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BLEACHING CHEMICAL PAPER PULP

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1

This invention relates to an improved method for bleaching chemical wood pulps.

Various multi-stage methods have been proposed for bleaching chemical wood pulps, using calcium hypochlorite in one or more stages and alkaline peroxide in one or more others. The present invention relates to such prior processes in which one or more treatments of the pulp with a calcium compound, e. g., calcium hypochlorite, precedes a treatment with alkaline peroxide, and particularly to an improved modification of such processes whereby increased bleaching efficiency is realized.

An object of the invention is to provide an improved method of bleaching chemical wood pulps. A further object is to provide a modification of prior multi-stage methods for bleaching such pulps involving a treatment with a calcium compound in a stage prior to that in which the pulp is treated with an alkaline peroxide solution, by which modification substantially better bleaching results. A particular object is to provide an improved multi-stage method for bleaching kraft pulp in which an alkaline peroxide bleaching stage follows one or more earlier stages in which calcium hypochlorite is used. Still further objects will be apparent from the following description.

The present invention is based on the discovery that in the multi-stage bleaching of chemical wood pulps, substantially better bleaching results are obtained if the pulp is acidified intermediate an earlier stage (or stages) in which the pulp is treated with a calcium compound, and a subsequent stage in which it is treated with alkaline peroxide. The improved results include a higher and more stable degree of brightness. Furthermore, the efficiency of the alkaline peroxide treatment is substantially improved by such intermediate acidification. Accordingly, the above objects are accomplished in accordance with the invention by acidifying the chemical pulp after it has been subjected to a treatment with a calcium compound, and before it is treated with an alkaline peroxide solution.

Acidification of the pulp may be effected by intimately contacting the pulp with an aqueous solution of an acid in such amounts and concentrations that the resulting mixture will be distinctly acid, i. e., have a pH not greater than 6. Generally the pulp will be slurried with the acid solution but any other convenient or desired method of obtaining intimate contact may be used. Any acid or acid yielding material which will produce the required acidity may be used.

2

The invention is further illustrated by the following examples.

Example 1

The pulp samples used in Examples 1 to 4 were taken from various stages of a mill bleaching process in which kraft pulp from northern mixed hardwoods is bleached in conventional manner in two separate stages, employing in each about 2% of active chlorine (based on the dry weight of the pulp) in the form of calcium hypochlorite at a pulp consistency of about 12%. The pulp is washed with water after each bleaching stage. Washed pulp from the first stage had an air brightness of 64.5 and an oven brightness of 57.5. Washed pulp from the second stage had air and oven brightnesses of 75.0 and 67.5, respectively.

(*a*) Washed pulp from the first stage of the above mill process was bleached at a pulp consistency of 12% with an alkaline peroxide bleach solution containing 0.05% Epsom salts, 5.0% 41.6° Bé. sodium silicate (containing 8.9% Na_2O, 29% SiO_2 and the balance water), 1.33% sulfuric acid and 2.0% sodium peroxide, all based on the dry weight of the pulp. A beaker containing a slurry of the pulp and bleach liquor was placed in an oven. The temperature of the slurry rose in 2 hours from 70 to 160° F. Since at this point the residual active oxygen content was only 19% of that originally added, bleaching was discontinued and the air and oven brightnesses were found to be 71.0 and 67.0, respectively. The pH of the slurry during the peroxide bleach ranged from about 10.5 to 10.8.

(*b*) A second sample of washed pulp from the first stage of the mill process was slurried (at about 2% consistency) with water containing hydrochloric acid in an amount equal to 3.0% hydrochloric acid of about 35% strength, based on the dry weight of the pulp. The resulting slurry had a pH ranging from about 2.0 to 2.6. After about 10 minutes, the pulp was washed thoroughly with water then subjected to an alkaline peroxide bleach under the same conditions as in (*a*) above. The residual active oxygen content was still 44% after 5 hours in the oven, at which time the temperature had risen to 180° F. After this 5 hour period, the air and oven brightnesses of the pulp were 79.5 and 77.5, respectively.

Example 2

(*a*) Example 1 (*a*) was repeated using pulp from the second stage of the mill process. After 2 hours in the oven, the temperature of the slurry

of pulp and peroxide bleach liquor had risen to 160° F. Because the residual active oxygen content then was only 12%, bleaching was discontinued. The air and oven brightnesses of the peroxide bleached pulp were 74.5 and 69.5 respectively.

(*b*) Example 1 (*b*) was repeated using pulp from the second stage of the mill process. After 5 hours in the oven, the temperature was 180° F. and the residual active oxygen content was 44%. The final air and oven brightnesses of the pulp were 82.0 and 79.5, respectively.

