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# UNITED STATES PATENT OFFICE

#### 1,970,065

#### PROCESS OF BLEACHING PULP AND OTHER LIGNIFIED MATERIALS

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10 Claims. (Cl. 8-2)

This invention relates to processes of bleaching wood pulps; and it comprises a method of removing lignin and color from wood pulp wherein the

- pulp is first treated with chlorine in a more or less hydrolyzed aqueous solution, then with hypochlorous acid in an aqueous solution free of hydrochloric acid, and finally with hypochlorite in an alkaline solution; treatment being ordinarily in transit with a flowing stream of pulp in aque-
- .10 ous suspension and with an initial addition of all the chlorine needed, an intermediate addition of calcium carbonate to neutralize HCl, but not HOCl, and a later addition of caustic alkali to neutralize the HOCl and make an alkaline solu-
- 15 tion; said method also being applicable to making clean strong cellulose directly from wood; all as more fully hereinafter set forth and as claimed. The present invention provides a rapid and economical process for removing lignin and color-
- 20 ing matter from various wood pulps, including those classed as hard bleaching pulps, without impairing the strength or other desirable characteristics of the cellulose fibres.
- Wood pulps are frequently classed as easy or 25 hard bleaching according to the effects of the cooking or chemical process by which they are produced. If the process is carried to the point where practically all of the lignin and related compounds are removed from the cellulose, the
- 30 result is an easy bleaching pulp. However, with the methods now available for the production of this class of pulp, it is necessary to subject the material to such drastic conditions of treatment
- as to impair the strength and other characteris-35 tics of the cellulose fibres. In producing what is known as hard bleaching pulps the cooking or pulping process is usually conducted under such conditions that the chemical action upon the cellulose is minimized; is reduced to a point where
- 40 degradation of quality is substantially avoided. This produces a strong pulp but one containing residual lignin and related compounds or coloring matter which are exceedingly difficult to remove.
- 45 Where this removal is attempted by the usual methods of bleaching attacking lignin, an oxidation of the cellulose occurs with consequent degradation or loss of strength in the final product.
- 50 The problem of removing residual lignin and related compounds from hard bleaching pulps without direct oxidation has been the subject of considerable investigation by workers in this art and numerous processes have been developed in
- 55 which hard bleaching pulps are subjected to the

action of solutions of chlorine under varying conditions of operation. These processes are primarily based upon the assumption that chlorine directly combines with lignin to produce chlorinated derivatives of undefined composition and proper- 60 ties. It is now generally recognized that these chlorinated derivatives or reaction products exhibit somewhat altered characteristics such as an increased solubility in alkalies and this recognition has lead to the development of processes in- 65 volving various combinations of chlorine and alkaline treatments. So far as I am aware none of these processes has achieved any considerable commercial success due, apparently, to the fact that, in the absence of specific knowledge con- 70 cerning the nature of the reactions between lignin and chlorine, it has been impossible to avoid undesirable secondary reactions which have the effect of causing the final product to exhibit undesirable characteristics which can be corrected 75 only by resorting to expensive and complicated after treatments such as alkaline treatments to which reference has been previously made.

It is known that lignin has the characteristics of an aromatic phenolic substance as in its be- 80 havior toward caustic soda and the like, and in the light of recent investigation, I have been able to establish the fact that lignin will react with a dilute aqueous solution of chlorine and also with a dilute solution of hypochlorous acid to produce, 85 in each instance, a chlorinated product which is insoluble in water but somewhat soluble in dilute alkalies. Another characteristic of these products is that, under the influence of alkaline bleaching or oxidizing agents, they undergo a transforma- 99 tion into the deleterious colored substances. The purpose of the bleaching is, of course, to obtain a pulp consisting only of pure cellulose free from the lignin and from the coloring matters which are originally present in the wood or are pro- 95 duced by secondary reactions occurring during the bleaching process. The present invention accomplishes this by a methodical use of chlorine, the pulp or other lignified material being treated under conditions yielding a final chlorinated lig- 100 nin derivative which is readily soluble in alkaline solutions and in alkaline oxidizing media without production of color.

