

[54] **TREATMENT OF ALKALINE PULP
WITH AN ACIDIC MEDIUM
FOLLOWED BY OXYGEN BLEACHING
AND DELIGNIFICATION**

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[56]

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[57]

ABSTRACT

A method of delignifying and bleaching alkaline pulp which comprises the steps of pretreating the pulp with an acidic medium having a pH from 1.2 to 4.8, such as an aqueous sulphur dioxide solution or a mineral acid, and thereafter subjecting the pulp in an alkaline medium, preferably sodium hydroxide, to the action of oxygen gas at elevated temperature and pressure. Preferably, the pretreated pulp is subjected to the action of oxygen gas in the alkaline medium in the presence of a protector, such as magnesium carbonate or sodium silicate, which is operative to inhibit degradation of the physical strength properties of the pulp.

13 Claims, No Drawings

TREATMENT OF ALKALINE PULP WITH AN ACIDIC MEDIUM FOLLOWED BY OXYGEN BLEACHING AND DELIGNIFICATION

This application is a continuation of Ser. No. 738,132, filed June 19, 1968, now abandoned.

This invention relates to the bleaching and delignification of alkaline pulps, such as soda, kraft and sulphate pulps, with oxygen gas.

It is well known that cellulose chemical pulp may be produced by an alkaline process, such as the conventional soda, kraft, counter-current kraft, or sulphate process, from suitable starting material which may, for example, be derived from conifers, such as pine; from deciduous woods, such as eucalyptus, or from fibrous non-woody plants, such as bagasse. For the purpose of this specification, a cellulose chemical pulp produced by an alkaline process will simply be referred to as an "alkaline pump".

It is well known that untreated alkaline pump normally contains impurities, such as lignins, and has a dark brown color and is generally bleached to some degree before use in all but the roughest of papers. The pulp is thus often lightly treated to remove only a portion of the color or it may be fully treated in a multiplicity of bleaching operations to obtain the highest white possible by present art, or it may be treated in any intermediate manner as needed. In all but special cases, care is taken to preserve as far as possible the physical strength properties of the fibers.

Unfortunately, in all currently practiced methods of brightening alkaline pulps, caustic soda and chlorine compounds are almost exclusively used in some form or other in the first delignification stages. The waste waters from these stages, in particular, lead to serious effluent disposal problems.

In order to delignify and semi-bleach an alkaline pulp, it is well known in the art to subject untreated pulp successively to the following stages of treatment:

- a. Chlorination,
- b. Alkali extraction, and
- c. Hypochlorite treatment.

This sequence is generally referred to as the C-E-H sequence.

Chlorination converts lignins into water- and alkali-soluble chlorinated lignin compounds which are removed by water washing and by the alkali extraction step. The delignified pulp is bleached during the hypochlorite treatment to produce a so-called semi-bleached pulp.

In order to effect full bleaching, the semi-bleached pulp may be subjected to the following additional stages of treatment after the C-E-H sequence:

- d. Chlorine dioxide treatment,
- e. Alkali extraction, and
- f. Chlorine dioxide treatment.

The full bleaching sequence is generally referred to as the C-E-H-D-E-D sequence.

The above sequences suffer from the following disadvantages:

- i. Effluents containing large quantities of chlorine and sodium ions are produced during stages (a) and (b) and (c) listed above. The disposal of these effluents is a serious problem.
- ii. Color reversion is relatively high at the semi-bleached stages as well as at the fully bleached stage.

iii. Degradation of the physical strength properties of the pulp occurs during the hypochlorite stage.

iv. In certain cases, the capital outlay for chemical plant for the production of the chemicals is high, or alternatively, the cost of purchasing the chemicals is relatively high.

Certain modifications of, or deviations from, the fundamental sequences are possible. Thus, in order to obtain a stronger pulp with a higher degree of whiteness and less color reversion, as well as to permit some degree of effluent recovery, the basic C-E-H sequence may be modified by using mixtures of chlorine and chlorine dioxide or even chlorine dioxide alone in the chlorination stage.

"Active oxygen" compounds, such as hydrogen peroxide, have been used in the final bleaching of alkaline pulp as a substitute for, or an addition to, chlorine dioxide. It has been found that, for all practical purposes, "active oxygen" compounds are not effective for delignification and are, therefore, not suitable in the early delignification stages of purification. However, "active oxygen" compounds can be used to advantage in the later bleaching stages to give the sequence C-E-H-D-P-D or the sequence C-E-H-D-E-D-P, where "P" denotes the peroxide or other "active oxygen" stage. It has also been found that sulphur dioxide may be used to advantage in a final bleaching stage to give the sequence C-E-H-D-E-D-SO₂.

It is also known that alkali pulps can be delignified and bleached by subjecting it in an alkaline medium to the action of oxygen gas or any other gas containing free oxygen, such as air. When this treatment is carried out at elevated temperature and pressure, good delignification and bleaching can be obtained but it has been found that the physical strength properties of the pulp are affected adversely.

Among the latest publications on oxygen gas treatment of pulps in an alkaline medium are the work of Nikitine and Akim (Proc. Leningrad Acad. of Forestry 75/1956 — 77/1958 — 85/1960 and Bum. Prom. 12/1960) and U.S. Pat. No. 3,251,730 in the name of S. Watanabe.

