

UNITED STATES PATENT OFFICE

2,030,384

METHOD OF BLEACHING PULP

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No Drawing. Application October 18, 1934,
Serial No. 748,923

7 Claims. (Cl. 8—2)

This invention relates to a method of bleaching pulp and more particularly to a method of bleaching pulp prepared by the sulphate process, or by some similar alkaline process using a sulphide as an active cooking ingredient.

The coloring matter in sulphate pulp is largely composed of complex phlobotannin bodies containing sulphur in their constitutions. While the exact chemical constitutions of the phlobotannin bodies are not known with certainty, certain facts have been observed with respect to the phlobotannin bodies. In general, the sulphur content of the complex phlobotannin bodies increases as the sulfidity of the cooking liquor increases. As the concentration of sulphur in the cooking liquor increases, and as the cooking conditions are made more drastic by the use of higher temperatures, the substitution of sulphur in the coloring matter, which has been identified as sulphur derivatives of phlobotannin bodies, increases and makes the coloring matter darker brown or black.

The bleachability of sulphate pulp is quite largely dependent upon the concentration of phlobotannin bodies in the pulp. Furthermore, the difficulty in bleaching sulphate pulp increases as the sulphur content of the phlobotannin bodies increases. The sulphuretted phlobotannin bodies may be considered as sulphur dyes, which must be removed or altered before bleaching, if the bleach requirements are to be reduced and a white pulp is to be obtained.

The coloring matter comprising these sulphur derivatives of phlobotannin bodies is acidic in nature. In alkaline solution, the coloring matter is a darker red brown, while in acid solution it is a lighter brownish yellow. The coloring matter is darkest in color at pH 10.5 or above and lightest in color at pH 2.8 or below. The greatest percentage of color change occurs at pH 6.9 to 6.1.

It is interesting to note that the coloring matter in sulphate or kraft pulp does not obtain its characteristic brown color until it comes in contact with oxygen, which may be introduced in the wash liquors, in the water used, or from the air. Before contact with oxygen, the coloring matter is a bright yellow, more or less dark depending upon the sulphur content.

In order to improve the bleachability of sulphate pulp and obtain a bleached pulp of the desired degree of whiteness, and preferably a white pulp having a bluish cast, we have found that a portion of the phlobotannin bodies can be removed prior to bleaching by the use of a strong

caustic solution, as described in our copending application, "Method of treating pulp", filed October 18, 1934, Serial No. 748,921. It has also been found that upon chlorination, the coloring matter is rendered soluble in caustic soda, but not in lime, so that if the bleaching liquor is maintained alkaline, the coloring matters can be washed out.

We have now found that the addition of oxygen liberating compounds, such as alkali metal peroxides, to the caustic soda solution used in the treatment of the sulphate pulp prior to bleaching makes it possible to obtain a bleached sulphate pulp of a high degree of whiteness, and of a white color that is on the bluish rather than the yellowish side. A small percentage of a peroxide of an alkali metal is added to the caustic soda solution that is used for treatment of the sulphate pulp in the diffuser and is also added to the caustic soda solution used for treatment of the pulp between the chlorination and bleaching steps.

By the method of our invention, a bleached pulp is produced that can be satisfactorily used in the manufacture of high grade bond, ledger and writing papers. The bleached pulp is of an exceptionally high purity, having a high alpha cellulose content and a low copper number. It also has very desirable paper making characteristics, in that it resists the mechanical action of beaters and Jordans to such an extent as to be capable of withstanding longer beating times and thus of requiring a higher degree of hydration. A pulp having these improved paper making characteristics can be manufactured into high grade papers having surface characteristics similar to those of rag paper.

It is therefore an important object of this invention to provide a method of bleaching sulphate pulp to obtain a bleached sulphate pulp of a high degree of whiteness and of improved characteristics, capable of being made into high grade papers possessing surface characteristics similar to those of rag papers.

It is a further important object of this invention to provide a method of bleaching sulphate pulp wherein the phlobotannin bodies are subjected to oxygen in nascent form, and are probably converted, in part, into a blue coloring matter that imparts a bluish cast to the bleached pulp.

Other and further important objects of this invention will become apparent from the following description and appended claims.

In the usual sulphate process for the manufacture of pulp, the pulp is blown from the di-

gester in which the wood is cooked, into a diffuser, where the pulp is washed to remove the cooking liquor, or black liquor, as it is commonly known. In accordance with our present invention, prior to washing the pulp in the diffuser, an aqueous solution of caustic soda containing a suitable alkali metal peroxide is introduced into the top of the diffuser in the space above the level of the pulp and gradually forced downwardly through the mass of pulp, displacing the black liquor ahead of it. The body of caustic soda solution is, in turn, displaced by a following body of water or weak liquor introduced into the diffuser under pressure.

