cellulose pulp obtained at a given degree of delignification are superior to those of cellulose pulp obtained using the known alkaline oxygen gas bleaching process. This is especially observed when the impregnation step is effected in two zones, in the first of which the cellulose degradation inhibitor is introduced, such as magnesium compound, and in the second of which an alkaline solution is introduced, at a pH such that precipitation of insoluble magnesium compounds such as magnesium hydroxide and magnesium carbonate can take place. Any desired replenishment of magnesium ion should take place in the first impregnation zone, by addition of a magnesium compound, such as magnesium sulfate, magnesium carbonate or magnesium oxide, which however should have been fully dissolved in the waste bleaching liquor before this is brought into contact with the cellulose pulp.

The total amount of magnesium compound applied to the cellulose pulp during the impregnation is preferably adjusted so that the total quantity of magnesium both in the dissolved and in the precipitated state remaining in the pulp after the final impregnating step is within the range from about 0.05 to about 1%, preferably from about 0.05 to about 0.3%, calculated as MgO, and based on the dry weight of the pulp. During the impregnation, a portion of the magnesium compounds may be precipitated as, for example, magnesium hydroxide, while a portion of the magnesium compounds can exist in solution, preferably as soluble complex magnesium compounds, such as when the magnesium complex has been formed with hydroxy acids, and acids containing at least two carboxylic acid groups. Preferably, an amount within the range from about 0.03% to about 1% and preferably from about 0.05 to about 0.1% of magnesium, calculated as MgO, and based on the weight of the dry pulp, should be in solution in the form of soluble magnesium salts following the final impregnation step, while in the first impregnation step the major proportion of the magnesium content and preferably the entire magnesium content should be in dissolved form, so that the pulp will be uniformly impregnated therewith prior to the alkaline oxygen gas bleaching.

In addition to the magnesium complexes of hydroxy acids and acids containing at least two carboxylic groups, such are disclosed in U.S. Pat. No. 3,652,386, other magnesium complex forming compounds can be added to the waste alkaline oxygen bleaching liquor, such as for example, polyphosphates, nitrogenous polycarboxylic acids such as imino diacetic acid or nitrilo triacetic acid.

In the case of cellulose pulps containing cobalt, ethylenediamine can be added in a small amount within the range from about 0.1 to about 1 kilograms per ton of pulp.

As the waste alkaline oxygen gas bleaching liquor, there can be used not only the alkaline liquor remaining in the bleaching system upon completion of the alkaline oxygen gas bleaching process, after separation of the pulp therefrom, but any aqueous solution which contains liquor from this bleaching process. For example, an aqueous solution obtained by washing out the contents of the bleaching system with for instance water or a mixture of water and liquor obtained from the bleaching process can be used. Solutions obtained in the washing system for the alkaline oxygen gas bleached pulp are also included in the term "waste alkaline oxygen gas bleaching liquor," as used herein.

In accordance with one embodiment of the invention, waste alkaline bleaching liquor is recovered from the alkali oxygen gas bleaching stage under pressure, so that the liquor contains significant quantities of dissolved oxygen gas. This waste bleaching liquor is then used to wash and to partially displace pulping liquor from the pulp in displacement equipment operating at superatmospheric pressures. Because of the superatmospheric pressures maintained, the oxygen gas dissolved in the bleaching liquor does not escape, but is present for oxidation purposes in the displacement apparatus, so that the amount of oxygen gas consumed in the alkali oxygen gas bleaching process can be further reduced.

The amount of the waste alkali oxygen gas bleaching liquor that is used is determined by the amount of alkali to be introduced during the bleaching stage, and the amount of organic substances that are to be recovered, and the amount of discharge of waste alkali oxygen gas bleaching liquor that can be tolerated under the environmental pollution regulations, as well as the construction of the washing plant, that is, the number of washing stages included therein.

It is often suitable to add enough waste liquor from the alkali oxygen gas bleaching stage to replenish the alkali lost in the pulping process.

