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BLEACHING CELLULOSIC MATERIALS

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It has hitherto been proposed to bleach cellulosic materials with aqueous solutions of chlorites. Such bleaching processes have the general advantage that, properly applied, the degradation of the cellulosic material normally incident to the use of conventional bleaching agents, such as chlorine, hypochlorites and permanganates, particularly when a high degree of bleaching is required, is avoided. My invention relates to improvements in the bleaching of cellulosic materials with chlorites and in completing the bleaching of materials partially bleached with such conventional bleaching agents.

I have discovered that cellulosic materials can be bleached to an exceptionally high degree, as reflected by whiteness, for example, without substantial degradation, as reflected by loss of strength, for example, by subjecting the cellulose material to the joint action of chlorites and aldehydes in aqueous solution at a pH of about 3-9.

The useful chlorites comprise the chlorites of the alkali metals and the alkaline earth metals, such as sodium chlorite (NaClO_2) and calcium chlorite ($\text{Ca}(\text{ClO}_2)_2$). The useful aldehydes comprise, for example, formaldehyde, acetaldehyde, paraformaldehyde, furfural, benzaldehyde, the 5- and 6-carbon atom aldose sugars and inverted sucrose. All of these compounds are characterized by the CHO group. Temperatures and concentrations are widely variable. Increased temperature increases the rate of bleaching. The ratio of chlorite to aldehyde may vary widely, although a molar ratio of 1:1 is generally useful. An excess of the aldehyde does no damage to the bleached product. The consistency of the bleaching solution, the ratio of the weight of the cellulosic material to the weight of the solution, may also vary over a wide range. For example, the bleaching can be carried on at consistencies of about 5%, as in conventional practice, or at much higher consistencies such as 15% and 25%. At higher consistencies, higher concentrations of chlorite and aldehyde can also be used to accelerate the bleaching rate.

I have also discovered that the consumption of chlorites, in such bleaching of cellulosic materials, is reduced when phosphates, of the alkali metals, are present.

For example, the effect appears when phosphates, such as monosodium phosphate and disodium phosphate, are used to control the pH of the bleaching solution. In the presence of such phosphates, comparable whiteness with a consumption of chlorite less than half that otherwise required can frequently be obtained.

The improvements of my invention are applicable to cellulosic materials generally. My invention is particularly applicable to the bleaching of cellulose fibers derived from wood or woody material by any of the generally practiced fiber

liberation processes and for bleaching cellulose fibers commonly used in textile manufactures. My invention is applicable to the bleaching of wood pulp produced by the kraft process, the sulfite process and the soda process, to the bleaching of cotton linters, of hemp, of derivatives of cellulose such as rayon and of woven fabrics produced from cellulose fibers.

The bleaching of my invention is useful, with particular advantage, in a combined operation in which the cellulosic material is partially bleached with one or more conventional bleaching agents and in which the bleaching is completed with a chlorite and an aldehyde in accordance with my invention. The partial or preliminary bleaching can be carried to a degree short of that at which substantial degradation of the cellulosic materials begins and the bleaching then carried to a high degree to produce a product of the combined steps of exceptional whiteness, for example, and of unusually high strength. For example, kraft pulp can usually be bleached to a degree characterized by a whiteness of the range of 70-78 (G. E. reflectometer) without substantial degradation by conventional practices with chlorine or a hypochlorite. By applying my invention, such partially bleached pulp can be brought to a whiteness of 85 or better, for example, without loss of strength or other degradation.

My invention will be further illustrated by the following examples:

Example I

125 grams of Swedish kraft pulp were added to 2500 cc. of an aqueous solution containing 0.48 gram of sodium chlorite and 1.25 grams of formaldehyde. This suspension, of 5% consistency, was buffered at a pH of 8 by the addition of half normal sodium hydroxide, the pH being checked at regular intervals by the use of a Beckman meter. The suspension was maintained at a temperature of 60° C. for two hours and the pulp was then separated and washed. The following physical tests were conducted at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied, percent.....		0.5
Total formaldehyde applied.....do.....		1.0
Bursting strength (Mullen).....	67.0	66.4
Tearing strength (Elmendorf).....	57	61
Tensile strength (Schopper).....	244	242
Brightness (percent reflectance with #1 filter in G. E. reflectometer).....	82.7	87.1

Example II

100 grams of a kraft pulp were added to 2000 cc. of an aqueous solution containing 0.177 gram of sodium chlorite and 2 grams of formaldehyde.