It is now definitely established that when pulp containing lignin or related lignin compounds is 105 treated with chlorine in a dilute acid solution it reacts very rapidly to produce a chlorinated derivative or reaction product which is somewhat soluble in the presence of alkaline bleaching agents but yields difficultly removable color 119 formations. Treatment with chlorine in an acid 4 per cent chlorine based on the bone dry weight solution, whether the acidity results from hydrolysis of chlorine or is due to another cause, is equivalent to the action of chlorine as such. I

- have discovered that a primary chlorinated derivative or reaction product so produced, after the neutralization of any hydrochloric acid present or formed in the reaction, is capable of undergoing a further energetic change or reaction
- 10 with free hypochlorous acid. Free hypochlorous acid results when the solution still containing free chlorine is neutralized with calcium carbonate or like neutralizing agent incapable of reacting with free HOCl. This second reaction yields a
- 15 hitherto unknown secondary chlorinated derivative or reaction product which has entirely different properties as compared with the product of the initial reaction. Practically speaking, the most important properties characterizing this new
- 20 secondary reaction product are (1) its greater solubility in alkaline oxidizing media and (2) the fact that it does not yield colored products when treated with such reagents. The formation of such a secondary product and its proper-
- 25 ties has not been previously recognized. The lignin of unbleached pulp reacts in two stages. The first stage of reaction occurs in acid solution; usually in the presence of hydrochloric acid resulting from hydrolysis of chlorine, while the
- 30 second stage is brought about by subjecting the primary chlorinated product to the action of hypochlorous acid in the absence or substantial absence of hydrochloric acid. This two-stage reaction is utilized in the present invention wherein
- **35** pulp is first acted on by chlorine in an acid solution, and then the chlorinated products formed at the expense of the lignin, are acted on by hypochlorous acid in a solution substantially free of other acids; that is, in a neutral or substan-40 tially neutral medium. Both the successive reac-
- tions proceed at relatively high velocity and there is formed a new chlorinated reaction product which can be completely and easily bleached to a white color with very small quantities of alka-
- 45 line bleaching agents and without danger of impairing the strength or other desirable characteristics of the cellulose. This result is presumably due to the fact that the chlorination of the pulp, in two stages as described herein, avoids 50 undesirable secondary reactions, including the
- production of resistant color. The new reaction product has substantially greater solubility in alkaline bleaching agents than the products of chlorinating methods in the prior art.
- 55 Proceeding now to a more detailed description reference will be had to the accompanying drawings, wherein-

Figure 1 is a curve diagram illustrating the. progress of the reactions characterizing my im-60 proved process in comparison with other processes, and

Figure 2 is a diagrammatic view of a simple form of apparatus which may be used in carrying out the process in a continuous manner.

- 65 The graphs of Fig. 1 are plotted from data obtained in a number of tests on various ways of bleaching, including this invention. In order to make the results strictly comparable so far as possible, conditions were made identical as re-
- 70 gards amount of chlorine, amount of water, proportion of dry pulp, agitation, time, temperature. etc. All tests were made with the same unbleached pulp: a particular kraft pulp containing a minimum of 4 per cent lignin. In each 75 case, treatment was with a solution containing

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of the pulp. An aqueous suspension was made containing 5 parts of dry pulp to 800 parts of water. This was treated at room temperature with the stated amount of chlorine; 4 per cent 80 of the bone dry weight of the pulp.

In Fig. 1, the ordinates represent the amount of chlorine consumed; the proportion of the total 4 per cent which was used in the time indicated. For example, 3.6 per cent on this curve would 85 represent 90 per cent consumption of the 4 per cent used. The abscissæ represent the time in minutes in these particular tests. The lowermost full line curve A represents an ordinary bleaching operation in alkaline hypochlorite un-90 der these particular conditions, the aqueous suspension being treated with 4 per cent of chlorine in the presence of a slight excess of alkali. Curve B shows the rate of chlorine consumption when the pulp was treated with 4% of chlorine in 95 the presence of hydrochloric acid. Curve C shows the rate of chlorine consumption when the product obtained by the treatment represented by curve B was further subjected to the action of hypochlorous acid in the solution resulting 100 from the addition of an excess of calcium carbonate to the mixture after the reaction according to curve B had proceeded for a period of four minutes, the curve of the reaction during such period being represented by the full 105 line portion of the curve B. Curve D shows the rate of chlorine consumption following the addition of an excess of alkali to the mixture left after the reaction represented by curve C had proceeded for a period of four minutes, as in- 110 dicated by the full line portion of said curve C. These determinations apparently support the conclusion that the rapid consumption of chlorine occurring during the first few minutes of the first and second stages, as represented by the 115 full line portions of curves B and C is presumably due to the combination of lignin with chlorine. Following this, the reactions occurring in each of the stages represented by curves B and C are presumably secondary chlorination and 120 progressive oxidation. As indicated on curve chart it is also found that the rate of chlorine consumption, when the original pulp was treated with 4% of chlorine, in a solution containing an excess of calcium carbonate, follows substantially 125 the same curve as curve B.