Only partial removal of the waste pulping liquor by washing with recycled waste alkali oxygen gas bleaching liquor gives in general a better bleaching, and surprisingly, under suitable conditions, frequently may give a considerably better bleaching than alkali oxygen gas bleaching of pulp which has been completely freed from spent pulping liquor. Thus, the presence of spent pulping liquor with the waste alkali oxygen gas bleaching liquor can be quite advantageous.

The amounts of waste alkali oxygen gas bleaching liquor and of spent pulping liquor that can be present during the alkali oxygen gas bleaching of the invention are calculated in terms of organic substances therein.

The amounts of organic substance by weight of the total quantity of solids are determined as evaporation residue, according to TAPPI, minus the quantity of sodium calculated as Na_2O. The amount of such substances per 100 kg. of dry unbleached pulp is within the range from about 1 to about 50 kg.

For optimum results, when applying the bleaching process of the invention to sulfate pulp or soda pulp, the amount of organic substances derived from the original spent cooking liquor and present during the bleaching preferably is within the range from about 1 to about 20 kg., suitably from about 1 to about 10 kg., per 100 kg. of dry unbleached pulp.

When the bleaching process of the invention is applied to alkali oxygen gas digested pulp, the amount of organic substances can be somewhat higher, and preferably quantities of up to 30 kg. per 100 kg. of dry unbleached pulp are used for optimum results.

When the process of the invention is applied to sulfite pulp, the preferred upper limit with regard to the amount of organic substances is somewhat lower, and is approximately 15 kg. per 100 kg. of dry unbleached pulp.

The consumption of alkali increases markedly if the content of organic substance exceeds these limits, and moreover, the degree of delignification during the alkali oxygen gas bleaching is impaired.

The washing is suitably carried out in a plurality of washing zones, waste liquor of the highest solids content being recovered as effluent from the first zone, and passed to the chemicals recovery system for evaporation and subsequent combustion, for example, while waste effluent from the last washing zone can be used as an ingredient in reformulating pulping or digestion liquor for reuse. The waste pulping liquors can also be cycled to a wet combustion step under pressure, which may be carried out without preceding evaporation, as desired, in known manner.

For a good heat economy, it is desirable to wash the alkaline oxygen gas bleaching liquor from the bleached cellulose pulp countercurrently to the flow of the bleached pulp, so that a high content of organic substances is retained in the waste alkaline oxygen gas bleaching liquor which is then better suited for use in the process of the invention.

The temperature at which the washing and displacement of waste digestion liquor from the pulp is carried out is in no way critical. Elevated temperatures cause more rapid displacement of the waste digestion liquor, and consequently, a temperature within the range from about 50° C. to about 170° is normally employed. An alkaline pulp such as, for example, a sulfate pulp, can be washed at a temperature within the range from about 80 to about 150°, while a somewhat lower temperature within the range from about 50 to about 110° C., can be used for acid pulps such as sulfite pulp.

The temperature during impregnation likewise is in no way critical. It is convenient to use a temperature similar to the washing temperature. The alkali impregnation may, however, be carried out at a lower temperature than the washing for alkaline pulps, such as sulfate pulp, in which event the temperature can be within the range from about 70 to about 130° C. In the case of acid pulps, such as sulfite pulps, it is convenient to employ a temperature within the range from 30 to about 100° C., preferably from about 40 to about 60° C.

The superatmospheric pressure that is employed during the washing and impregnation steps is likewise not critical, but should be at least 3 kg./cm.^{2}, and normally is within the range from about 3 to about 30 kg./cm.^{2}, preferably from about 5 to about 20 kg./cm.^{2}. This pressure is suitably the same superatmospheric pressure as is used during the digestion, to minimize heat and gas losses. This simplifies transport of the cellulose pulp from the digester through the washing and impregnating zones to the alkaline oxygen gas bleaching reactor. Moreover, a more uniform alkaline oxygen gas bleaching is obtained, with less decomposition of the carbohydrates, when impregnation with the alkali is carried out under superatmospheric pressure.