In their French patent specification No. 1,387,853 and their corresponding Canadian patent specification No. 743,847, L'Air Liquide S.A. discloses that by treating a chemical pulp with oxygen gas in an alkaline medium in the presence of certain "catalysts" or "protectors" the physical and mechanical strength properties of the pump can be preserved, and in some cases even improved, while giving a very complete delignification and a significant increase in brightness. More particularly, the pulp is treated with oxygen gas in an alkaline medium in the presence of a "catalyst" used at a concentration from 0.5 to about 3 percent by weight of the pulp and selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, zinc carbonate, alkali metal borates and titanium dioxide.

The L'Air Liquide method gives improved results, but still suffers from the disadvantage that if higher brightnesses are required, there is still a tendency for undesirable degradation in the physical strength properties to occur so that the limits of operation have to be carefully defined. Also, it is normally necessary to conduct the treatment over extended periods of time of up to 2 hours. On alkaline pulps, brightnesses over 45

percent are rarely obtained and then only with undesirable degradation in physical strength properties.

There is no method known to the applicants for the further bleaching of oxygen semi-bleached alkaline pulps to full brightness of 86 percent or more, without having to use the conventional chlorination stage and the subsequent extraction stage.

It is an object of the present invention to provide an adjunct to an oxygen gas treatment of an alkaline pulp in an alkaline medium, with which a semi-bleached pulp with a higher brightness can be obtained substantially without loss in physical strength properties, than is possible with the oxygen gas treatment on its own, or with which an even higher brightness can be obtained without any substantial loss in physical strength properties.

It is a further object of the present invention to produce a fully bleached pulp with adequate strength properties by further treatment of such a semi-bleached pulp without the use of a chlorination stage and a subsequent extraction stage.

According to the invention a method of delignifying and bleaching an alkaline pulp includes the steps of pretreating the pulp with an acidic medium, and thereafter subjecting the pulp in an alkaline medium to the action of oxygen gas.

The oxygen gas acts to delignify and bleach the pretreated pulp. If only a semi-bleached pulp is required, no further treatment need be effected. However, the oxygen gas treatment may easily be followed by any suitable bleaching stage or stages. Thus, if the semi-bleached pulp is bleached by the known D-E-D treatment, it can lead to full-bleached brightnesses with a saving in time and bleaching chemicals due to more efficient bleaching that can be achieved.

The method according to our invention can replace the C-E-H or C-E stages of conventional semi- and full-bleaching procedures to achieve a saving in expensive treating chemicals and to minimize the effluent problem and the color reversion problem, while still obtaining high brightnesses and maintaining the physical strength properties of the pulp.

It is known that an acid treatment prior to bleaching by conventional bleaching agents other than oxygen gas, does not exhibit any appreciable beneficial effect, but it has been found quite unexpectedly that an acid pretreatment of an alkaline pulp, prior to oxygen gas treatment in an alkaline medium, materially enhances the brightness that can be obtained after the oxygen stage and at the same time acts to preserve physical strength properties.

It is preferable for the pretreated pulp to be well washed, preferably with water, before being subjected to oxygen gas bleaching. The wash water should be substantially free from any deleterious or interfering elements, such as manganese.

In order to permit a saving in chemicals and some recovery of the acidic wash waters, fresh pulp to be pretreated may be slurried in water recycled from the washing operation, without any deleterious results.

The pretreating action is a function of the pH of the acidic medium and it has been found that for most pulps, the required duration of the pretreatment decreases with decreasing pH when all other conditions remain constant. The acidic medium may have a pH

from 1.2 to 4.8, and preferably from 2.5 to 4.8. The duration of the pretreatment may be from 5 to 60 minutes. The pulp consistency during pretreatment may be about 5 percent, but there is nothing inherent in the pretreatment which restricts the consistency to this value if suitable equipment is used.

Any suitable acidic medium may be used for the pretreatment. Sulphur dioxide or mineral acids, such as hydrochloric acid or sulphuric acid, have been found to give good results. It is also possible to use an acidic material such as alum, or a mixture of acidic media. Sulphur dioxide is preferably used at a concentration from 0.5 to 1 percent by weight of the pulp on a dry basis.

An alkaline pump may be pretreated by adding an aqueous sulphur dioxide solution to a pulp slurry, preferably at ambient temperature. It has been found that no significant improvement in the bleaching or the protection of the physical strength properties against degradation is obtained if the SO_2 content is increased above 1% by weight on a dry pulp basis. On the other hand, if the SO_2 content is reduced below 0.5 percent by weight on a dry pulp basis, the results obtained are, although significant, not as satisfactory as in the preferred range of SO_2 concentration of 0.5 to 1 percent.

Experiments have shown that less satisfactory results are obtained if the contact time between the alkaline pulp and the SO_2 is less than 30 minutes and that no significant improvement is obtained if the contact time exceeds 60 minutes.

