METHOD OF SUPERBLEACHING CHEMICAL PULP

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This invention relates to a method of treating partially bleached chemical wood pulps of the sulfate and sulfite type in order to produce superbleached chemical pulp fibers which possess unimpaired or improved physical properties.

Partially bleached pulps of the sulfate or sulfite types are generally prepared by treating the original pulps with bleaching agents in single or multiple stages. In general, these partially bleached sulfate or sulfite pulps are comprised of long, clean, good forming, medium or strong fibers, depending on the nature of the original pulp and the bleaching treatment thereon, and by reason of these properties are desirable for use in high grade papers. However, in the production of the highest quality papers constituted or comprised essentially of fibers of this class, for esthetic reasons, and also for purposes of ink contrast, it is often desirable that the chemical fiber be bleached or brightened to a markedly higher degree. Thus, sulfate and sulfite pulps which are to be employed in top quality paper production often require bleaching to a very high degree of whiteness designated as superbleached; i.e., possessing a diffuse reflectance as compared to magnesium oxide in the range of 80 to 80% brightness as measured by standard brightness meters.

Although a great many oxidizing agents, under various conditions, have been suggested for employment as bleaches for raising partially bleached pulps of the sulfate and sulfite type to the superbleached brightness level, only chlorine or its compounds presently enjoy any measure of commercial usage. It is well known in the trade, however, that when attempts are made with chlorites to produce so-called superbleached pulp, this chemical tends seriously to degrade or damage the pulp fiber.

As a means for reducing the adverse action of chlorine upon the partially bleached chemical fibers, many expedients have been suggested for the employment of this bleaching agent. The more commonly selected expedient is the treatment of the partially bleached chemical pulp in single or multi-stage systems, using intermediate washing with either water or dilute caustic, or both. Often, the superbleaching stage or stages are merely continuations of normal partial bleaching procedures using chlorine and/or hypochlorite.

For instance, sulfate or sulfite pulp partially bleached in multiple stages with chlorine and hypochlorite in the normal manner, may be subjected to one or more additional chlorine or hypochlorite treatments with a water or caustic wash after each treatment. When such a procedure is used, the resultant fiber may possess a brightness which classifies it in the superbleached brightness range, but the characteristic high fiber strength has been progressively reduced to a degree with each succeeding treatment, and a considerable proportion of the inherent characteristic of high strength sacrificed in favor of high brightness. Furthermore, additional multi-stage treatments of this nature result not only in fiber damage, due to the action of bleaching chemicals on the pulp, but also in mechanical loss by reason of attendant washing steps. A further resultant disadvantage arises by reason of the fact that these additional treatments require extensive equipment occupying considerable floor space.

It is an object of the present invention to provide a simple method of preparing high strength pulps of the grade designated as superbleached from partially bleached chemical pulps of the class consisting of sulfate pulps and sulfite pulps.

It is also an object of the invention to produce superbleached pulps from either moderately bleached sulfate or sulfite pulps without materially affecting the physical strength thereof.

It is also an object of the invention to produce superbleached sulfate or sulfite pulps of unimpaired physical properties and with strengths superior to those possessed by similar pulps bleached to the same high degree in conventional single or multiple stage chlorine systems.

In accordance with the broad concept of the invention, the partially bleached chemical wood pulp of either the sulfate or sulfite type having a brightness in the range of 65 to 85% as measured on a standard brightness meter is, at a density above about 30%, impregnated with alkaline peroxide and permitted to bleach in the cold, that is, at temperatures below about 135° F. for an extended period of time, that is, from about 1 day to 20 days or until maximum brightness is produced, the pulp density being maintained above about 30% on a dry pulp basis.

In general, desirable physical characteristics of a finished paper, and the pulp therein, may be judged from an observation of the results of certain standard physical measurements of the paper as, for instance, burst, tear, and tensile strength. In a general way, the viscosity of pulp in a cuprammonium solution, as determined by standard procedure, is proportional to the combined physical characteristics and throughout
the following experiments, the cuprammonium viscosity in centipoises has been determined and used as a measure of the fiber strength and cellulose degradation of a particular pulp. Brightness as hereinafter expressed refers to the percent reflectance as measured by a Hunter Multipurpose reflectometer, calibrated to a General Electric brightness meter.

Example I

As mentioned hereinafore, it is possible by means of active chlorine treatments to prepare superbleached chemical pulps of the sulfite or sulfite type but at a sacrifice of fiber strength. As a specific example, a Southern pine sulfite pulp which had been treated in the conventional manner with multiple chlorine-hypochlorite steps and intermediate washes to reach a partially bleached brightness of 77.0 units, was found to possess a cuprammonium viscosity of 22.8 centipoises.