It will be seen that the process of the present invention can be carried out in apparatus comprising:

(a) One or more cellulose pulp washing vessels constituting a washing zone;

(b) One or more cellulose pulp impregnating vessels for impregnating the pulp with cellulose degradation inhibitors, constituting an impregnation zone; and

(c) One or more cellulose pulp impregnating vessels for impregnating the pulp with alkali, constituting an impregnation zone (which may be combined with (b)); and

(d) Means for conveying cellulose pulp and the liquor in which it is suspended between the different vessels, and from the cellulose pulp digester to the first washing vessel, and from the last impregnation vessel to the alkaline oxygen gas bleaching reactor.

In accordance with a preferred embodiment of the invention, the washing and impregnation vessels constitute zones in a continuous digester. In this case, the pulp is transferred from zone to zone without disturbance, and without any change in superatmospheric pressure, as well as without need for special apparatus for transporting or conveying the pulp between the zones.

If the washing and impregnation process of the instant invention are a part of the continuous digester, the digester includes a zone (a) for continuously washing pulp, and one or more zones (b) and (c) for impregnating pulp, following the washing zone.

The apparatus for carrying out the process of the invention can be adapted for attachment to an existing pulp digester for continuously cooking pulp. Separate apparatus can then be located externally of the digester to carry out the washing (a) and impregnation (b) and (c) operations, such as, for example, one or more diffusors operating under superatmospheric pressure. In this case, the impregnation apparatus (b) and (c) are connected immediately following the washing apparatus (a), which can, if desired, be connected directly to the digester. The washing apparatus (a) and the impregnation apparatus (b) and (c) can also be combined in a single vessel, in which the pulp passes through the various operations in a series of zones, first a washing zone (a) and then one or more impregnating zones (b) and (c).

In the case of impregnating zones which form an integral part of a continuous digester, the pulp is normally fed to the top of the digester, and caused to pass downwardly therethrough, and proceeds in the same manner through the washing zones which are below the digestion zones. If a separate impregnating apparatus is used, however, it may be suitable instead to pass the pulp upwardly from the bottom of the vessel through the impregnating zones, displacement of the pulp upwardly being effected by means of the pressure prevailing in the digester below. In certain cases, it may be suitable to combine either before or with the impregnating zone a mechanical agitator for defibrating the pulp, and thereby expediting the impregnation. In the event that defibration increases the risk of blockage of the screens, double screens may be used, or flow may be altered between separate screens, or means can be added for sweeping the screens clear of blocking material.

Suitable apparatus for impregnating zones is in principle the same as that used in the washing zones incorporated in a continuous cellulose pulp digester with continuously operating diffusers, and comprises among other things screens and conduits for introducing, distributing and discharging the treating liquors. It is suitable to provide in such a system conduits, pumps, and other necessary devices to enable the alkaline liquor and other impregnating liquor of chemicals, such as alkali and cellulose decomposition inhibitors, to be impregnated in the pulp in the impregnating zones, and means for carrying away the effluent from the impregnating zones, and transferring this to the digester system or to a washing zone.

Means can also be included with the impregnating apparatus to make it possible to carry out the impregnation at pulp concentrations that are suitable, by regulating the quantity of liquors supplied to and removed from the systems, as well as the relative quantity of pulp. A suitable pulp concentration during impregnation is within the range from about 8 to about 25%, preferably from about 10 to about 18%.

The impregnation in which the washed cellulose pulp is treated with an aqueous solution containing magnesium ions can be carried out to advantage in a manner in which the aqueous solution is circulated through the impregnating zone, and is replenished by adding magnesium compounds thereto. If the impregnation process is carried out in such a way that a surplus of impregnating liquor is used, the surplus can be withdrawn and passed to the washing process, to be used for displacing waste digestion liquor from the pulp. This can be carried out in a separate final washing zone, or by mixing the surplus liquor from the impregnation step with waste alkaline oxygen gas bleaching liquor from the alkaline oxygen gas bleaching step.

