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BLEACHING PULP

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This invention relates to improvements in the bleaching of cellulosic material with chlorites. It relates more particularly to the bleaching of cellulosic materials with chlorites at high pulp densities, that is, pulp densities in execess of about 15%, with important savings in bleaching costs and with the usual advantages of chlorite bleaching, particularly freedom from fibre injury.

The bleaching of various cellulosic materials, including paper and paper pulp, such as sulfite, kraft or sulfate pulp, pulped wood, cotton linters, hemp and cellulosic derivatives, such as rayon, with the chlorites as bleaching agents is known. The outstanding advantage of the use of chlorites for bleaching such materials is that the desired bleach is readily obtained without any substantial degradation of the fibres. The present invention provides for the bleaching of such cellulosic materials with chlorites, with the known advantages of such bleaching, but at a greatly reduced cost.

In accordance with the present invention, cellulosic materials are bleached by forming a high density plup having a pulp density in excess of about 15%, for example, from 15 to 50%, containing the necessary amount of chlorite to effect the desired bleaching, under conditions such that the chlorite is substantially inactive with respect to bleaching, and subsequently activating the chlorite by raising the temperature of the pulp, by the addition of an acid or acidic material, or, advantageously, by both raising the temperature and adding an acid or acidic material. In this way, the high density plup is formed under conditions of temperature, etc., such that substantially no bleaching takes place, and the chlorite in the high density pulp is subsequently activated by raising its temperature or the addition of acid or both until the desired bleaching takes place. The cellulosic material may, of course, be partially bleached with chlorine or hypochlorites prior to the bleaching with chlorites in accordance with this invention.

By this method of operation, substantial economies are obtained. If the activation is effected by heating the pulp, with or without the addition of acid, there is a substantial saving in steam cost, because the amount of steam required to heat the pulp to an effective bleaching temperature is much less than where low density pulps are treated, as the high density pulp contains much less water per pound of cellulosic material than the low density pulp. There is also a substantial saving in chlorite cost, because a much larger percentage of the available chlorine of the chlorite is used before the concentration has been reduced to a point where the bleaching action stops. This latter saving follows from the fact that the bleaching action of chlorites apparently stops after the concentration of the chlorite has been reduced, but while there is still an appreciable amount of the chlorite remaining in the bleaching solution. If the pulp density is high, the concentration of chlorite for a given percentage of available chlorine based upon the weight of the cellulosic material is greater than if a low density pulp is treated, and accordingly, a larger proportion of the chlorite is utilized before its concentration is reduced to the point where bleaching action stops. Further economy is obtained by the new process as higher temperatures, which increase the rate of reaction, and hence increase the yield or output from given equipment and decrease labor costs, may be used.

The chlorites which may be used in bleaching in accordance with the present invention include the alkali metal chlorites, such as sodium chlorite, and the alkaline earth metal chlorites, such as calcium or magnesium chlorite. The chlorites at temperatures below 50° C., e. g. at room temperature, and particularly in neutral or alkaline solution, are without substantial bleaching effect on pulp. Accordingly, a high density pulp containing the necessary amount of chlorite to produce the desired bleach is readily prepared at room temperature, particularly if the pulp is maintained in a neutral or somewhat alkaline condition. Such a high density pulp, containing the necessary amount of chlorite, may be prepared in various ways, such as by forming a low density pulp containing the chlorite and removing the proper amount of water by filtration, expression, or in other ways to form the high density pulp, or by spraying pulp with an aqueous solution of the chlorite, etc. In any event, the high density pulp having a pulp density in excess of about 15% and containing the proper amount of chlorite to effect the desired bleach is first produced under conditions of temperature and acidity which preclude any substantial bleaching action, and the resulting pulp is then activated by heating, or by adding acid, or by adding acid and heating. In general, if heat activation is used, the high density pulp will be heated to temperatures in excess of 50° C., advantageously in excess of 80° C., for example, from 80° C. to 100° C. or somewhat higher. If temperatures in excess of 100° C. are used, the

bleaching must be carried out in pressure equipment to prevent vaporization of the water. If acid activation is used, one or more of a number of acids or acidic materials may be used, including hydrochloric acid, sulfuric acid, boric acid, phosphoric acid, acid phosphates, aluminum silico fluoride, alum, etc. The acid or acidic materials may be added to the pulp in aqueous solution, or may be brought into contact with the pulp as gases, for example, as hydrochloric acid gas or carbon dioxide. In general, the acid or acidic material will be added to the high density pulp after the chlorite or chlorite solution, although where activation by both acid and heat is used, and insufficient acid or acidic material is added to activate the pulp without heating it to relatively high temperatures, the acid or acidic material may be added to the pulp prior to, or at the time of, the addition of the chlorite with subsequent activation by heat.

The amount of acid or acidic material which will be used for acid activation may be varied over a wide range, and is such as to give the pulp a pH ranging from 1 or 2 to 7. Where activation is by adjustment of acidity alone, without the use of the high temperatures, somewhat more acid is required than where both heat and acid are used, to produce a proper bleach in a reasonable time; and in such cases, the amount of acid or acidic material used is such as to bring the pH within the lower part of the range 1 to 7. Where both acid and heat are used, less acid or acidic material is advantageously used; and the amount of acid may be insufficient to activate the chlorite at room temperature, so that the acid may be added prior to or at the same time the chlorite is added. It is advantageous to use both acid and heat, with the use of an amount of acid proportioned to give the pulp a pH of about 5. Such amounts of acid may be added to the pulp prior to the heating, e. g., when the chlorite is added, or even before the chlorite is added, without causing such activation of the chlorite at low temperatures as to interfere with the process; but the addition of the acid or acidic material to the pulp when hot, as by bringing it in gaseous form into contact with the pulp has important operating advantages. With many high density pulps, it is difficult or impossible to measure the pH value, and in such cases it is difficult to specify the amount of acid or acidic material added in terms of pH. In general, an amount of acid which will produce a good bleaching effect in 30 to 40 minutes, or which is equivalent to an amount of hydrochloric acid gas about ¼ the weight of the available chlorine in the pulp to be bleached, whether activation is by acid alone or by both heat and acid, is advantageously used.