The subsequent oxygen gas treatment may be carried out in any suitable alkaline medium, preferably sodium hydroxide. Generally speaking, about 6 percent by weight sodium hydroxide on a dry pulp basis is preferred for most pulps if maximum bleaching and delignification is required. However, with pulps with a low lignin content, the quantity of sodium hydroxide may be reduced. The sodium hydroxide content will generally vary from 2% to 12% by weight on a dry pulp basis.

The oxygen gas treatment may be carried out at an operating temperature from 90°C to 135°C (although for most purposes a temperature of 130°C will be preferred) and at an oxygen pressure from 70 to 400 p.s.i. During oxygen gas treatment, the pulp consistency may be from 4 to 30 percent, preferably from 8 to 18 percent. The pulp may be subjected to the oxygen gas treatment for a period of time ranging from 10 to 100 minutes depending on the results required or the nature of the pulp being treated.

It is a further feature of the present invention that the acid pretreated pulp may be subjected to the action of oxygen gas in the alkaline medium in the presence of a protector operative to inhibit degradation of the physical strength properties of the pulp. Generally speaking, about 1 percent by weight of protector on a dry pulp basis is preferred, but the amount of protector may vary from 0.5 to 3.0 percent by weight on a dry pulp basis.

The protector may be selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, zinc carbonate, alkali metal borates and titanium dioxide, which is disclosed in French patent specification No. 1,387,853. In this group, magnesium carbonate is the preferred protector.

The protector may also be selected from the group consisting of silica; an alkali metal silicate, such as sodium silicate; an alkali earth silicate, such as magnesium silicate; an alkali earth oxide, such as magnesium oxide; an alkali earth hydroxide, such as magnesium hydroxide; and an alkali earth salt, preferably a magnesium salt, such as magnesium phosphate, magnesium acetate, or magnesium chloride. In this group, sodium silicate, magnesium oxide and magnesium silicate are particularly advantageous, sodium silicate being preferred because of its solubility.

It will be appreciated that in carrying out the method according to the invention, no quantities of deleterious or interfering elements, such as manganese, should be introduced at any stage.

Although it is preferred to use a protector, the acid pretreatment according to the invention may be used without a protector being employed in the subsequent oxygen treatment. It has been found that without a protector, the acid treatment can result in a higher brightness after the oxygen treatment than is possible with the oxygen treatment on its own, substantially without any sacrifice of physical strength properties of the pulp. This will be apparent from the results shown in table I below.

By increasing the solubility of the oxygen gas used, faster and improved bleaching and delignification can be obtained. Since such solubility of oxygen at any selected temperature is a function of the partial pressure of the oxygen, it is advantageous to carry out the oxygen treatment at as high an oxygen concentration and/or as high a total gas pressure as is practically feasible. In order to protect the pulp against degradation of its physical strength properties when it is subjected to severe conditions of time, temperature and pressure to obtain higher brightnesses and improved delignification, it is advantageous to use a protector during the oxygen gas treatment.

The acid pretreatment plus the use of a protector permits pressures up to 400 p.s.i. and even higher and temperatures as high as 130°C to be used in order to obtain higher brightnesses substantially without increase in degradation of the physical strength properties of the pulp as compared with the same oxygen gas treatment but without the acid pretreatment and without the use of a protector. Generally speaking, the operating temperature may range from 90°C to 135°C (although for most purposes a temperature of 130°C will be preferred) and the operating pressure may be from 70 to 400 p.s.i. during the oxygen gas treatment in the presence of a protector after acid pretreatment. The effect of a protector will be apparent from the results shown in tables I and II below.

With the method according to the invention, the time required for the oxygen treatment to achieve a given brightness is reduced as compared with hitherto known oxygen gas bleaching and delignification methods. This is apparent from the results shown in table III below.

Since the solubility of oxygen in the alkaline solution is a function of the partial pressure of the oxygen which can be increased by either increasing the total gas pressure or the oxygen content, or both, and since the method according to the invention permits the pressure to be increased considerably in relation to known methods, the method according to the invention is not limited to the use of relatively pure oxygen, but may

also be used with compressed air or any other gas containing free oxygen, provided no detrimental materials are present.

The oxygen gas treatment is best carried out in any suitable pressure apparatus which will ensure intimate contact or adequate exposure of the pulp mass with or to oxygen in the gas phase, thus to ensure adequate resaturation of the liquid medium with oxygen.

It is not necessary to maintain the temperature constant during oxygen gas treatment and it may be advantageous to allow it to rise continuously or stepwise during the treatment so that a portion of the alkali is consumed at a lower temperature. Also, the alkaline medium may be added stepwise during the treatment.

The oxygen gas treated pulp may be washed in any suitable manner. The choice of the washing operation is largely governed by whether recovery of chemicals in the effluent or subsequent bleaching is contemplated. It is advantageous for the washing operation to be done carefully and for the effluent to be treated in a chemical recovery process. Further economies in recovery of this filtrate can be achieved if portion of this filtrate is recirculated for dilution of pulp which is to be oxygen gas treated. This has been found to have no deleterious effects on the brightnesses obtained.