After leaving the last impregnating zone, the washed and impregnated cellulose pulp is fed to an alkaline oxygen gas bleaching reactor. To do this, the pulp can be discharged in conventional manner from the digester, and any separate vessels brought into contact with ambient air, and then fed into the reactor by using known feeding devices, such as screw conveyors, piston presses, or thick-pulp pumps, by way of known metering devices. Between the final impregnating zone and the alkaline oxygen gas bleaching reactor there can be arranged means for washing the pulp in preses, such as screw presses, and means for defibrating and fluffing the pulp, such as disintegrators.

The alkaline oxygen gas bleaching reactor may comprise a reaction tower devoid of all movable devices, other than those required for feeding the pulp thereto, and removing the pulp therefrom. This type of reactor is especially suitable when the alkaline oxygen gas bleaching is carried out with pulps of high pulp concentration, of the order of from about 25 to about 40%. The reactor may also be provided with mechanical devices for agitating the pulp in the reactor, and for transporting the pulp therethrough. Reactors based on the bleaching of pulp in fluidized beds can also be used.

In accordance with a further preferred embodiment of the invention, simplifying the treatment apparatus, the impregnating zones are maintained at a superatmospheric pressure, of such magnitude as to enable an alkali-impregnated cellulose pulp to be fed to the alkaline oxygen gas bleaching reactor by means of this pressure. In this case, a transporting means such as thick-pulp pump can be arranged between the impregnating zone and the alkaline oxygen gas bleaching reactor. The pulp is fed against the superatmospheric pressure prevailing in the bleaching reactor to within the range from about 3 to about 10 kg./cm.^{2}. A metering valve such as a rotating dispensing valve is suitably arranged between the last impregnating zone and the alkaline oxygen gas bleaching reactor, to prevent gas from the alkaline oxygen gas bleaching reactor from feeding back to the impregnating zone. A thick-pulp pump can also serve as the metering means.

The pulp may pass through devices located between the impregnating zone and the alkaline oxygen gas bleaching reactor for dewatering the pulp, and for mechanically exposing the fibers. The effluent solution recovered from the dewatering zone is returned to the impregnating zone, or it can also be used for the preparation of digestion liquor for the wood digestion. However, these devices are not necessary. The washed and impregnated cellulose pulp can be subjected to a bleaching process in the alkaline oxygen gas bleaching reactor, directly from the last impregnating zone. This reduces investment cost in apparatus, and improves operation economy, since the costs involved in the maintenance and care of disintegrators and pressers are thereby avoided.

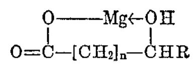
The alkali used in the impregnation of the washed cellulose pulp with alkali can be any alkali metal hydroxide, such as sodium hydroxide or potassium hydroxide, as well as alkaline-reacting salts of the alkali metals, especially sodium salts, and mixtures of such salts, such as sodium carbonate, sodium bicarbonate, sodium sulfide and sodium hydrosulfide. Solutions containing other chemicals such as white liquor, green liquor and mixtures thereof, optionally fortified by adding any of the above mentioned salts, can also be employed. This simplifies recovery of chemicals, since it is unnecesary to further process such liquors for reuse. For chemical balance, the alkali used is suitably in the form of white liquor, or a mixture of white liquor and sodium hydroxide and/or sodium carbonate.

An excess of alkaline impregnating solution is advantageously used during the impregnation, since it provides a more uniform impregnation. The excess effluent impregnating liquor can be cycled to the digestion process, or can be cycled to a suitable stage in the waste digestion liquor chemicals recovery process, to prepare fresh digestion liquor. When manufacturing sulfate pulp, the use of the white liquor optionally replenished with sodium hydroxide or sodium carbonate affords the advantage that the excess liquor can be effectively utilized when digesting the wood without the need for an intermediate chemicals treatment process.