Example 3

A sample of washed pulp from stage one of the above mill process was acidified as in Example 1 (*b*), except that 2.5% hydrochloric acid was used. The pH of the acidic slurry ranged from about 2.6 to 3.0. The acidified pulp was washed, then bleached with alkaline peroxide as in Example 1 (*b*) except that no sulfuric acid was added to the bleach liquor, the silicate and sodium peroxide contents were reduced to 2.0% and 1.0%, respectively, and the slurry of the pulp in the bleach liquor was heated on a hot plate instead of in an oven for 1 hour. During this time the temperature rose to 200° F. and the pH ranged from about 11 to 11.3. The residual active oxygen content at the end of the treatment was 5%. The air and oven brightnesses of the bleached pulp were 76.0 and 74.5, respectively.

Example 4

Example 3 was repeated using washed pulp from the second stage of the mill process. Here again, the final temperature during the peroxide bleach was 200° F. and the residual active oxygen content after 1 hour was 5%. The final air and oven brightnesses were 80.0 and 78.0, respectively.

In the preceding examples, brightnesses were determined using handsheets prepared from pulp slurries acidified with dilute sulfuric acid to a pH of 4.5 at 0.3–0.5% consistency. Brightnesses were measured using a General Electric Reflectometer, which measures brightness on a scale ranging from 0 for minimum reflectance to 100 for maximum reflectance. "Air" brightnesses were determined using handsheets dried at atmospheric temperature. "Oven" brightnesses were determined after drying freshly prepared handsheets for 1 hour in an oven heated to 105° C. (221° F.). The smaller the difference between the air and oven values for a given sample, the greater is the stability of the brightness of that sample.

The results of Examples 1 and 2 show that the final peroxide bleach is much more effective if preceded by acidification. They also show that preacidification substantially and effectively decreases peroxide decomposition in the final bleach. These observations hold for pulp from either the first or second hypochlorite stage of the mill process. However, it will be noted from Example 2 that whereas the brightness of pulp from the second stage was increased only slightly by the peroxide bleach in the absence of preacidification, the brightness increase from the final peroxide bleach was very substantial when the pulp was preacidified. These results accord with general experience in applying the present invention, i. e., that the value of the acidification treatment increases the more the pulp has been contacted previously with calcium compounds. Thus, the invention is most advantageously applied to pulp which has been previously subjected to a plurality of calcium hypochlorite bleaching stages, or previously contacted in several stages with calcium compounds, e. g., with calcium containing liquors recycled from various stages of commercial processes. Repeated contact with calcium-containing liquors appears to be particularly harmful to bleaching in a subsequent alkaline peroxide bleach, unless the latter is preceded by the present acid treatment.

It will be noted that 1% peroxide with preacidification gave much higher brightnesses in Examples 3 and 4, than did twice that amount of peroxide without preacidification in Examples 1 (*a*) and 2 (*a*). Also, 1% peroxide with preacidification gave substantially higher brightnesses starting with pulp from stage 1 of the mill process (Example 3), than did 2% peroxide without preacidification when starting with pulp from stage 2 (Example 2 (*a*)).

Example 5

A kraft pulp composed of about 80% northern softwood (spruce and fir) and about 20% northern hardwood (poplar), was used in this example after it had been partially bleached by a multi-stage method in a commercial pulp mill. The partial bleach involved in the following order: (1) a chlorination with about 5% chlorine at about 3 to 3.5% consistency; (2) a second chlorination at about the same consistency with about 2.5% chlorine, in which the pulp is alkalized after a few minutes with lime to a pH of about 9 to 11; (3) a caustic extraction using 2% caustic at about 12% consistency and 180° F.; (4) an alkaline soak; and (5) a calcium hypochlorite bleach equivalent to about 1.5% chlorine for about 1 hour at 100° F. and 12% consistency. In all of the above treatments, the stated amounts of reagents are based on the dry weight of the pulp. Also, the pulp was washed following each step. Samples of pulp pretreated in the mill in this manner had air brightnesses ranging from about 78–79 and oven brightnesses ranging from about 69–71. (In this case and in all subsequent examples, the oven brightness was determined for handsheets which had been dried for 1 hour at 120° C. (248° F.)).

(*a*) A washed sample of pulp partially bleached in the mill as indicated above was slurried at about 2% consistency with water containing hydrochloric acid in an amount sufficient to give the slurry a pH of 2.0. After about 10 minutes, the pulp was washed free of acid then bleached at 12% consistency at 160° F. and a pH of 11.3 with a peroxide solution containing 0.025% Epsom salts, 1% 41.6° Bé. sodium silicate solution and 1% sodium peroxide. After 1 hour, the residual active oxygen was 73% and the air and oven brightnesses were 84.3 and 81.1 respectively. After 3 hours, the residual active oxygen content was 60% and the air and oven brightnesses were 86.3 and 82.0, respectively.