This pulp was then treated with an additional 1% available chlorine as hypochlorite and then washed to produce a pulp with a brightness of 64.8, a figure sufficiently high so that the pulp fell within the range of pulps designated as superbleached. The cuprammonium viscosity of this pulp had dropped to 21.8 centipoises indicating that considerable fiber damage is associated with the action of the last hypochlorite treatment.

Example II

A partially bleached softwood sulfite pulp produced by conventional means possessed a brightness of 53.6 units and a cuprammonium viscosity of 22.3 centipoises. The partially bleached pulp was dewatered to 50% pulp density and thereafter treated with sufficient peroxide solution to add to the pulp 1% hydrogen peroxide, 4% sodium silicate 42° Bé, and 1% caustic soda all based on oven dried pulp. The resulting pulp possessed a pulp density of 43% and was maintained at this density for several days at room temperature. A maximum brightness of 90.8 units occurred after five days standing in the damp condition. The cuprammonium viscosity of the pulp was found to be 29.6.

Example III

Another sample of partially bleached sulfite pulp was found to have a pulp brightness of 70.3 units and a cuprammonium viscosity of 13.2 centipoises. When superbleached at a pulp density of 48% with 1% hydrogen peroxide, 4% silicate of soda, and 1% caustic soda, a brightness of 87.2 was obtained after 14 days at room temperature. In this case, the cuprammonium viscosity of the pulp was substantially unchanged. On the other hand, when the original partially bleached sulfite pulp at 70.3 brightness was superbleached at 5% density for four hours at 35° C. with 1% available chlorine as hypochlorite, based on oven dry pulp, and finally washed, there was obtained a finished product possessing a brightness of 97.4 units. In this latter instance, however, the cuprammonium viscosity had dropped to 9.9.

Example IV

A partially bleached hardwood sulfite pulp possessed a brightness of 75.5 units and a cuprammonium viscosity of 43.4. When superbleached at 5% density for 8 hours at 35° C. with 1% available chlorine as hypochlorite and washed, the brightness of the pulp had increased to 86.4 but the cuprammonium viscosity had dropped to 24.1.

However, when another sample of the pulp partially bleached to 75.5 was given a 14 day, room-temperature, 45% density superbleaching treatment employing 1% hydrogen peroxide, 4% silicate of soda, 41° Bé, and 1% caustic soda, based on oven dry pulp, the resultant product possessed a brightness of 90.0 units and the cuprammonium viscosity was measured as 48.8.

The invention as set forth herein requires, for best results, that a specific peroxide treatment procedure be employed for various brightnesses of moderately or partially bleached sulfite and sulfite pulps at 65 to 85 brightness to the superbleached range of 80 to 90+. In general, the peroxide superbleaching treatment shall be performed at a relatively high pulp density, i.e., about 30%. Further, the bleaching operation shall be performed at low temperature, preferably at room temperature and, in no instance, at a temperature higher than 130° F. Furthermore, to obviate excessive damage to the pulp, the bleaching should be carried out over a relatively extended period of time as, for instance, from 1 to 20 days, and the fibers preferably accumulated in order to prevent evaporation of substantial quantities of moisture from the high density pulp which may be in the form of crumbs or as a lap. The latter form of accumulation, by reason of the ease of handling, is preferred.

In order to maintain pulp damage at a minimum, it is advisable to employ only that quantity of bleaching and attendant reagents as is required to produce the desired maximum brightness. Thus, the chemical content on a dry pulp basis for the peroxide superbleaching treatment should be preferably within the following ranges:

<table>
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<tr>
<th>Per cent Peroxide as H₂O₂ (100%)</th>
<th>0.10 to 1.5</th>
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<tr>
<td>Total alkali calculated as NaOH</td>
<td>0.30 to 3.25</td>
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It will be understood that hydrogen peroxide is the preferred superbleaching reagent and should never be used as such or may be prepared from an inorganic peroxide, preferably sodium peroxide, although other metallic peroxides such as potassium peroxide, barium peroxide, sodium perborate and the like, may be employed since they generate hydrogen peroxide in aqueous solution.

The peroxide solution should contain an alkali.

The alkali is preferably caustic soda although other materials generating available alkali in aqueous solutions may be employed as, for instance, trisodium phosphate, sodium carbonate, sodium silicate, as well as sodium pyrophosphate.