During the alkali oxygen gas bleaching process, the carbohydrates of the pulp may be subjected to a considerable attack, leading to degradation of the cellulose during processing, a diminution of pulp viscosity, and related effects. This may be advantageous in the manufacture of viscose pulps, for example. However, when paper pulps are being manufactured, especially when it is desired that these pulps retain a high mechanical strength, a cellulose degradation inhibitor can be added to the pulp so as to obtain a uniform controlled degradation and a controlled viscosity. In accordance with this invention this is done in an impregnation zone under superatmospheric pressure. For this purpose, complex magnesium compounds can be used.

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.

It is known that aliphatic alpha-hydroxycarboxylic acids of the type RCHOHCOOH and the corresponding beta-hydroxycarboxylic acids $RCHOHCH_2COOH$ have the property of forming chelates with metals. These chelates are of the type:



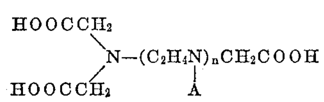
In the above formula, *n* is zero or one. When *n* is zero, the acid is an alpha-hydroxy acid, and when *n* is one, the acid is a beta-hydroxy acid.

R in 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 saccharinic 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, glutaconic 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 complex magnesium aminopolycarboxylic acid salts cellulose degradation inhibitors are formed from aminopolycarboxylic acids having the formula:



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.

The polyphosphoric acids are also good complexing agents for magnesium, and the magnesium salts of these acids are useful in the process of the invention. Exemplary are disodium-magnesium pyrophosphate, trisodium-magnesium tripolyphosphate and magnesium polymetaphosphate.

Especially advantageous from the standpoint of cost are the acids naturally present in waste liquors obtained from the alkaline treatment of cellulosic materials, which of course include the waste alkali-oxygen gas bleaching liquor. 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 alkali-oxygen gas bleaching or pulping 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,* in the waste liquor, for example, from a water-soluble or water-insoluble magnesium salt, oxide or hydroxide, in admixture with the complexing acid, or acid-containing waste liquor, and this mixture can be added to the pulp. Preferably, the waste liquor employed as the 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. It is also possible to add the magnesium salt, oxide or hydroxide to the pulp, and then bring the pulp 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.

Some waste liquors are particularly high in magnesium ion because of the nature of the pulp or of the pulping process. For example, unbleached pulps produced by the cooking of wood with magnesium bisulfite or magnesium sulfite usually contain enough magnesium ion so that no addition of magnesium compound need be made. Such waste liquors 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 magnesium compound can be used, such as, for example, magnesium sulfate, magnesium chloride, magnesium bromide, magnesium chlorate, magnesium potassium chloride, magnesium formate, 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 corrosive 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 alkali-oxygen gas reaction. Any other water-insoluble magnesium compounds can be used in this way, for instance, magnesium phosphate, magnesium silicate and magnesium sulfide.

The alkali-oxygen gas bleaching of the pulp is carried out in the normal way. 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 treatment 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 presure, the more rapid the reaction. Usually, an oxygen gas pressure within the range of 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 proces.

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 treatment 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.

When using an alkali charge in which sodium hydroxide and sodium sulfide are the principle ingredients, the alkaline oxygen gas bleaching is preferably carried out at a temperature within the range from about 90 to about 120° C. When green liquor, sodium carbonate and sodium bicarbonate are used, a somewhat higher temperature, from about 100 to about 140° C., is preferably used.

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 is 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.

The amount of alkali required in the treatment 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, 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 alkali charge within the range of about 7 to about 12% can be used. When treating 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%.