By this preliminary treatment with caustic soda and an alkali metal peroxide, before the color bodies have had an opportunity to become oxidized, the color bodies are quite largely dissolved or kept in solution and subsequently removed. The action of the alkali metal peroxides appears to be one that results in the conversion of part of the coloring matter into color bodies of a bluish shade.

The caustic soda solution used in treating the sulphate pulp in the diffuser is preferably one that has been prepared by dissolving caustic soda in fresh water, although so-called "white liquor", as it is known in the sulphate process, which is a strongly alkaline liquor produced by causticizing green liquor, may be used. The amount of caustic soda solution used in our method will vary considerably, depending upon the time of contact of the caustic liquor with the pulp, the concentration of the caustic liquor or solution, and the temperature of the mass in the diffuser. Ordinarily, however, between 2.5 and 15% of caustic soda (NaOH) by weight of the air dry pulp undergoing treatment constitutes the most satisfactory operating range. A caustic solution of a concentration of approximately 50% of NaOH by weight of the solution may be used. Into this caustic solution is incorporated by dissolving a quantity of sodium peroxide equivalent to 0.5% or over of the air dry weight of the pulp undergoing treatment. Other peroxides of alkali metals or perborates may be used in place of sodium peroxide.

As previously stated, the treatment of the pulp in the diffuser with caustic solution containing sodium peroxide is started as soon as possible after the pulp has been blown into the diffuser, so as to avoid any substantial oxidation of the phlobotannin bodies. A caustic solution of the concentration above indicated is introduced into the space above the pulp in the diffuser and is gradually forced downwardly through the mass of pulp and cooking liquor, displacing the cooking liquor ahead of it. After all of the caustic solution has been introduced into the diffuser, it is followed by weak liquor from the process, or by wash water, introduced under sufficient pressure, say about 15 pounds per sq. in., to displace the body of caustic solution ahead of it at the desired rate, such that the operation may be completed in from 12 to 16 hours. The action of the caustic soda solution is to dissolve the phlobotannin bodies and sulphur derivatives thereof, and these bodies and derivatives are largely removed by the caustic soda solution and by the weak liquor or wash liquor following the caustic soda treatment.

After the pulp in the diffuser has been thoroughly washed, it is subjected to the usual screening operation, being first passed through a knotter and then through screens to prepare

the pulp for bleaching. The bleaching process is preferably of a multi-stage type, including at least one treatment with gaseous chlorine at a comparatively low pulp density and a subsequent, and preferably final, treatment, also at low density, with bleaching solutions containing calcium hypochlorite and of maintained caustic alkalinity, as taught in the Wells Patent No. 1,883,193. Multi-stage bleaching operations of this type are not in themselves new, but the method of our invention includes an intermediate treatment of the pulp with a caustic alkali solution containing an alkali metal peroxide to aid in the removal or conversion of the color bodies. This treatment with caustic alkali and alkali metal peroxide between the chlorinating and calcium hypochlorite bleaching process supplements the treatment of the pulp in the diffuser in the manner already described, and is apparently necessary to obtain the best results from the diffuser treatment.

The first chlorination step may be carried out with the use of gaseous chlorine and at a consistency of between $3\frac{1}{2}$ and 5%. Chlorine is introduced into the aqueous suspension of pulp in any suitable manner, as by bubbling chlorine gas into a downwardly flowing column of pulp at a rate such that the bubbles of chlorine gas do not rise substantially in the column before being absorbed. Sufficient chlorine is introduced in this manner to equal about 45% of the chlorine required for complete bleaching of the pulp. The temperature of the pulp mass during chlorination is preferably maintained at between 70° and 75° F.

After the preliminary bleaching step just described, the pulp is washed with a caustic soda solution of 40 to 50% concentration, which is used in such an amount as to provide between 0.5 and 3% of caustic soda by weight of the air dry pulp undergoing treatment. The caustic solution is preferably added continuously to the stock while it is being moved along in the system.

After the addition of the caustic solution, the stock is passed through a reacting tower, or vessel, wherein it is allowed to remain for 10 to 20 minutes to permit the reaction between caustic soda and any chlorinated bodies, such as lignin and ligno celluloses, to take place. Chlorination of the phlobotannins renders them soluble in strong alkalies, such as caustic soda, after they have been oxidized, whereas they are rendered insoluble and precipitated by the hydroxides of alkaline earth metals, such as lime.