Such filtrate, or recirculated filtrate, may then, for example, be used as portion of the wash water used in the normal washing stages applied to the pulp as produced by the pulping process concerned, or may be added directly to the liquors at any stage in the recovery process concerned. Alternatively, the caustic soda in the filtrate may be recovered by any of the known methods of recovery. It is a big advantage of this process that despite the load of organic matter in these filtrates, they are substantially free of chlorides which are normally always present in bleach plant effluents. This enables the chemical recovery process to be conducted readily without the serious interferences caused by chlorides, and allows, if necessary, any recovered sodium carbonate to be converted to caustic soda for repeated re-use. The very heavy pollution load caused by normal multi-stage bleaching operations will in this way be very beneficially reduced.

Higher brightness semi-bleached pulp may be produced by following the oxygen gas treatment with a second acidic treatment similar to the pretreatment. Alternatively, the oxygen gas treated pulp may be subjected to any of the conventional bleaching agents, such as hypochlorite, chlorine dioxide or peroxide, with a considerable saving in these agents as compared with conventional processes. The results achieved with a single additional bleaching stage after the oxygen gas treatment, are indicated in table IV below.

Hitherto it has not been possible to obtain full bleaching of oxygen gas treated alkaline pulp by means of the conventional D-E-D sequence only. Chlorination was still necessary, thus giving a sequence such as O₂-C-E-D-E-D. It is an advantage of our invention that, quite unexpectedly, due to better delignification, full bleaching may be more readily obtained by subjecting pulp which has been semi-bleached in accordance with our invention, to the conventional D-E-D sequence only and so directly to obtain full bleaching. The type of pulp which is conventionally subjected to the C-E-H-D-E-D sequence may in accordance with our invention

be subjected to the sequence $\text{SO}_2\text{-O}_2\text{-SO}_2\text{-D-E-D}$ or to the sequence $\text{SO}_2\text{-O}_2\text{-H-D-E-D}$. The type of pulp which is conventionally subjected to the C-E-D-E-D sequence may be subjected to the sequence $\text{SO}_2\text{-O}_2\text{-D-E-D}$.

The results of full bleaching according to the invention are indicated in tables V and VI below.

In accordance with the present invention it is now possible for the first time fully to bleach alkaline pulp to accepted maximum brightness without a chlorination stage and a subsequent extraction stage being required. The caustic soda from the oxygen bleaching stage and sulphur from the sulphur dioxide pretreatment are recoverable as make-up in a conventional Kraft Pulp Chemical Recovery Process or in other processes involving incineration, without the interference normally caused by the presence of chlorides. The replacement or modification of the C-E-H stages can thus be effected with a substantial or almost complete reduction in the effluent problem, since the caustic soda used in our method may be recovered and re-used, or the caustic soda and/or Sulphur Dioxide may be used as make-up in the conventional recovery process concerned, without any attendant problems caused by chloride contamination.

The capital outlay for a full bleaching plant could in certain circumstances be reduced considerably for the following reasons:

- i. no chlorine electrolytic cells are required;
- ii. the main chemical required is caustic soda which can be recovered readily and re-used;
- iii. the only other chemicals required are those needed to produce chlorine dioxide and such chemicals are only required in relatively small quantities.

The following examples are illustrative of the invention without in any way limiting the scope thereof. In the examples and throughout this specification, concentrations are given as percentages by weight on a dry pulp basis, and oxygen pressures are those pertaining at maximum temperature during oxygen gas treatment. Pulp consistency is the ratio, expressed as a percentage, of the weight of the dry pulp to the weight of the wet pulp.

All tests for the examples were carried out in accordance with TAPPI specifications, unless otherwise stated. For all the examples, the heating-up time to reach maximum temperature during the oxygen gas treatment, was 60 minutes, but it will be appreciated that a shorter or longer heating-up period may be employed.

EXAMPLE I

The lignin content, the brightness and the physical strength properties of the following pulps are compared in table I below:

- a. untreated, unbleached, industrial softwood (pine) kraft pulp of KAPPA 23.9 (hereinafter referred to as Pulp A);
- b. the pulp of (a) above after oxygen gas treatment in an alkaline medium without a protector and without an acid pretreatment (hereinafter referred to as Pulp B);
- c. the pulp of (a) above after an acid pretreatment followed by the same oxygen gas treatment in an alkaline medium as in (b) above, but without a protector (hereinafter referred to as Pulp C);

d. the pulp of (a) above after the same acid pretreatment followed by the same oxygen gas treatment in an alkaline medium without a protector as in (c) above, but with the exception that the oxygen gas treatment was carried out for a shorter period of time (hereinafter referred to as Pulp D);

e. the pulp of (a) above after the same oxygen gas treatment in an alkaline medium as in (b) and (c) above, but with a protector and without an acid pretreatment (hereinafter referred to as Pulp E);

f. the pulp of (a) above after the same acid pretreatment as in (c) above followed by the same oxygen gas treatment in an alkaline medium and with a protector as in (e) above (hereinafter referred to as Pulp F).

The results of Pulps B, C and D show that the physical strength properties of the pulp are degraded by oxygen gas treatment without a protector. With Pulps C and D which were subjected to acid pretreatment, higher brightnesses were obtained as compared with Pulp B which did not have an acid pretreatment.