When using sulfide or sulfide-containing alkaline solutions such as white liquor and/or green liquor, it is suitable with respect to the attack on carbohydrates during the alkaline oxygen gas bleaching to oxidize the sulfide either totally or partially prior to contact with the cellulose pulp. This can be done in known manner, obtaining alkali metal thiosulfate and/or alkali metal sulfate. This pretreatment step for oxidation of the sulfides is suitably carried out separately, before the sulfide-containing solutions are brought into contact with the pulp to be bleached, but the oxidation step can also be carried out after impregnating the pulp with the sulfide-containing solution. The oxidation also provides a reduction in oxygen gas-consumption during the alkaline oxygen gas bleaching. The oxidation can be effected with air or oxygen gas, at atmospheric pressure or at superatmospheric pressure. A peroxide compound such as hydrogen peroxide can be added as an initiator.

Elementary sulfur can be charged to the system in lieu of the sulfide-containing solution, or in combination with oxidative pretreatment of the sulfide-containing solution, the elementary sulfur in the alkaline solution react rapidly with sulfide to produce polysulfide. This method is particularly suitable when the process of the invention is applied to acid cellulose pulps, such as sulfite pulps.

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 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 decreases with an increased 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, treatment 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 pulp treated in accordance with the process of the invention can be further processed in accordance with known methods, as desired. It can, for example, be bleached with chlorine and/or sodium hypochlorite and/or chlorine dioxide, and it may also be subjected to continued refinements, in accordance with known procedures.

In order to lower still further the discharge of organic substances at the conclusion of the process, the cellulose pulp can be washed subsequent to the alkali-oxygen gas bleaching process using an aqueous solution containing an organic substance. A suitable aqueous solution in this respect is one obtained by separating suitably by washing cellulose pulp from waste bleaching liquors and/or extraction liquors from other bleaching stages, and/or extraction stages of the same or another pulp. Examples of such aqueous solutions are those obtained from alkali extraction and hot and cold alkali cellulose treatment processes. Solutions obtained from bleaching cellulose with hydrogen peroxide also can can used for this purpose, as well as bleaching solutions from chlorine, hypochlorite, chlorine dioxide, and chlorite bleaching stages, in any combination. If desired, the chlorine content of the recovery system can be reduced by known methods, for instance, by the absorption of hydrochloric acid from flue gases obtained when burning waste liquor, or by crystallizing out sodium chloride. The aqueous solution containing the organic substance can also be an evaporation condensate, which is optionally pre-treated in a known manner to remove volatile and/or colored materials.

In accordance with another embodiment of the invention, the aqueous solution containing organic substances or a portion of this solution is pretreated before being used to wash the cellulose pulp subsequent to bleaching the same with an oxygen-containing gas. The pretreatment process is preferably in the form of an oxidation process, suitably with an oxygen-containing gas. Other conventient pretreatment methods include biological purification using an activated sludge or a biological bed and/or treatment with lime and/or alkali, filtering, separation by means of membranes, for example, reverse osmosis or ultrafiltration, treatment with activated carbon or treatment with polymers having absorbing and/or ion-exchanging properties, or with in organic ion exchanges.

The following Examples represent preferred embodiments of the invention. Reference is made to FIG. 1 as illustrating a suitable apparatus for carrying out the method of the invention.

EXAMPLE 1

Pine wood chips were cooked in a conventional manner in the digestion zone **1** of the continuously operated sulphate digester of FIG. 1. The resulting pulp, which after the digestion had a Kappa number of 30, was passed continuously to the washing zone **2** provided with screens (not shown) and divided into two parts, zones A and B, in which the pulp arriving from the cooking zone was passed countercurrently to waste bleaching liquor from the alkaline-oxygen-gas bleaching zone, introduced through the line **3**. The dry solids content of the waste bleaching liquor was 1%. Waste digestion liquor mixed with bleaching liquor was removed from the lower end of zone B through the line **4**. The waste liquor removed through the line **4**, amounting to 2 $m.^3$ per ton of pulp, was recycled to the digestion zone. Waste digestion liquor was removed from the upper zone A through the line **5**, the digestion liquor being displaced through the line **5** by the charged waste bleaching liquor, and slightly diluted thereby. The solids contents in this liquor was 16%. The liquor removed through the line **5** was passed to an evaporation and combustion stage. The temperature in the washing zone was approximately 130° C., and the total residence time for the pulp was 5 hours. The total quantity of bleaching waste liquor charged to the washing zone was 3 $m.^3$ per ton of pulp.