(*b*) Example 5 (*a*) was repeated, omitting the acid pre-treatment. After only 1.5 hours the residual active oxygen content had dropped to 10%, in view of which bleaching was discontinued. The air and oven brightnesses were then 83.0 and 77.7, respectively.

(*c*) Example 5 (*b*) was repeated except that 2% each of silicate and sodium peroxide were used in the bleach liquor (pH 11.3). The residual active oxygen after 1 hour bleaching was only 12% and the air and oven brightnesses were 85.0

and 77.3, respectively. The oven brightness in this instance using twice the amount of peroxide was substantially lower than the value obtained in the same time in Example 5 (*a*) in which the pulp was preacidified.

Example 6

Pulp from the source described in Example 5 was bleached without preacidification at 12% consistency and 120° F. with a bleach liquor containing 0.025% Epsom salts, 1% 41.6° Bé. silicate and 1% sodium peroxide. Even at this relatively low temperature the residual active oxygen was only 15% after 1.5 hours, at which time the air and oven brightnesses were 82.0 and 76.9, respectively.

Example 7

Four washed pulp samples from the source described in Example 5 were bleached at 150° F., a consistency of 12% and a pH of 11.3, using a bleach liquor containing 0.012% Epsom salts, 1.0% 41.6° Bé. sodium silicate and 1.0% sodium peroxide. Sample 1 was bleached without acid pretreatment. The remaining samples were pretreated with hydrochloric acid in the manner described in Example 5. The amounts of 35% hydrochloric acid used, based on the weight of the pulp were: 1.0% for sample 2, giving a pH of 4.8; 1.25% for sample 3, giving a pH of 3.5; and, 2.5% for sample 4, giving a pH of 2.5. After acidifying, samples 2,3 and 4 were washed free of acid then bleached as indicated. The residual active oxygen contents after 1.5 hours for samples 1 to 4 were 11%, 22%, 35% and 46% respectively. Final oven brightnesses for samples 1 to 4 were 76.7, 79.4, 81.1 and 80.9, respectively.

Example 8

(*a*) A pump sample from the source described in Example 5 was pretreated with hydrochloric acid as described in Example 5 to a pH of 3.3. After 10 minutes at 60° F. the acid was removed by washing and the pulp bleached at 190° F. and 12% consistency using a bleach liquor containing 0.05% Epsom salts, 3.0% 41.6° Bé. sodium silicate and 1.0% sodium peroxide. After 1.5 hours, the residual active oxygen content was 40% and the air and oven brightnesses of the pulp were 88.3 and 83.3, respectively.

(*b*) Example 8 (*a*) was repeated except that chlorine was substituted for hydrochloric acid as the acidifying agent in the pretreatment step. 3% Cl_2, based on the weight of the pulp, was required to give a pH of 3.3. After a peroxide bleach time of 1.5 hours, the residual active oxygen content was 40% and the air and oven brightnesses were 88.3 and 83.2, respectively.

The results of Examples 8 (*a*) and (*b*) show that chlorine can be used in place of hydrochloric acid in the acid pretreatment step with substantially identical results. In other experiments substantially the same as those of Examples 8 (*a*) and (*b*), except that the peroxide bleach step was omitted, it was found that the acidifying treatment, using either hydrochloric acid or chlorine, did not itself result in any substantial increase in brightness, the maximum increase being at best about 1 point.

While the foregoing examples illustrate applications of the invention in bleaching kraft pulps, the invention can also be applied advantageously in the bleaching of other chemical pulps such as soda pulp, sulfite pulp and semi-chemical pulps. In the case of any of these chemical pulps, the acid treatment of the invention should follow one or more preliminary treatments in which a calcium compound, such as lime or calcium hypochlorite, is used, and will of course precede a subsequent alkaline peroxide bleach. This acid treatment is, however, particularly well suited for use in bleaching kraft (sulfate) pulps which are normally darker in color and are more difficult to bleach to a high permanent brightness. Kraft pulps may be bleached to excellent and more permanent brightnesses by the present improved process than is possible with corresponding prior combination calcium hypochlorite-peroxide processes. Furthermore, the same degree of brightness may be obtained by the present process, as compared to corresponding prior processes, employing smaller amounts of peroxide or calcium hypochlorite, thus permitting a substantial reduction in costs. Reduction in the amount of hypochlorite used is known to reduce pulp degradation.