A comparison of the results for Pulps C and D shows that the duration of the oxygen gas treatment affects the brightness and the physical strength properties that are obtained. A comparison of the results for Pulps B and D show that with an acid pretreatment according to the invention, a semi-bleached pulp with a higher brightness can be obtained substantially without loss in physical strength properties, than is possible with the oxygen gas treatment on its own.

The results for Pulps E and F show that where oxygen gas treatment is carried out in the presence of a protector, the physical strength properties of the pulp are preserved to a marked degree. With Pulp F which was subjected to an acid pretreatment, the brightness was materially enhanced in relation to Pulp E which was not subjected to an acid pretreatment.

It will also be noticed that the acid pretreatment enhances the color reversion properties despite the much higher brightnesses obtained.

It will be appreciated that the various operating factors during pretreatment and/or oxygen gas treatment are variable relative to one another depending on the results required or the nature of the pulp being treated.

EXAMPLE II

The lignin content, the brightness and the physical strength properties of an industrial softwood (pine) kraft pulp of KAPPA 23.1 after an acid pretreatment followed by oxygen gas treatment in the presence of an alkaline medium without a protector, are compared below in table II with those of the same pulp after the same acid pretreatment followed by the same oxygen gas treatment in an alkaline medium but in the presence of different protectors, namely magnesium carbonate, sodium silicate and magnesium trisilicate.

In the case of sodium silicate, only 4% NaOH was actually added to constitute the alkaline medium for the oxygen gas treatment, since the sodium silicate contributed sufficient additional alkali to the reaction.

EXAMPLE III

Table III compares the required duration of an oxygen gas treatment to bleach an industrial softwood (pine) kraft pulp of KAPPA 32 to a brightness of 50 by the following treatments:

- a. oxygen gas treatment in an alkaline medium with a protector at an oxygen pressure of 200 p.s.i.g., but without an acid pretreatment (hereinafter referred to as Pulp G);
- b. the same oxygen gas treatment as in (a) above after an acid pretreatment in H_2SO_4 at pH 3.0 for 15 minutes (hereinafter referred to as Pulp H);
- c. the same oxygen gas treatment as in (a) above after an acid pretreatment in H_2SO_4 at pH 1.6 for 15 minutes (hereinafter referred to as Pulp I);
- d. the same oxygen gas treatment as in (a) above after an acid pretreatment in SO_2 at pH 3.0 for 60 minutes (hereinafter referred to as Pulp J);
- e. the same pretreatment and oxygen gas treatment as in (d) above with the exception that the oxygen gas treatment was carried out at 400 p.s.i.g. (hereinafter referred to as Pulp K).

A comparison of the results for Pulps H, I and J with the results for Pulp G shows that with an acid pretreatment according to the invention, the required duration of the oxygen gas treatment at a given oxygen pressure to obtain a given brightness is reduced considerably as compared with oxygen gas treatment without an acid pretreatment.

The results for Pulps H and I show that with H_2SO_4 as acidic pretreating medium, the contact time between H_2SO_4 and pulp may be as short as 15 minutes. This is also true for other mineral acids.

The results for Pulps J and K show the marked reduction in the required duration of the oxygen gas treatment which is brought about by an increase in the oxygen pressure, when all other factors remain constant.

EXAMPLE IV

Table IV below given an indication of the potential of oxygen gas bleached pulps produced in accordance with the present invention, to further bleaching in a single additional bleaching stage after the oxygen gas treatment, by comparing the brightnesses and physical strength properties of an industrial softwood (pine) kraft pulp of KAPPA 20.0 after the following treatments:

- a. a conventional C-E-H treatment (hereinafter referred to as Pulp L);
- b. the same oxygen gas treatment in an alkaline medium with a protector but without an acid pretreatment as Pulp E in Example I above, followed by a hypochlorite treatment (hereinafter referred to as Pulp M);
- c. the same acid pretreatment and the same oxygen gas treatment in an alkaline medium with a protector as Pulp F in Example I above, followed by a hypochlorite treatment (hereinafter referred to as Pulp N);
- d. the same acid pretreatment and the same oxygen gas treatment in an alkaline medium with a protector as in (c) above, followed by a more concentrated hypochlorite treatment than in (c) above (hereinafter referred to as Pulp O).

Although Pulp N was subjected to a lower dosage of hypochlorite than Pulp M, a higher brightness was obtained as a result of the acid pretreatment.

The brightness of 67.0 obtained with Pulp M after the hypochlorite treatment is the maximum obtainable for the pulp in question with a hypochlorite treatment after an oxygen gas treatment without an acid pretreat-

ment. Although Pulp M was subjected to a higher dosage of hypochlorite than Pulp N, a higher brightness was obtained with the latter pulp which was subjected to an acid pretreatment.

The saving in expensive bleaching chemicals that can be achieved with a method in accordance with the present invention as compared with the conventional C-E-H treatment, is apparent from a comparison of the chemicals used for Pulps M, N and O in relation to the chemicals used for Pulp L. The caustic soda used on the oxygen gas bleaching of pulps M, N and O is readily recoverable since it is free from chlorides.