The stock is thereafter again washed and concentrated to a consistency of between 12 and 20%, as by means of a screw press. To the concentrated mass of stock there is added a quantity of caustic soda solution in an amount equivalent to about 5% of caustic soda (NaOH) on the air dry weight of the pulp present. This caustic soda solution contains an amount of sodium peroxide equivalent to about 0.5% or over by weight of the air dry pulp undergoing treatment. The thus treated stock is heated to a temperature of between 100° and 120° F., preferably about 100° F., and maintained at that temperature for approximately one hour. During this treatment, the strong caustic solution dissolves any remaining impurities, such as lignin and phlobotannin bodies that have been chlorinated during the bleaching operation. It also appears that any remaining coloring matter is converted by the action of the sodium peroxide into a bluish color body.

After this treatment with caustic soda and sodium peroxide, the pulp is again washed and then

bleached at low density, say from 3 to 6%, with an aqueous bleaching solution of calcium hypochlorite. The amount of bleaching solution added is that calculated to complete the bleaching of the pulp. Bleaching is carried out at a temperature of between 100° and 120° F., preferably at about 115° F. During this final bleaching step, the stock is maintained alkaline to phenolphthalein by the addition of caustic soda if necessary.

When the stock has been completely bleached, it is removed from the bleacher and washed. During washing, a dilute mineral acid, such as sulphuric acid, may be added as a neutralizing agent to remove the last traces of alkali in the stock.

Bleached sulphate pulp made in accordance with the method above described is of a high degree of purity and is more on the bluish shade of white than bleached sulphate pulp produced by methods not employing an alkaline metal peroxide or other oxygen liberating compound in the treatment of the pulp.

We are aware that numerous details of the process may be varied through a wide range without departing from the principles of this invention, and we, therefore, do not purpose limiting the patent granted hereon otherwise than necessitated by the prior art.

We claim as our invention:

1. The method of obtaining bleached pulp of improved characteristics from pulp prepared by the use of an alkaline cooking liquor containing an active sulphide ingredient, which comprises treating the pulp before it is washed and before it is exposed to the oxidizing influences of dissolved and atmospheric oxygen with a caustic alkali solution containing an oxygen liberating alkali metal compound, subjecting the treated pulp after washing to a multi-stage bleaching operation and treating said pulp between successive bleaching steps with a caustic alkali solution also containing an oxygen liberating alkali metal compound.

2. The method of obtaining bleached pulp of improved characteristics from pulp prepared by the use of an alkaline cooking liquor containing an active sulphide ingredient, which comprises treating the pulp in a closed vessel under pressure before the pulp has been exposed to the oxidizing influences of dissolved and atmospheric oxygen with a fresh caustic alkali solution containing sodium peroxide, subjecting the treated pulp after washing to a multi-stage bleaching operation and treating said pulp between suc-

cessive bleaching steps with a caustic alkali solution containing sodium peroxide.

3. In a method of obtaining bleached pulp of improved characteristics from pulp prepared by the use of an alkaline cooking liquor containing an active sulphide ingredient, which comprises treating the pulp in a closed vessel under pressure before being exposed to the oxidizing influences of dissolved and atmospheric oxygen with a fresh caustic alkali solution containing sodium peroxide, the sodium peroxide being present in an amount equivalent to 0.5% and over on the air dry weight of the pulp undergoing treatment, subjecting the treated pulp after washing to a multi-stage bleaching operation and treating said pulp between successive bleaching steps with an alkaline solution containing sodium peroxide in an amount equivalent to 0.5% and over on the air dry weight of the pulp undergoing treatment.

4. In the process of obtaining a bleached sulphate pulp of improved characteristics, the step of subjecting freshly blown pulp before it is exposed to the oxidizing influences of dissolved and atmospheric oxygen to the action of a solution of caustic soda containing an oxygen liberating alkali metal compound.

5. In the process of obtaining a bleached sulphate pulp of improved characteristics, the step of subjecting freshly blown pulp before it is exposed to the oxidizing influences of dissolved and atmospheric oxygen to the action of a solution of caustic soda and sodium peroxide.

6. In the process of obtaining a bleached sulphate pulp of improved characteristics, the step of subjecting freshly blown pulp before it is exposed to the oxidizing influences of dissolved and atmospheric oxygen to the action of an aqueous solution of caustic soda and sodium peroxide, the amount of caustic soda being equivalent to 2.5 to 15% of NaOH on the air dry weight of the pulp and the amount of sodium peroxide being equivalent to 0.5% and higher on the air dry weight of the pulp.

7. In the process of obtaining a bleached sulphate pulp of improved characteristics, the steps of subjecting freshly blown pulp before it is exposed to the oxidizing influences of dissolved and atmospheric oxygen to the action of an aqueous solution of caustic soda and sodium peroxide and subsequently between successive bleaching operations again subjecting the pulp to the action of a similar solution containing caustic soda and sodium peroxide.

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