The invention is not restricted to processes employing any specific number or types of steps except that the acid treatment must be intermediate a treatment with a calcium compound and a later treatment with alkaline peroxide. The common practices of first partially purifying the pulp by prechlorination treatments, by alkali treatments, or combinations thereof, are included, as are also combination partial bleaches using both sodium and calcium hypochlorites. Also, the alkaline peroxide bleach after the present acid treatment, may be supplemented by subsequent treatments, e. g., with hypochlorite, peroxide and/or other treating agents, including reducing agents.

As previously indicated, any acid or acid yielding substance may be used in the acidification step which will give the required acidity. To be effective, the acidity should correspond to a pH no higher than 6. In most applications, acidities corresponding to a pH of about 2 to 5, preferably 2.5 to 4.0, will be used. Acidities greater than a pH of about 2 offer no particular advantages and increase costs. Illustrative of suitable acidifying agents are hydrochloric, nitric and phosphoric acids, and chlorine. Acids which give the more soluble calcium salts, such as hydrochloric acid, and chlorine are preferred. These will ordinarily and most conveniently be applied as aqueous solutions at low pulp consistencies, e. g., 0.5 to 5%, and at ordinary temperatures. However, pulp consistency and temperatures appear not to be critical with respect to the acid treatment and high or low consistencies and temperatures substantially higher or lower than ordniary may be used if desired. When using chlorine, temperatures above about 100° F. are generally avoided, temperatures below about 80° F. being preferred. Under these conditions the chlorine functions primarily as an acidifying agent and does not oxidize or degrade the pulp to any substantial extent. Prolonged contact of the acid with the pulp is not necessary, 5 to about 15 minutes being generally suitable. Longer times may, however, be used.

The bleaching and other steps of the prior processes to which the present acidification step is applicable may be carried out in any desired manner according to well-known procedures. Also, as is well known, the alkaline peroxide bleach which follows the acidification step may be practiced using any peroxygen compound which yields hydrogen peroxide in aqueous alkaline solutions, examples of which are hydrogen peroxide, percarbonates, perborates, perphos-

phates and alkali metal peroxides. Because of its relative cheapness, sodium peroxide is preferred, although a combination of hydrogen peroxide and an alkali may be used with equally good results. Ordinarily, the alkaline peroxide bleach will be effected at a pH of 9.5 to 13, preferably 10 to 12; and at temperatures of 100–200° F., preferably 150–190° F. Higher or lower alkalinities and temperatures may also be used. The various bleaching stages may be carried out at any pulp consistencies customary or desirable for any given process.

I claim:

1. In a process for bleaching chemical wood pulps wherein the pulp is treated under alkaline conditions with a calcium compound yielding calcium ions and then treated with alkaline peroxide, the improvement comprising acidifying said pulp intermediate said treatments, without simultaneously bleaching said pulp to any substantial extent, with an agent from the group consisting of hydrochloric acid and chlorine to a pH not higher than 6.

2. In a process for bleaching chemical wood pulps wherein the pulp is treated with calcium hypochlorite and then treated with alkaline peroxide, the improvement comprising acidifying said pulp intermediate said treatments, without simultaneously bleaching said pulp to any substantial extent, with an agent from the group consisting of hydrochloric acid and chlorine to a pH not higher than 6.

3. In a process for bleaching chemical wood pulps wherein the pulp is treated under alkaline conditions with a calcium compound yielding calcium ions and then treated with alkaline peroxide, the improvement comprising acidifying the pulp intermediate said treatments, without simultaneously bleaching said pulp to any substantial extent, with an agent from the group consisting of hydrochloric acid and chlorine to a pH of 2 to 5.

4. In a process for bleaching kraft pulp wherein the pulp is treated under alkaline conditions with a calcium compound yielding calcium ions then treated with alkaline peroxide, the improvement comprising acidifying said pulp intermediate said treatments, without simultaneously bleaching said pulp to any substantial extent, with an agent from the group consisting of hydrochloric acid and chlorine to a pH of 2 to 5.

5. A process for bleaching kraft pulp comprising partially bleaching said pulp with calcium hypochlorite, acidifying the partially bleached pulp, without simultaneously bleaching said partially bleached pulp to any substantial extent, with an agent from the group consisting of hydrochloric acid and chlorine to a pH of 2 to 5 and further bleaching the pulp with an alkaline peroxide solution.

6. The process of claim 5 wherein the pulp is acidified to a pH of 2.5 to 4.

7. The process of claim 5 wherein the alkaline peroxide bleach is carried out at a temperature of 150 to 190° F. and at a pH of 10 to 12.

8. The process of claim 5 wherein the acidifying agent is hydrochloric acid.

9. The process of claim 5 wherein the acidifying agent is chlorine.

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