In a modification of the present process I begin with a larger percentage of chlorine than that used in the described experiment (4%). A proportionately greater amount of chlorine is 130 available for alkaline oxidation in stage 3 and produces conditions under which complete bleaching may be effected in this state without the addition of any other step provided that sufficient time is allowed. In a second alternative 135 modification, useful under certain conditions, particularly when handling pulps which are difficult to bleach, I commence the process with less than the total amount of chlorine which may be required to remove the lignin and then, 140 after subjecting the pulp to the preliminary reactions provided for by stages 1, 2 and 3 I wash the pulp and complete the bleaching in a fourth stage, in which a fresh supply of alkaline bleach is added to the washed pulp. In carrying out 145 this fourth or final stage, I prefer to employ from 2% to 6% or more of 35% bleaching powder based upon the dry weight of the pulp. This final stage can be conveniently carried out with the aid of standard bleaching equipment and 150

in accordance with the methods usually employed in the handling of exceptionally easy bleaching pulps. In carrying out this fourth stage a batch system is preferably employed, thus facilitating

- 5 the preparation of a pulp with a standard degree of whiteness. In view of the extreme rapidity with which the various reactions, more particularly those involved in stages 1 and 2, proceed to completion it is obvious that the process of
- 10 this invention is particularly adapted to be carried out in a continuous manner and with the aid of comparatively simple and inexpensive equipment.

Considering the different stages of the process 15 in the order of their occurrence, it will be under-

stood that stage 1 involves the addition of chlorine to a pulp suspension in a neutral liquid so that the chlorine reacts in equilibrium with water in accordance with the formula

#### $Cl_2+H_2O \rightleftharpoons HCl+HOCl;$

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that is, is more or less completely hydrolyzed. The chlorine may be added either as an aqueous solution or as a gas introduced directly into the 25 pulp suspension. The method usually employed

- is to introduce chlorine gas into the flowing stream of pulp with violent agitation which tends towards rapid promotion of the desired reactions. The amount of chlorine used should be substan-30 tially enough to remove the amount of lignin
- contained in the pulp. The desired reaction which takes place at this stage of the process is exceedingly rapid and requires only a contact period of from one to five minutes which may be
- 35 conveniently provided for by the employment of a reaction vessel through which the pulp is caused to pass, said vessel being of such size as to afford a contact period of the desired duration. In stage 2 of the process, a regulated supply of calcium 40 carbonate is introduced into the flowing pulp
- stream as it leaves the reaction vessel employed in stage 1. This reagent may be in the form of a suspension of ground marble, precipitated chalk, or a colloidal form of calcium carbonate and
- 45 should be added in such quantity as to provide a slight excess over the amount necessary to neutralize the HCl, which ensures neutrality in the mixture. During this addition of ground marble or precipitated chalk the pulp stream is subjected
- 50 to violent agitation to ensure proper mixing, following which the pulp stream is conducted to a second reaction vessel similar to that employed in stage 1. For present purposes the reaction vessel used in stage 2 may be assumed to be of
- 55 a size permitting a contact period of approximately four minutes. The use of calcium carbonate in stage 2 is recommended rather than that of caustic alkalies, such as lime, for the reason that it avoids the necessity for closely controlling
- 60 the desired condition of neutrality in the mixture since an excess of calcium carbonate does not react with HOCI and does not affect the completeness of the reaction. The present invention is not, however, limited to the use of calcium
- 65 carbonate in stage 2 but contemplates the use of any other agent capable of bringing about substantially complete neutralization of the hydrochloric acid while leaving hypochlorous acid in the free state. It is desired to have the liquid
- 70 in a substantially neutral state during stage 2 as regards all other acids than HOCl. During the progress of stage 2, the product obtained in stage 1 is subjected to the action of free hypochlorous acid in a substantially neutral solution due to

75 the neutralization of the hydrochloric acid.

When the reactions occurring in stage 2 have proceeded to the desired point as represented by the full line portion on curve C, the reaction in stage 3 is initiated by adding an excess of lime or any other suitable caustic alkali to the flowing pulp suspension as it leaves the reaction vessel employed in stage 2. A reaction vessel is also used in stage 3 to provide for a contact period of from ten to thirty minutes or even longer. The purpose of this stage is to bring about a definite 85 alkaline condition in the mixture immediately after the completion of stage 2 in order to convert the free hydrochlorous acid into hypochlorite and prevent undesirable secondary reactions.

