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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 cellulosic material to the joint action of chlorites and persulfates in aqueous solution at a pH of about 3–11. The useful chlorites comprise the chlorites of the alkali metals and the alkaline earth metals, such as sodium chlorite, $NaClO_2$, and calcium chlorite, $(Ca(ClO_2)_2$. The useful persulfates comprise the persulfates of the alkali metals, such as sodium persulfate, $Na_2S_2O_8$, and potassium persulfate, $K_2S_2O_8$, and the persulfates of the alkaline earth metals. Temperatures and concentrations are widely variable. Increased temperature increases the rate of bleaching. The ratio of chlorite to persulfate may vary widely, although a molar ratio of 2:1 is generally useful. 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 of pulp can be carried out at pulp 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 persulfate can also be used to accelerate the bleaching rate. The bleaching is with advantage carried out at elevated temperatures, temperatures of about 60°–80° C. being particularly useful, and, particularly when using such elevated temperatures, it is advantageous to effect the bleaching at a pH upwards of about 7, that is at a pH of about 7–11. 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 to the bleaching of 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 a persulfate 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 in 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 a kraft pulp were added to 2500 cc. of an aqueous solution containing 0.96 grams of sodium chlorite and 1.25 grams of sodium persulfate. This suspension, of 5% consistency, was buffered at a pH of 5.8 by required additions of hydrochloric acid and sodium hydroxide during the bleaching, the pH being checked at regular intervals with a Beckman meter. The suspension was maintained at a temperature of 75°–80° 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	.....	0.76
Bursting strength (Mullen)	51.0	50.7
Tearing strength (Elmendorf)	48	50
Tensile strength (Schopper)	207	191
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	78	87.16

Example II

125 grams of the same kraft pulp were added to 2500 cc. of an aqueous solution containing 0.96

gram of sodium chlorite and 1.25 grams of sodium persulfate. This suspension was brought to and maintained at a pH of 7.5 with half normal sodium hydroxide, the pH being checked at regular intervals. The suspension was maintained at a temperature of 70°–80° C. for two hours and the pulp was then separated and washed. The following physical tests were made at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied.....percent		1.0
Total available chlorine consumed.....do		0.31
Bursting strength (Mullen)	51.0	50.0
Tearing strength (Elmendorf)	48	47
Tensile strength (Schopper)	207	209
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	78	87.67

Example III

125 grams of the same kraft pulp were added to 2500 cc. of an aqueous solution containing 0.96 gram of sodium chlorite and 1.25 grams of sodium persulfate. The suspension was buffered at a pH of 8.5 with half normal sodium hydroxide, the pH being checked at regular intervals. This suspension was maintained at a temperature of 75°–80° 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		0.19
Bursting strength (Mullen)	51.0	48.5
Tearing strength (Elmendorf)	48	45
Tensile strength (Schopper)	207	207
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	78	87.42

Example IV

125 grams of kraft pulp were suspended in 2500 cc. of an aqueous solution containing 4.8 grams of sodium chlorite and 6.25 grams of sodium persulfate. This suspension was buffered at a pH of 9 with half normal sodium hydroxide, the pH being checked at regular intervals. The suspension was maintained at a temperature of 24° 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		5.0
Bursting strength (Mullen)	51.0	51.1
Tearing strength (Elmendorf)	48	47
Tensile strength (Schopper)	207	191
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	78	83.97

Example V

125 grams of another kraft pulp were mixed with 840 cc. of an aqueous solution containing 1.44 grams of sodium chlorite and 1.5 grams of sodium persulfate, buffered at a pH of 8.5 with half normal sodium hydroxide, the pH being checked at regular intervals. This suspension had a consistency of 15%. The suspension was maintained at a temperature of 35°–43° C. for two hours and the pulp was then separated and washed. The following physical tests were conduced at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied.....percent		1.5
Bursting strength (Mullen)	51.0	49.8
Tearing strength (Elmendorf)	48	46
Tensile strength (Schopper)	207	217
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	78	83.42

Example VI

125 grams of another kraft pulp were added to 2500 cc. of an aqueous solution containing 0.96 gram of sodium chlorite and 1.25 grams of sodium persulfate. The suspension was buffered at a pH of 9.1 with half normal sodium hydroxide, the pH being checked at regular intervals. This suspension was maintained at 60° C. for two hours and the pulp was then separated and washed. The following physical tests were made at 70° F. and 50% relative humidity:

	Original pulp	Bleached pulp
Total available chlorine applied.....percent		1.0
Bursting strength (Mullen)	51.0	49.6
Tearing strength (Elmendorf)	48	45
Tensile strength (Schopper)	207	200
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	78	84.5

Example VII

A piece of untreated greige cotton muslin, 80 x 80 threads per inch, weighing 36 grams and measuring 12 inches by 38 inches, was placed in 500 cc. of water containing 1.5 grams of sodium chlorite, 2.0 grams of sodium persulfate, 1.0 gram of trisodium phosphate and 1.0 gram of sodium ethane 1-palmitate 2-sulfonate. This solution, with the cloth in it, was maintained at a temperature of 80°–90° C. for thirty minutes. The cloth was then washed, soured in aqueous sulfuric acid containing 1% H_2SO_4, rewashed and ironed dry. The brightness was increased from 56.8 to 82.5, the absorbency was good, the starch removal was quite complete, all motes had been removed and the cloth had not been tendered.