The pulp was passed from the washing zone **2** to the first impregnating zone **6**, where the pulp was impregnated with a circulating liquor comprising mainly waste bleaching liquor, but which also contained 20% of waste digestion liquor, accompanying the pulp into the impregnating zone. Approximately 30 kg. per ton of pulp of dissolved organic substances obtained from the digestion liquor were passed from the washing zone to the impregnating zone **6**. The circulating liquor was passed through a buffer container **7** and admixed at this point with magnesium sulphate dissolved in circulating liquor. The resulting solution was forced through line **9** into the impregnating zone **6** by the pump **8** and displaced liquor was removed through the line **10** and returned to the buffer container **7**. Excess liquor was removed through the line **11**, and introduced as displacement liquor through the line **3**. The quantity of magnesium charged, calculated as MgO, as 2 kg. per ton of dry pulp. The temperature in the impregnating step **6** was 110° C., and the pulp concentration 15%. The residence time was 60 minutes.

The pulp was continuously transferred from the first impregnating zone **6** to the second impregnating zone **12**, where the pulp was treated with alkali dissolved in a solution which also contained mainly waste bleaching liquor obtained from the alkaline-oxygen-gas bleaching step. The alkali was charged as 35% sodium hydroxide in the buffer container **13**, in a quantity corresponding to 25 kg. sodium hydroxide per ton of dry pulp. By means of a pump **14**, the diluted liquor obtained in the buffer container **13** was driven into the impregnating zone **12** through the line **15**, and liquor displaced from the impregnating zone was removed through a line **16** and returned to the buffer container **13**, where the liquor was replenished with sodium hydroxide supplied through a line **18**. The temperature in the impregnating zone **12** was maintained at 95° C. and the pulp concentration at 15%. The residence time in zone **12** was 60 minutes. Excess liquor was removed through the line **17**, and used to displace waste digestion liquor from pulp, or for preparing digestion liquor.

The treated pulp was discharged from the bottom of the second impregnating zone **12** through the line **19**, and transferred, under its own pressure, to an alkaline-oxygen-gas bleaching reactor (not shown) provided with agitating means. The pulp was treated in the reactor with alkali (NaOH) at a pH of and oxygen-gas at a partial pressure of 4 $kg./cm.^2$ for 30 minutes at a temperature of 100° C. The alkaline-oxygen-gas bleached pulp was washed with water in countercurrent flow to recover the waste bleaching liquor, which was continuously returned to the process. A bleached pulp was obtained having a Kappa number of 14 and a brightness of 44, according to SCAN, corresponding to a reduction in the Kappa number of 2 Kappa number units, and an increase in brightness of 4%, as compared with conventional bleaching using the same alkali charge.

EXAMPLE 2

Pine wood chips were digested to a pulp of the same Kappa number as the pulp of Example 1, and bleached in an analogous manner, except that the alkali used in the alkali-oxygen-gas bleaching was white liquor having a sulphidity of 35%, instead of sodium hydroxide. The alkali charged was calculated as the quantity of alkali determined by acidimetric titration to pH 10. The alkali charged was calculated as NaOH, although sulphide and sodium carbonate were also included as active chemical ingredients. The white liquor had an alkali content calculated as NaOH of 130 grams per liter, determined in the aforementioned manner. In order to obtain the same Kappa number as that obtained when charging 25 kg. NaOH per ton pulp, the alkali charge was increased to 28 kg. NaOH, determined in the aforementioned manner. The brightness of the bleached pulp was the same as when pure sodium hydroxide was used.