EXAMPLE V

Table V below compares the brightnesses and the physical strength properties obtained with an industrial softwood (pine) kraft pulp of KAPPA 22.6 after the following treatments:

- a. the same oxygen gas treatment in an alkaline medium with a protector and without an acid pretreatment as applied to Pulp E in Example I above, followed by a D-E-D sequence (hereinafter referred to as Pulp P);
- b. the same treatment as in (a) above preceded by the same acid pretreatment as applied to Pulp F in Example I above (hereinafter referred to as Pulp Q);
- c. the same treatment as in (b) above, but with an acidic treatment similar to the acid pretreatment interposed between the oxygen gas and chlorine dioxide stages (hereinafter referred to as Pulp R);
- d. the same treatment as in (c) above, but with a hypochlorite stage instead of the additional acidic treatment (hereinafter referred to as Pulp S);
- e. a conventional C-E-H-D-E-D sequence (hereinafter referred to as Pulp T);

With the SO_2 - O_2 - SO_2 -D-E-D sequence of Pulp R, good physical strength properties, high brightness and low color reversion are obtained, while at the same time a saving in bleaching chemicals as compared with the conventional C-E-H-D-E-D sequence is achieved.

Acceptable brightnesses are also obtained with the SO_2 - O_2 -D-E-D and SO_2 - O_2 -H-D-E-D sequences of pulps Q and S respectively, Pulp Q showing a better preservation of physical strength properties.

The acid pretreatment according to the invention results in improved color reversion properties as compared with the conventional C-E-H-D-E-D sequence of Pulp T.

EXAMPLE VI

Table VI below compares the brightnesses and the physical strength properties obtained with an industrial eucalyptus-acacia hardwood kraft pulp of KAPPA 20 after the following treatments:

- a. a conventional C-E-H-D-E-D sequence (hereinafter referred to as Pulp U);
- b. the same acid pretreatment and oxygen gas treatment in an alkaline medium with a protector as applied to pulp F in Example I above, followed by an additional acidic treatment similar to the pretreatment and a D-E-D sequence (hereinafter referred to as Pulp V).

The high brightness of 65.6 for Pulp V after the SO_2 - O_2 sequence, is typical of the brightness obtainable with that sequence on hardwood kraft pulps.

TABLE I

Characteristics of an industrial softwood (pine) kraft pulp of kappa 23.9 after oxygen gas treatment in an alkaline medium with and without acid pretreatment and a protector

	Pulp A	Pulp B	Pulp C	Pulp D	Pulp E	Pulp F
Pretreatment:						
Pulp consistency			8	8		8
Acidic medium (percent SO ₂)			1	1		1
pH of acidic medium			3.2	3.2		3.2
Operating temperature			Ambient	Ambient		Ambient
Duration (mins.)			60	60		60
Elrepho brightness	24.1	24.1	26.5	26.5	24.1	26.5
Oxygen gas treatment:						
Pulp consistency			8	8		8
Alkaline medium (percent NaOH)			6	6		6
Operating temperature (°C.)			130	130		130
Oxygen pressure at max. temp. (p.s.i.g.)			190	190		190
Duration at temperature (mins.)			100	80		100
Protector					(1)	(1)
Elrepho brightness	24.1	51.2	58.4	56.3	51.6	59.6
Colour reversion* (18 hours at 105° C.)		0.6	0.4	0.4	0.5	0.4
Physical strength properties (all results at 9,090 revs. Lampen):						
Canadian freeness (cc.)	640	330	545	505	424	588
Breaking length (metres)	11,400	9,650	10,330	10,630	10,610	11,500
Double folds (under 800 g.)	576	244	173	173	475	500
Burst factor	70.4	59.5	56.1	58.1	63.3	66.3
Tear factor	91	74	71	73	94	99
Permanganate No. (AFNOR)	23.9	4.6	3.3	3.4	4.3	3.1

¹ 1% MgCO₃.

*Pulps produced by a conventional C-E-H sequence normally have a colour reversion value of 4.3 for a brightness of 52 and a colour reversion value of 8.2 for a brightness of 60.

TABLE II

CHARACTERISTICS OF AN INDUSTRIAL SOFTWOOD (PINE) KRAFT PULP OF KAPPA 23.1 AFTER ACID PRETREATMENT AND OXYGEN GAS TREATMENT WITH DIFFERENT PROTECTORS

PRETREATMENT						
Pulp Consistency:	5.0					
Acidic Medium:	1%SO ₂					
pH of Acidic Medium:	3.0					
Operating Temperature:	Ambient					
Duration:	60 mins.					
OXYGEN GAS TREATMENT						
Pulp Consistency:	8.0					
Alkaline Medium:	6%NaOH					
Operating Temperature:	130°C					
Oxygen Pressure at max.temp:	200 p.s.i.g.					
Duration:	100 mins.					
	Pulp treated without protector	Pulp treated with 1%MgCO ₃	Pulp treated with 2% Sodium silicate	Pulp treated with 1% magnesium trisilicate		
Elrepho Brightness	51.6	56.7	55.3	60.3		
Canadian Freeness (cc):	320	515	560	565		
Breaking Length (meters):	9580	9850	10,400	10,900		
Double Folds (under 800g):	244	793	1,200	614		
Burst Factor:	58.4	63.1	65.3	64.5		
Tear Factor:	84	99	102	101		
Permanganate No. (AFNOR):	5.1	4.1	4.3	3.8		

TABLE III

DURATION OF OXYGEN GAS TREATMENT TO BLEACH AN INDUSTRIAL SOFTWOOD (PINE) KRAFT OF K.A.P.P.A. NUMBER 32 TO AN ELREPHO BRIGHTNESS OF 50.