In commencing stage 1, it is desirable to add 90 chlorine in excess of the amount actually consumed in stages 1 and 2 so that sufficient chlorine is available in stage 3 for the production of the class of pulp desired. According to one modifica-95 tion of my invention, stage 3 may be eliminated and the pulp washed at the end of stage 2 and then subjected to the action of a fresh alkaline bleaching reagent. This washing and bleaching of the pulp with fresh alkaline bleaching reagents may also be resorted to at any suitable point in 100 the progress of stage 3. However, the method regarded as best is to proceed with stage 3 to a rather advanced point, until the reaction slackens materially, as indicated in the curve diagram at the point corresponding to a chlorine consump- 105 tion of 3.5 per cent and a time of 20 minutes. The pulp may be washed in a suitable way as, for example, by passing the pulp over a rotary vacuum filter. At this point the pulp may be sufficiently bleached to answer the purpose for which 110 it is to be used but, if a particularly bright color is desired, it is advisable to follow stage 3 with the fourth stage treatment previously mentioned herein as an alternate form of my process. This fourth stage lends itself to the use of standard 115 bleaching equipment and is preferably conducted, by a batch process, in the presence of an excess of alkali and under conditions usually characterizing the handling of very easy bleaching pulps.

When handling certain classes of pulp, it may 120 be desirable to modify the process so that stage 1, as represented by curve B, is preceded by a preliminary treatment of the pulp with an alkaline hypochlorite so that the initial reaction proceeds to a certain point along the line of curve 125 A prior to initiation of the reaction stage represented by curve B. Under certain conditions and when dealing with certain classes of pulp, this initial treatment reduces the time required for bleaching the pulp to a particular degree 230 of whiteness and does not appear to adversely affect the reactions occurring in the subsequent stages originally designated as stages 1 and 2.

Proceeding now to a description of the apparatus appearing in Fig. 2, 11 designates a pulp 135 supply regulating box divided into three compartments by weirs 12. The stock is delivered to the central compartment 13 through pipe 14. and flows over the weirs into the overflow compartment 15 or into the discharge compartment 140 16. From the compartment 15 the stock is returned to the source of supply through an over flow pipe 17. The stock delivered to the discharge compartment 16 is conducted through pipe 18 to the inlet of a centrifugal pump 19 in which 185 it is subjected to violent agitation.

A regulated quantity of chlorine, preferably in the form of gas, is introduced into the pulp stream as the latter enters the zone of violent agitation afforded by the pump 19. In the pres- 150

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ent instance the chlorine is conveniently conducted to the inlet side of the pump through a pipe 20 under the control of a suitable regulating device indicated at 21. The mixture of

- 5 pulp stock and chlorine leaving the pump 19 is conducted through a pipe 22 to a reaction vessel 23 which is designed to afford the duration of contact required for the completion of stage 1. In carrying out stage 2 of the process the pulp
- 10 is first conducted from the reaction vessel 23 through a pipe 24 to a mixing vessel 25 where calcium carbonate or other suitable alkali is added to the mixture to neutralize the hydrochloric acid. This addition of calcium carbonate or
  15 other agent may be conveniently accomplished
- through the medium of the pipe 26 and the controllable feeding device 27. The resulting mixture passes from the mixing vessel 25 through a pipe 28 to the inlet side of a pump 29 which
- 20 affords a second zone of violent agitation in which the calcium carbonate is mixed with the reaction product of stage 1. From the pump 29 the mixture is conducted through a pipe 30 to a second reaction vessel 31. designed so as to
- 25 allow the mixture to remain therein long enough to complete stage 2.

The product of stage 2 is then conducted through a pipe 32 into a second mixing vessel 33 wherein an excess of lime or other suitable 30 alkali is added to the mixture as by means of the pipe 34 and the feeding device 35. In leav-

- ing the mixing vessel 33 the pulp mixture is conducted through a pipe 36 to a third reaction vessel 37 which affords the duration of contact
- **35** required for the completion of stage 3 in the course of which the mixture is brought to a definite alkaline condition. The product of stage 3 is then conducted through a pipe 38 to a vacuum filter or washer 39 and from thence
- 40 to any suitable form of conveyor 40. If the third stage is to be followed by the fourth stage of treatment previously mentioned herein, the pulp after being washed is delivered by the conveyor 40 to any standard type of bleaching ap-
- 45 paratus in which the fourth stage of treatment is to be conducted. In addition to its usefulness, in connection with

the removal of lignin and color formations from previously prepared pulps, the process describedherein is advantageous when applied to the treat-