Example VIII

36 grams of the same muslin in 500 cc. of water containing 1.0 gram of sodium chlorite, 2 grams of sodium persulfate, 1.0 gram of trisodium phosphate and 1.0 gram of sodium ethane 1-palmitate 2-sulfonate were maintained at a temperature of 95° C. for thirty minutes. The cloth was then washed, soured with aqueous 1% H_2SO_4, rewashed and ironed dry. The brightness was increased from 56.8 to 83.5, the absorbency was good, starch removal was quite complete, the motes had been removed and the cloth had not been tendered.

Example IX

36 grams of the same muslin in 500 cc. of water containing 0.5 gram of sodium chlorite, 1.0 gram of sodium persulfate, 1.0 gram of trisodium phosphate and 1.0 gram of sodium ethane 1-palmitate 2-sulfonate were maintained at a temperature of 95° C. for one hour. The cloth was then washed, soured with aqueous 1% H_2SO_4, rewashed and ironed dry. The brightness was increased from 56.8 to 82.3, the absorbency was good, the starch and mote removal was quite complete and the cloth had not been tendered.

Example X

18 grams of the same muslin were soaked in an aqueous solution containing 10 grams per liter of sodium chlorite, 20 grams per liter of sodium persulfate and 50 drops per liter of sodium diamyl sulfosuccinate as a wetting agent, buffered at a pH of 8.8. The cloth was then drained until it held about its own weight of solution and then hung in a vessel through which steam was passed for ten minutes. The cloth was then washed, soured, rewashed and ironed dry. The brightness was increased from 56.8 to 78.

Example XI

18 grams of the same muslin were soaked in an aqueous solution containing 20 grams per liter of sodium hydroxide, 2 grams per liter of sodium chlorite and 50 drops per liter of sodium diamyl sulfosuccinate as a wetting agent. The cloth was then drained until it contained about its own weight of solution and hung in a vessel through which steam was passed for ten minutes. The cloth was then washed and soaked in an aqueous solution containing 10 grams per liter of sodium chlorite and 20 grams per liter of sodium persulfate, drained until it contained about its own weight of solution and again hung in a vessel through which steam was passed for ten minutes. The cloth was then washed, soured, rewashed and ironed dry. The brightness was increased from 56.8 to 83, the starch and mote removal was quite complete, the absorbency was good and the cloth had not been tendered.

Example XII

125 grams of a Swedish kraft pulp were added to 2500 cc. of an aqueous solution containing 0.19 gram of sodium chlorite and 0.37 gram of sodium persulfate. This suspension was buffered at a pH of 8 with half normal sodium hydroxide, the pH being checked at regular intervals. 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	.....	0.20
Bursting strength (Mullen)	67.0	63.0
Tearing strength (Elmendorf)	57	69
Tensile strength (Schopper)	244	217
Brightness (percent reflectance with No. 1 filter in G. E. reflectometer)	82.7	87.3

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 but none of them has been entirely satisfactory when applied to produce high degrees of bleaching, and 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 with substantial cost savings and without substantial degradation of the cellulosic material. Also, the bleaching process of my invention will produce exceptionally high degrees of whiteness with relatively short bleaching times as compared to a number of such processes.

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 containing a compound selected from the group consisting of chlorites of the alkali metals and alkaline earth metals and a compound selected from the group consisting of persulfates of alkali metals and alkaline earth metals at a pH of about 3–11.

2. 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 containing a compound selected from the group consisting of chlorites of alkali metals and alkaline earth metals and a compound selected from the group consisting of persulfates of alkali metals and alkaline earth metals at a pH of about 3–11.

3. In the bleaching of cellulosic material, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution containing a compound selected from the group consisting of chlorites of alkali metals and alkaline earth metals and a compound selected from the group consisting of persulfates of alkali metals and alkaline earth metals at a pH of about 3–11 and at a temperature of about 60°–80° C.

4. In the bleaching of cellulosic material, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution containing a compound selected from the group consisting of alkali metal chlorites and alkaline earth metal chlorites and also containing a compound selected from the group consisting of alkali metal persulfates and alkaline earth metal persulfates at a pH of about about 7–11 and at a temperature of about 60°–80° C.

5. In the bleaching of cellulosic material, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution containing a compound selected from the group consisting of alkali metal chlorites and alkaline earth metal chlorites and also containing a compound selected from the group consisting of alkali metal persulfates and alkaline earth metal persulfates at a pH of about 7–11.

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