	Pulp G	Pulp H	Pulp I	Pulp J	Pulp K
Pretreatment pulp consistency	-	5.0	5.0	5.0	5.0
acidic medium	-	0.8%H ₂ SO ₄	5%H ₂ SO ₄	1%SO ₂	1%SO ₂
pH of Acidic medium	-	3.0	1.6	3.0	3.0

25	operating temperature	-	ambient	ambient	ambient	ambient
	duration (mins)	-	15	15	60	60
	oxygen gas treatment					
	pulp consistency	8.0	8.0	8.0	8.0	8.0
30	alkaline medium	6%NaOH	6%NaOH	6%NaOH	6% NaOH	6%NaOH
	operating temperature (°C)	130	130	130	130	130
	oxygen pressure at max. temp as p.s.i.g.	200	200	200	200	400
35	duration at max. temp (mins)	60	22	25	30	16
	protector:	1%MgCO ₃	1%MgCO ₃	1%MgCO ₃	1%MgCO ₃	1%MgCO ₃
40	* color reversion (18 hours at 105°C)	0.5	0.1	0.1	0.2	0.6
	* Pulps produced by a conventional C-E-H sequence normally have a color reversion value of 4.1 for a brightness of 50.					

TABLE IV

THE POTENTIAL OF OXYGEN GAS BLEACHED PULPS TO BE FURTHER BLEACHED IN A SINGLE ADDITIONAL BLEACHING OPERATION

Basic Pulp: Industrial Softwood (Pine) Kraft of KAPPA 20.0.					
Bleaching sequence:	Pulp L	Pulp M	Pulp N	Pulp O	
Chemical usage:	C-E-H	O ₂ -H	SO ₂ -O ₂ -H	SO ₂ -O ₂ -H	
55	Acidic pretreatment	-	-	1%SO ₂	1%SO ₂
	Alkali	-	6%NaOH	6%NaOH	6%NaOH
	Protector	-	1%MgCO ₃	1%MgCO ₃	1%MgCO ₃
	Chlorination	5.65	-	-	-
	Alkaline extraction	3.0% NaOH	-	-	-
60	Hypochlorite as av. Cl ₂	2.35	1.0	0.5	1.0
	Elrepho brightness				
	Untreated	25.5	25.5	25.5	25.5
	After acid pretreatment	-	-	27.0	27.0
65	After oxygen gas treatment	-	53.5	58.5	58.5
	After Hypochlorite stage	75.9	67.0	69.7	76.0
	Color reversion	12.8	2.1	1.2	3.3

**Physical strength
Properties**(all results at 9000
revs Lampen)

Canadian freeness (cc)	510	525	545	615
Breaking length (meters)	9620	9950	10200	8470
Double folds (under 800g)	420	227	404	221
Burst Factor	49.6	56.0	61.6	45.1
Tear Factor	87	95	93	100

TABLE V.

**FULL BLEACHING OF AN INDUSTRIAL SOFTWOOD
(PINE) KRAFT PULP OF KAPPA 22.6**

	Pulp P	Pulp Q	Pulp R	Pulp S	Pulp T
Bleaching Sequence:	O ₂ -D-E- D	SO ₂ -O ₂ - D-E-D	SO ₂ -O ₂ - SO ₂ -D-E-H-D-E-D	SO ₂ -O ₂ - D-E-D	C-E-H- D-E-D
Brightness:					
Untreated	25.5	25.5	25.5	25.5	25.5
SO ₂	—	27.0	27.0	27.0	—
O ₂	53.0	58.0	58.0	58.0	—
SO ₂	—	—	63.9	—	—
H	—	—	—	78.2	75.9
D	76.0	77.3	77.9	83.8	79.9
E	—	—	—	—	—
D	78.0	86.6	88.7	86.7	88.0
Physical Strength properties after D-E-D sequence					
Canadian freeness (cc)	427	535	510	615	510
Breaking length (meters)	10,210	9,760	8,990	8,470	9,260
Double folds (under 800g)	296	441	397	221	420
Burst factor	58.9	56.2	55.8	45.1	49.6
Tear factor	75	108	103	100	87
Color reversion (18 hr. at 105°C)	Nil	2.7	3.2	2.7	6.5
Chemical usage					
C	—	—	—	—	5.65
E	—	—	—	—	3.0
H	—	—	—	1.3	2.35
D	0.80	0.75	0.75	0.75	0.80
E	1.5	1.5	1.5	1.5	1.5
D	0.45	0.25	0.25	0.25	0.45