- ment of raw lignified materials including hard woods, excelsior and the like. In this particular application the removal of lignin and color formations is accomplished without injury to the 55 cellulose fibres so that the final pulp product
- 55 cellulose fibres so that the final pulp product is found to contain practically all of the hemicelluloses as well as the higher celluloses. The present invention, therefore, provides a process of treating raw lignified materials which gives
- 60 a greater yield as compared with the pulp processes now in use and which also makes possible the economical production of satisfactory pulp from hard woods and other lignified materials which have heretofore been considered more or
- 65 less unsuitable for this purpose. In this particular application of the process, the raw lignified material, after being shredded or otherwise reduced to a desired state of fineness, is preferably boiled in water or otherwise hydrated to produce
- 70 a certain swelling of the fibres. Following this, the material is treated in accordance with the process previously described herein and it is found that this treatment removes the lignin and color formations in such a way that an excep-
- 75 tionally high yield of cellulose is obtained. The

amount of chlorine employed in this treatment of raw lignified material is preferably enough to react with the total amount of lignin contained in said material.

Having thus described my invention, what I 80 claim is:---

1. A continuous process of bleaching pulp in transit which comprises conducting a moving stream of pulp in aqueous suspension and containing added chlorine through a plurality of successive reaction zones, these zones including (1) a zone where the chlorine is allowed to act until reaction slackens, (2) a zone in which HCl acidity of the moving stream is neutralized and the resulting HOCl is allowed to act until its activity **90** slackens and (3) a zone where base is added in sufficient amount to make the stream alkaline.

2. The process of bleaching wood pulp which comprises subjecting such pulp to the action of chlorine in dilute aqueous solution until the action slackens and then neutralizing the HCl acidity only and thereby subjecting the pulp to a treatment with hypochlorous acid in an aqueous solution substantially free of other acids.

3. The process of bleaching wood pulp which 100 comprises subjecting such pulp to the action of an excess of chlorine in dilute aqueous solution, then neutralizing hydrochloric acid in such solution, leaving hypochlorous acid in a free state, and subjecting the wood pulp to the action of 105 such hypochlorous acid.

4. In the process of claim 3, neutralizing hydrochloric acid with calcium carbonate.

5. The process of bleaching wood pulp which comprises subjecting such pulp to the action of 110 chlorine in a dilute aqueous solution, continuing the treatment of the pulp with hypochlorous acid in a dilute solution substantially free of other acids and bleaching the resultant products in an alkaline medium. 115

6. The process of bleaching wood pulp which comprises subjecting such pulp to the action of chlorine in a dilute aqueous solution, continuing the treatment of the pulp with hypochlorous acid in a dilute solution substantially free of other 120 acids and bleaching the resultant product in an alkaline medium, the amount of chlorine initially added being at least sufficient to react with the lignin of the wood pulp and to supply the hypochlorous acid of the second step and the 125 alkaline bleach of the third step.

7. The process of bleaching pulp fiber which comprises subjecting such pulp to the action of chlorine in a dilute aqueous solution, continuing the treatment of the pulp with hypochlorous 13C acid in a dilute solution substantially free of other acids, bleaching the resultant product in an alakline medium, washing the bleached product and subjecting the washed product to further bleaching with fresh alkaline bleaching solu-135

8: In the removal of lignin from cellulose in fibrous material containing both, the process which comprises exposing such fibrous material to the action of an aqueous solution of chlo-140 rine until action slackens substantially, then neutralizing hydrochloric acid present without neutralizing hypochlorius acid, continuing the exposure of the fibrous material till the new action instituted slackens materially, then neutralizing the hypochlorous acid with caustic alkali and forming an alkaline solution, and continuing the exposure of the fibrous material to the alkaline solution to remove chlorinated products.

9. A process as claimed in claim 1 in which 150

1 coincident with or immediately following the contact of the pulp with chlorine and to further violent agitation in zone 2 coincident with or

5 immediately following the introduction of the acid neutralizing agent.
10. The process of bleaching pulp fiber which comprises subjecting such pulp to the action of

the pulp is subjected to violent agitation in zone chlorine in a dilute aqueous solution, continuing the treatment of the pulp with hypochlorous acid in a dilute solution substantially free of other acids, bleaching the resultant product in an al-kaline medium, removing the alkaline medium 80 and subjecting the pulp to further bleaching with fresh alkaline bleaching solution.

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