This suspension, of 5% consistency, was buffered at a pH of 7.1 by the addition of sodium bicarbonate and monosodium phosphate, the pH being checked at regular intervals. The suspension was maintained at about 25° C. for three hours and the pulp was then separated and washed. The following physical tests were conducted at 70° F and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied...percent.....		0.23
Total formaldehyde applied.....do.....		2.0
Bursting strength (Mullen).....	51.0	51.4
Tearing strength (Elmendorf).....	48	41
Tensile strength (Schopper).....	207	207
Brightness (percent reflectance with #1 filter in G. E. reflectometer).....	78	84.1

Example III

125 grams of a kraft pulp were added to 2500 cc. of an aqueous solution containing 0.221 gram of sodium chlorite and 2.5 grams of formaldehyde. This suspension was buffered at a pH of 6.9 by the addition of sodium bicarbonate and monosodium phosphate, the pH being checked at regular intervals. The suspension was maintained at a temperature of 50° C. for one hour and the pulp was then separated and washed. The following physical tests were conducted at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied...percent.....		0.23
Total formaldehyde applied.....do.....		2.0
Bursting strength (Mullen).....	51.0	48.5
Tearing strength (Elmendorf).....	207	214
Brightness (percent reflectance with #1 filter in G. E. reflectometer).....	78	85.0

Example IV

125 grams of a kraft pulp were added to 2500 cc. of an aqueous solution containing 0.0625 gram of formaldehyde. The suspension was buffered at a pH of 7.1 with a phosphate buffer. The suspension was maintained at a temperature of 50° C. for one hour and the pulp was then separated and washed. This pulp was then added to 2500 cc. of an aqueous solution containing 0.20 gram of sodium chlorite and 0.0625 gram of formaldehyde. This suspension was buffered at a pH of 7.4 with a phosphate buffer. The suspension was maintained at a temperature of 50° C. for one hour and the pulp was then separated and washed. The following physical tests were conducted at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied...percent.....		0.25
Total formaldehyde applied.....do.....		0.10
Bursting strength (Mullen).....	41.5	42.0
Tearing strength (Elmendorf).....	41	41
Tensile strength (Schopper).....	176	194
Brightness (percent reflectance with #1 filter in G. E. reflectometer).....	74.3	83.1

Example V

100 grams of a kraft pulp were added to 2000 cc. of an aqueous solution containing 0.18 gram of sodium chlorite and 0.85 gram of acetaldehyde. The suspension was buffered at a pH of 7.1 with a phosphate buffer. The suspension was maintained at a temperature of 50° C. for one hour and the pulp was then separated and washed.

The brightness of the bleached pulp was then 82.5 as compared to 74.3 for the original pulp.

Example VI

23 grams of a cotton muslin cloth, previously klier boiled, was soaked in an aqueous solution containing 2.3 grams per liter of sodium chlorite and 0.72 gram per liter of formaldehyde. The cloth was drained until it contained only about its own weight of solution and was then placed in a closed vessel in which it was maintained at a temperature of 75° C. for one hour. It was then washed and ironed dry. The brightness had increased from 74 to 84.2, while the tensile strength was not affected.

Example VII

23 grams of the same cloth was soaked in the same solution (see Example VI) and was then drained until it contained about its own weight of solution (50% consistency). The cloth was then placed in a closed vessel and maintained at a temperature of about 25° C. for two hours. It was then washed and ironed dry. The brightness had increased from 74 to 84.2, while the tensile strength was not affected.

Example VIII

23 grams of the same cloth (see Example VI) was soaked in an aqueous solution containing 2.3 grams per liter of sodium chlorite and 0.72 gram per liter of formaldehyde, buffered at a pH of 7.0 with a phosphate buffer. The cloth was drained until it contained about its own weight of solution and placed in a closed vessel in which it was maintained at a temperature of 25° C. for one hour. It was then washed and ironed dry. The brightness had increased from 74 to 85.4, while the tensile strength was unaffected.