The invention will be further illustrated by the following specific examples, but it is not limited thereto.

Example 1.—16 parts (dry basis) of kraft paper pulp having a color of 50 on the G. E. Reflectometer in wet mat form was stirred into 500 parts of an aqueous solution containing 1.84 parts of sodium chlorite and 1.4 parts of concentrated sulfuric acid. The pulp was then immediately filtered and pressed until the pulp density was 18%. It then contained 2.6% of available chlorine based on the dry weight of the pulp. It was heated to 95° C. and allowed to remain at this temperature for five minutes, at which time the bleaching was complete. The pulp was then thoroughly washed with water. Sheets made from this bleached pulp had a color of 70 on the G. E. Reflectometer.

Example 2.—150 parts (dry basis) of kraft pulp in the form of wet crumbs was stirred into 3000 parts of a solution containing 10.6 parts of available chlorine as sodium chlorite and 12.2 parts of sodium di-hydrogen phosphate monohydrate. The pulp was then immediately filtered and brought to a density of 15%. It then contained 2% of available chlorine as sodium chlorite based on the dry weight of the pulp. The mat was shredded and placed in an heat insulated glass rotating container where it was heated with live steam to 100° C. and allowed to remain at this temperature for one hour, after which the pulp was washed several times. The pulp originally had a G. E. Reflectometer color of 56, and after bleaching a color of 82. The final product had a strength in percent Mullen of 136 whereas the original pulp had a strength in percent Mullen of 141.

Example 3.—150 parts (dry basis) of kraft pulp in the form of wet crumbs were stirred into 3000 parts of a solution containing 13.1 parts of available chlorine as sodium chlorite. The pulp was immediately filtered and brought to a density of 21.4%. It contained 1.6% available chlorine as sodium chlorite on the basis of the dry weight of the pulp. The pulp was shredded and placed in the apparatus used in Example 2 and heated to 100° C. with live steam. 0.6 part of chlorine gas was passed into the container over an interval of 60 minutes after which the pulp was thoroughly washed. After washing, it had a color of 80.2 on the G. E. Reflectometer as compared with an original color of 56. The percent Mullen of the final product was 128 as against 141 on the original. The chlorine gas was introduced into the container in which the pulp was heated to aid in the bleaching of the pulp. Such use of chlorine to assist in the bleaching of cellulosic material with chlorite is described and claimed in the application of John O. Logan, Serial No. 161,969, filed September 1, 1937.

Example 4.—16 parts (dry basis) of kraft pulp were stirred into 500 parts of a solution containing 42 parts of sodium chlorite. The pulp was immediately filtered and pressed to a density of 45%. The pulp then contained 2.6% of available chlorine as sodium chlorite based on the dry weight of the pulp. The pulp was broken into crumbs which were heated to 95° C. During heating, 0.1 part of hydrochloric acid gas was passed into the vessel containing the pulp. After about 10 minutes the bleaching was complete and the pulp was washed.

Example 5.—A pulp was treated under the same conditions as in Example 4 above except that no hydrochloric acid gas was passed in and the heating period was 1½ hours. The final product had a color of 73 on the G. E. Reflectometer as compared with its original color of 50.

Example 6.—16 parts (dry basis of kraft pulp in the form of wet crumbs were stirred into 500 parts of an aqueous solution containing 1.84 parts of sodium chlorite. The pulp was filtered and pressed to a density of 18%. It was heated to 95° C. and carbon dioxide was passed into the apparatus in quantities sufficient to displace most of the air. The heating was continued for 93 minutes. The pulp was then washed. It had a color on the G. E. Reflectometer of 74 as compared with an original color of 50.

We claim:

1. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material containing the chlorite at a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite.

2. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter substantially increasing the temperature of the pulp and maintaining the pulp at an elevated temperature until the desired bleaching is effected.

3. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter substantially increasing the acidity of the pulp and maintaining it under conditions of increased acidity until the desired bleaching is effected.

4. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter substantially increasing the temperature and the acidity of the pulp and maintaining it at an elevated temperature and under conditions of increased acidity until the desired bleaching is effected.

5. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% at a temperature substantially below 50° C. and thereafter raising and maintaining the temperature of the pulp above 50° C. until the desired bleaching is effected.

6. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite by the addition of acid and by increasing and maintaining the temperature of the pulp above about 50° C. until the desired bleaching is effected.

7. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite by the addition of hydrochloric acid and by increasing and maintaining the temperature of the pulp above about 50° C. until the desired bleaching is effected.

8. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter raising and maintaining the temperature of the pulp above about 80° C. until the desired bleaching is effected.

9. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter increasing the acidity by the addition of hydrochloric acid to activate the chlorite.

10. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite by bringing a gaseous acidic material into contact with the pulp.

11. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite by raising the temperature above 50° C. and bringing a gaseous acidic material into contact with it.

12. In the bleaching of cellulosic materials with chlorites, the improvement which comprises forming an aqueous pulp of the cellulosic material with the chlorite having a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite by raising the temperature above 80° C. and bringing a gaseous acidic material into contact with it.

13. In the bleaching of kraft pulp with chlorites, the improvement which comprises forming an aqueous kraft pulp containing chlorite at a pulp density in excess of about 15% under conditions such that the chlorite is substantially inactive and thereafter activating the chlorite.

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