TABLE VI

**FULL BLEACHING OF AN INDUSTRIAL
EUCALYPTUS-ACACIA HARDWOOD KRAFT
PULP OF K.A.P.P.A. 20**

Bleaching sequence	PULP U C-E-H- D-E-D	PULP V SO ₂ -O ₂ -SO ₂ - D-E-D
Chemicals used		
C	4.2	—
E	3.0	—
H	2.0	—
D	0.7	0.7
E	1.5	1.5
D	0.3	0.3
Brightnesses		
Untreated	24.6	24.6
SO ₂	—	25.8
O ₂	—	65.6 *
SO ₂	—	66.9
H	70.8	—
D	76.2	80.9
E	—	—
D	84.6	87.3
Physical strength properties (All Results at 9,000 revs. Lampen.)		
Canadian Freeness (cc)	—	480
Breaking Length (meters)	—	7,500

Double Folds (under
800 g)

Burst Factor	40	35
Tear Factor	42	38
Color Reversion	72	75
	8.8	2.9

*If no acid pretreatment is applied a brightness of only 61.0 is obtained.

We claim:

1. A method of delignifying and bleaching an alkaline pulp without a chlorination stage, comprising the steps of pretreating the alkaline pulp with an acidic medium having a pH from 1.2 to 4.8 for a time sufficient to enhance the ultimate brightness of the pulp after bleaching; washing the thus treated alkaline pulp; and thereafter subjecting same in an alkaline medium to the action of oxygen gas at a temperature of 90° to 135°C and a pressure in excess of 70 p.s.i.g.

2. A method according to claim 1, wherein after the oxygen gas treatment the pulp is subjected to an additional treatment in an acidic medium similar to the pretreatment.

3. A method according to claim 1, wherein the alkaline medium comprises sodium hydroxide.

4. A method of delignifying and bleaching an alkaline pulp without a chlorination stage, comprising the steps of pretreating the alkaline pulp with an acidic medium having a pH from 1.2 to 4.8 for a time sufficient to enhance the ultimate brightness of the pulp after bleaching and comprising at least one of the substances in the group consisting of sulphur-dioxide, a mineral acid and alum; washing the thus treated alkaline pulp; and thereafter subjecting same in an alkaline medium to the action of oxygen gas at a temperature of 90° to 135°C. and a pressure in excess of 70 p.s.i.g.

5. A method according to claim 4, wherein the acidic medium has a pH of 2.5 to 4.8.

6. A method according to claim 4, wherein the mineral acid is sulphuric acid.

7. A method according to claim 4, wherein the acidic medium comprises sulphur-dioxide at a concentration of from 0.5 to 1 percent by weight of the pulp on a dry basis.

8. A method of delignifying and bleaching an alkaline pulp without a chlorination stage, comprising the steps of pretreating the alkaline pulp with a mineral acid at a pH from 1.2 to 4.8 for a time sufficient to enhance the ultimate brightness of the pulp after bleaching; washing the thus treated alkaline pulp; and thereafter subjecting same in the presence of 2 to 12 percent by weight of sodium hydroxide on a dry pulp basis to the action of oxygen gas at a temperature of 90° to 135°C and a pressure in excess of 70 p.s.i.g.

9. A method of delignifying and bleaching an alkaline pulp without a chlorination stage, comprising the steps of pretreating the alkaline pulp with an acidic medium having a pH from 1.2 to 4.8 for a time sufficient to enhance the ultimate brightness of the pulp after bleaching; washing the thus treated alkaline pulp; and thereafter subjecting same in an alkaline medium to the action of oxygen gas at a temperature of 90° to 135°C and a pressure in excess of 70 p.s.i.g. and in the presence of an inorganic or organic protector operative to inhibit degradation of the physical strength properties of the pulp, the alkaline medium being constituted by a substance other than the protector.

10. A method of delignifying and bleaching an al-

kaline pulp without a chlorination stage, comprising the steps of pretreating the alkaline pulp with an acidic medium having a pH of 1.2 to 4.8 for a time sufficient to enhance the ultimate brightness of the pulp after bleaching; washing the thus treated alkaline pulp; and thereafter subjecting same in an alkaline medium to the action of oxygen gas at a temperature of 90° to 135°C and a pressure in excess of 70 p.s.i.g. and in the presence of a protector selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, magnesium acetate, zinc carbonate, alkali metal borates, titanium dioxide, silica, an alkali metal silicate, an alkali earth silicate, an alkali earth oxide, and an alkali earth hydroxide, the alkaline medium being constituted by a substance other than the protector.

11. A method according to claim 10, wherein the protector is present in the amount of 0.5 to 3.0 percent

by weight on a dry pulp basis.

12. A method of delignifying and bleaching an alkaline pulp without a chlorination stage, comprising the steps of pretreating the alkaline pulp with a mineral acid at a pH of 1.2 to 4.8 for a time sufficient to enhance the ultimate brightness of the pulp after bleaching; washing the thus treated alkaline pulp; and thereafter subjecting same in an alkaline medium comprising 2 to 12 percent by weight of sodium hydroxide on a dry pulp basis to the action of oxygen gas at a temperature of 90° to 135°C. and a pressure in excess of 70 p.s.i.g. and in the presence of up to 3 percent by weight on a dry pulp basis of a protector comprising a magnesium salt.

13. A method as claimed in claim 12 wherein the magnesium salt is magnesium oxide or magnesium hydroxide.

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