Example IX

45 grams of damp kraft pulp, containing 10 grams of dry pulp, were added to 165 cc. of water, buffered at a pH of 7.1 with a phosphate buffer. 1.4 cc. of an aqueous solution of sodium chlorite containing 0.0169 gram of available chlorine per cubic centimeter and 0.5 cc. of benzaldehyde (technical) were added to this suspension. The suspension was then maintained at a temperature of 50° C. for one hour and the pulp was then separated and washed. The brightness had increased from 78 to 81.0, while the strength of the pulp was not affected.

Example X

1.4 cc. of an aqueous solution of sodium chlorite containing 0.0169 gram of available chlorine per cubic centimeter and 0.1 cc. of furfural (technical) were added to 165 cc. of water, buffered at a pH of 7.1 with a phosphate buffer to which 10 grams of dry kraft pulp (similar to that used in Example IX) had been added. This suspension was maintained at a temperature of 50° C. for one hour and the pulp was then separated and washed. The brightness had increased from 78 to 81.1, while the strength of the pulp was not affected.

Example XI

125 grams of a kraft pulp were added to 2500 cc. of an aqueous solution containing 5 grams of NaH_2PO_4 and 30 grams of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 6.25 cc. of an aqueous solution containing 50 grams per liter of available chlorine as sodium chlorite and 7.5 cc. of an aqueous solution containing 9.16 grams per liter of formaldehyde. This suspen-

sion was maintained at a temperature of 56°-58° C. for one hour, during which period the pH remained between 6.95 and 7.0. The pulp was then separated and washed. The following physical tests were conducted at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied...percent	-----	0.25
Total available chlorine consumed...do	-----	0.196
Total formaldehyde applied...do	-----	0.055
Bursting strength (Mullen)	51.0	51.2
Tearing strength (Elmendorf)	48	45
Tensile strength (Schopper)	207	206
Brightness (percent reflectance with #1 filter in G. E. reflectometer)	78	85.66

Example XII

125 grams of the same kraft pulp used in Example XI were added to 2500 cc. of an aqueous solution containing 37.4 cc. of an aqueous solution containing 33.4 grams per liter of available chlorine as sodium chlorite and 30 cc. of an aqueous solution containing 9.16 grams per liter of formaldehyde. This suspension, of 5% consistency, was buffered at a pH of 7 by the addition of half normal sulfuric acid, the pH being checked at regular intervals by the use of a Beckman meter. The suspension was maintained at a temperature of 50° C. for two hours and the pulp was then separated and washed. The following physical tests were conducted at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied...percent	-----	1.0
Total available chlorine consumed...do	-----	0.246
Total formaldehyde applied...do	-----	0.22
Bursting strength (Mullen)	51.0	49.9
Tearing strength (Elmendorf)	48	42
Tensile strength (Schopper)	207	189
Brightness (percent reflectance with #1 filter in G. E. reflectometer)	78	86

In one aspect my invention affords important

economies. Many complicated processes, involving critical controls of time, temperature and concentrations, have been devised to effect high degrees of bleaching with minimum degradation. None of them has been entirely satisfactory, when applied to produce high degrees of bleaching, but all of them have been expensive to apply. As compared to a number of such processes, the bleaching process of my invention will produce comparable degrees of whiteness, for example, with cost savings of as much as 50% and more and without substantial degradation of the cellulosic material.

I claim:

1. In the bleaching of cellulosic material the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution having a pH of about 3-9 and containing an aldehyde and a compound selected from the group consisting of alkali metal chlorites and alkaline earth metal chlorites.

2. In the bleaching of cellulosic material, the improvement which comprises introducing the material to be bleached into an aqueous solution having a pH of about 3-9 and containing an aldehyde and a compound selected from the group consisting of alkali metal chlorites and alkaline earth metal chlorites.

3. In the bleaching of cellulosic material, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution having a pH of about 3-9 and containing an aldehyde, an alkali metal phosphate and a compound selected from the group consisting of alkali metal chlorites and alkaline earth metal chlorites.

4. In the bleaching of cellulosic material, the improvement which comprises completing the bleaching by subjecting partially bleached material to the action of an aqueous solution having a pH of about 3-9 and containing an aldehyde and a compound selected from the group consisting of alkali metal chlorites and alkaline earth metal chlorites.

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