As is usual, when employing a peroxide for bleaching purposes, it is desirable to incorporate a so-called stabilizer in the peroxide solution and the preferred stabilizer, by reason of its cheapness and by reason of its availability, is sodium silicate. The other stabilizers are soluble calcium or magnesium salts such as magnesium sulfate. Certain of these stabilizers contribute to the above described condition, where sodium peroxide is the source of hydrogen peroxide, it need not be completely neutralized but only to the extent desired to obtain a predetermined caustic content in the hydrogen peroxide solution resulting therefrom.

Therefore, in order to produce superbleached pulps from partially bleached sulfite or sulfite chemical pulps of above about 65 brightness, the preferred procedure is to treat the partially
bleached pulps with alkaline hydrogen peroxide in accordance with the special hydrogen peroxide bleaching method described above, in order to maintain chemical degradation at a minimum. In other words, all methods of hydrogen peroxide bleaching of partially bleached pulps are not effective for the purposes of the present invention. The following examples are designed to illustrate the point in question:

**Example V**

A sulfite chemical pulp, partially bleached by a standard chlorine-hypochlorite treatment, had a brightness of 72.1 and a cuprammonium viscosity of 34.5 centipoises.

A sample of this pulp was bleached at moderate density of 12% for three hours at 50° with 0.75% hydrogen peroxide, 4% silicate of soda, 42° Bé., and 1.26% caustic soda, all based on oven dried pulp. The resulting pulp possessed a brightness of 83.4 and a cuprammonium viscosity of 53.0 centipoises. In contrast to this, another sample of the partially bleached sulfite pulp, when given the preferred low temperature, long-time super-bleaching treatment with alkaline peroxide at a high density of 22% for seven days at room temperature, and with 0.5% hydrogen peroxide, 4% silicate and 0.5% NaOH, all on oven dried pulp basis, was found to have a pulp brightness of 65.1 units and a better viscosity, namely, 39.3 centipoises by the cuprammonium determination. Similar results are obtained on sulfate pulp:

**Example VI**

A sample of partially bleached Southern sulfite, prepared by a chlorine mill treatment, consisting of two stages of chlorination, each followed by a caustic wash and a final hypochlorite bleach, possessed a brightness of 68.5. A sample of this pulp, when treated at 12% density for one hour at 60° C., with 1.5% hydrogen peroxide, 5% silicate of soda, 42° Bé, and 1.5% caustic on oven dried pulp, produced a pulp having a maximum brightness of 81.6 and a cuprammonium viscosity of 16.1.

Another sample of the same pulp treated for four days at room temperature, at a pulp density of 45% with 1% hydrogen peroxide, 4% silicate of soda, 42° Bé, and 1% caustic, all on an oven dried basis, produced a superbleached sample having a brightness of 84.7 and a cuprammonium viscosity of 16.8.

The value of superbleaching with the low temperature, high density, long-time bleaching of the present invention, is even more striking when the physical properties of pulp obtained thereby are considered. In the example immediately above, it will be noted that both the final brightness and cuprammonium viscosity produced by the alkaline peroxide step of the present invention are higher than those produced by an alkali peroxide bleach at elevated temperature and at moderate density.

It will be understood that the above examples illustrate preferred operating conditions and are given merely for purposes of illustration, and are not intended to limit the scope of the invention as defined in the claims appended hereto.

What is claimed is:

1. The method of preparing a superbleached paper fiber from chemically purified fiber selected from the class consisting of sulfate fiber and sulfite fiber which comprises preliminarily prebleaching the chemically purified fiber with a hypochlorite to a brightness greater than 65 and then completing the bleach upon the chemically purified and hypochlorite prebleached fibers at a substantially constant pulp density not less than 30% and at temperatures below 130° F. with alkaline peroxide, the total alkalinity of which is 0.3% to 3.25% calculated as NaOH, the time for obtaining maximum brightness being between 1 and 20 days, whereby the physical properties of the so treated fibers at the higher brightness level remain substantially unchanged from those existing at the lower brightness level.

2. The method of preparing a superbleached paper fiber from chemically purified fiber selected from the class consisting of sulfate fiber and sulfite fiber which comprises preliminarily prebleaching the chemically purified fiber with a hypochlorite to a brightness greater than 65 and then applying an alkaline hydrogen peroxide solution to said purified and prebleached fibers at a high pulp density and thereafter maintaining the pulp density substantially constant and greater than 30% and the temperature below 130° F. for a bleaching period of between 1 and 20 days, the amount of peroxide being between 0.1% and 1.5% H₂O₂ (100%) and the total alkalinity calculated as NaOH, being between 0.3% and 3.25%, each based on the weight of dry fiber, whereby the physical properties of the so treated fibers at the higher brightness level remain substantially unchanged from those existing at the lower brightness level.

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