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

1. In the bleaching of cellulose pulp by the alkaline oxygen gas process, in which a gas containing oxygen is introduced into the pulp in the presence of alkali, which can be selected from the group consisting of sodium hydroxide and sodium carbonate and which optionally

may contain sodium sulfide, the improvement which comprises first impregnating under superatmospheric pressure cellulose pulp obtained from a continuous pulping or digestion process and containing spent pulping liquor with waste alkaline oxygen gas bleaching liquor in order to displace a major proportion of the pulping chemicals from the cellulose pulp but retain a minor proportion of such chemicals, and then impregnating under superatmospheric pressure the resulting pulp with alkali to be employed in the alkaline oxygen gas bleaching.

2. A process according to claim **1**, in which the alkali-impregnated pulp is impregnated also with a cellulose degradation inhibitor.

3. A process according to claim **2**, in which the cellulose degradation inhibitor is a magnesium compound.

4. A process according to claim **3**, in which the total quantity of magnesium in the pulp after the impregnation is within the range from about 0.05 to about 1%, calculated as MgO, and based on the dry weight of the pulp.

5. A process according to claim **3**, in which the impregnation is effected in two zones, in the first of which a magnesium cellulose degradation inhibitor is introduced, and in the second of which an alkaline solution is introduced, at a pH such that precipitation of insoluble magnesium compounds takes place.

6. A process according to claim **3**, in which the compound is a soluble complex magnesium compound.

7. A process according to claim **1**, in which the waste alkaline oxygen gas bleaching liquor is the alkaline liquor remaining in the bleaching system upon completion of the alkaline oxygen gas bleaching process, after separation of the pulp therefrom.

8. A process according to claim **1**, in which the amount of organic substances derived from the spent cooking liquor and remaining in the cellulose pulp after the displacement is within the range from about 1 to about 30 kg., per 100 kg. of dry unbleached pulp.

9. A process in accordance with claim **1**, in which the waste alkaline oxygen gas bleaching liquor is introduced into the pulp by washing the spent pulping liquor partially from the pulp.

10. A process according to claim **1**, in which the impregnation with the waste alkaline oxygen gas bleaching liquor is carried out in a plurality of washing zones, waste liquor of the highest solids content being recovered as effluent from the first zone, and passed to the chemicals recovery system for evaporation and subsequent combustion, waste effluent from the last washing zone being used in reformulating pulping liquor for reuse.

11. A process in accordance with claim **1**, in which the waste alkali-oxygen gas bleaching liquor is recycled within the pulp alkali-oxygen gas bleaching process in a cyclic or continuous operation.

12. A process according to claim **1**, in which the temperature at which the displacement of waste digestion liquor from the pulp is carried out is within the range from about 50° C. to about 170°.

13. A process according to claim **1**, in which the superatmospheric pressure that is employed during the impregnation steps is within the range from about 3 to about 30 kg./cm.^{2}.

14. A process according to claim **1**, in which the pressure during digestion is substantially the same pressure used during the impregnation.

15. A process in accordance with claim **1**, in which the cellulose pulp is from the sulfate pulping process.

16. A process in accordance with claim **1**, in which the cellulose pulp is from the sulfite pulping process.

17. A process in accordance with claim **1**, in which the cellulose pulp impregnated with the waste alkali-oxygen gas bleaching liquor and spent pulping liquor and with alkali is bleached by treatment with oxygen gas at a partial pressure of oxygen of at least about one bar and a temperture within the range from about 50° to about 140° C.

18. A process according to claim **1**, in which the impregnated pulp is fed to the oxygen gas bleaching reactor from the impregnating zone under superatmospheric pressure.

19. A process according to claim **1**, in which the impregnation is effected continuously and directly after digestion of the pulp.

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S. LEON BASHORE, Primary Examiner

A. CORBIN, Assistant Examiner

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