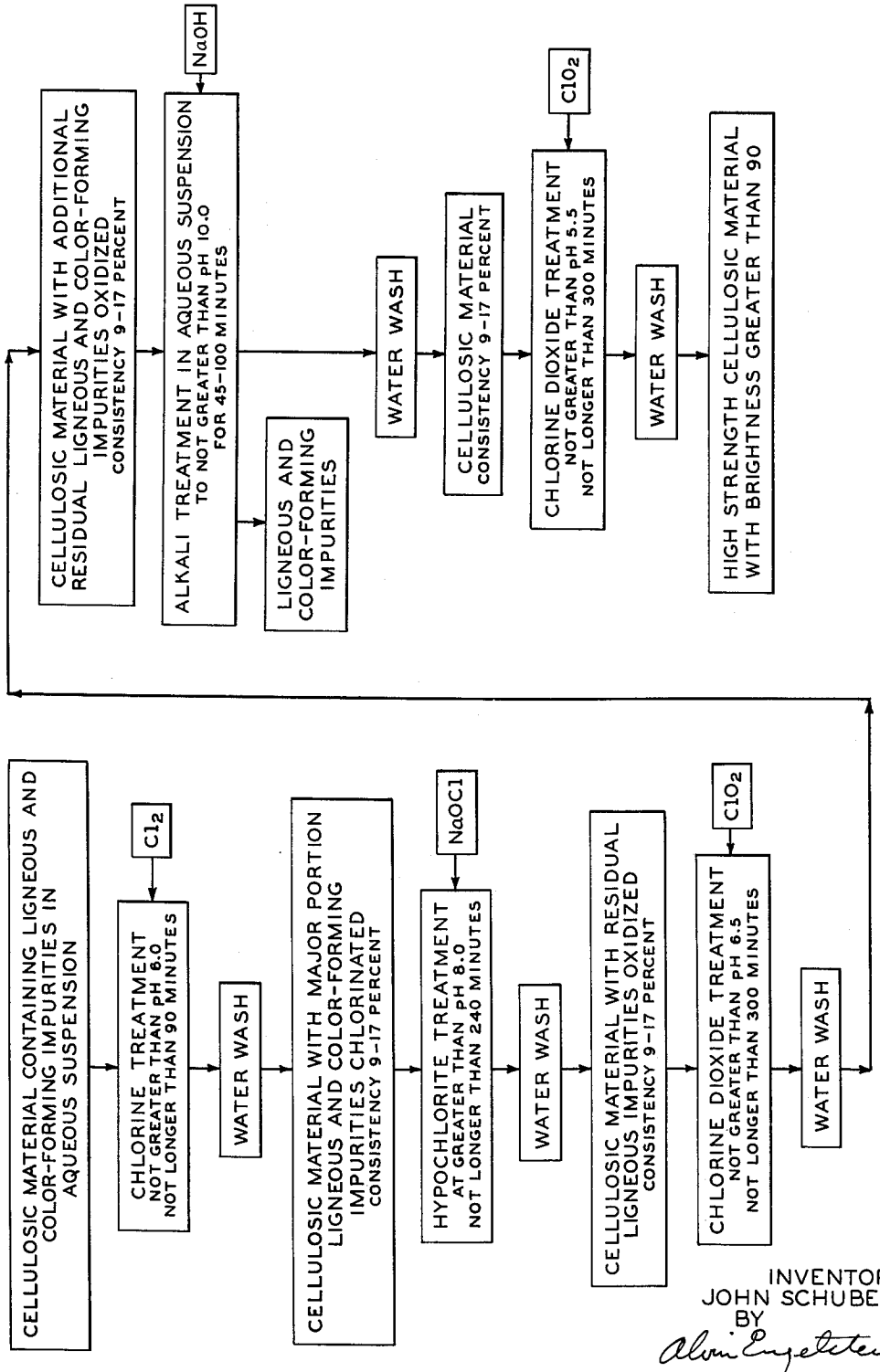
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PRODUCTION OF HIGH BRIGHTNESS HIGH STRENGTH WOOD PULPS

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PRODUCTION OF HIGH BRIGHTNESS HIGH STRENGTH WOOD PULPS

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This invention relates to the bleaching of ligneous cellulosic material and more particularly to the production of bleached cellulosic material having a very high brightness, improved color stability and high strength characteristics substantially unchanged from those of the unbleached cellulosic material.

Heretofore considerable work has been carried out in an effort to achieve a very high brightness pulp, viz. a pulp having a brightness above 90 while avoiding considerable loss in strength characteristics of the pulp. Single-stage, two-stage and multi-stage processes have been tried in an effort to obtain this high brightness pulp with retention of the pulp strength, but in general the processes have not been successful. In the first place, to attain a brightness in excess of 90 has been found extremely difficult to achieve with a brightness barrier generally being encountered at a brightness between 86–90. Secondly, even when this high brightness pulp in excess of 90 has been produced it has usually been done at the expense of the strength characteristics of the pulp due to oxidation and degradation of the cellulose with attendant considerable weakening of the strength characteristics of the pulp. Apparently as the ligneous and other non-cellulosic color-forming impurities are oxidized and removed from the pulp as the pulp approaches higher values of brightness, the cellulose becomes more susceptible to oxidation and degradation. Thirdly, when this high brightness has been obtained in one procedure, the bleaching was disadvantageous from a commercial standpoint because requiring excessively long time periods for the reaction, typically of more than one day and as long as 20 days.

One object of the present invention is to provide a process for production of bleached cellulosic material, for instance wood pulp, having a very high brightness and an improved color stability.

Another object is to provide a process for production of superbleached cellulosic material, for instance wood pulp, having high strength characteristics substantially unchanged from those of the unbleached pulp.

Another object is to provide a process for the production of high brightness high strength wood pulp, for instance wood pulp having a minimum G.E. brightness of about 91, with retention of high strength characteristics substantially unchanged from those of the unbleached pulp.

A further object is to provide a process for the production of very high brightness high strength wood pulp having strength characteristics unchanged from those of the unbleached pulp and having materially higher brightness and color stability than is possessed by bleached pulp obtained by methods currently practiced in the pulp and paper industry.

A further object is to provide a process for the production of very high brightness high strength wood pulp which is economical and efficient.

Additional objects and advantages will be apparent as the invention is hereafter described in detail.

I have carried out considerable experimental work on the bleaching of wood pulp in an effort to obtain high brightness pulp having a G.E. brightness in excess of 90 without material reduction in strength characteristics of

the cellulose due to oxidation and degradation of the cellulose. I have tried different procedures including single-stage, two-stage and multi-stage procedures in an effort to achieve this goal but the results have usually been the same, with the product pulp either having too low a brightness considerably below 90, its strength characteristics materially impaired, or both of these undesirable results.

In accordance with the present invention, it was found that by treating the unbleached ligneous cellulosic material by a novel procedure including a particular sequence of chlorination and oxidative brightening stages together with a careful observance of pH conditions, times of treatment and pulp consistencies, a high brightness, high strength superbleached cellulosic material was produced having a G.E. brightness of 90 and generally of about 91 or over together with high strength characteristics substantially unchanged from those of the unbleached cellulosic material. Additionally, the product bleached cellulosic material had an improved color stability.

The accompanying drawing diagrammatically illustrates the process of the invention.

The process of the invention involves, in the sequence specified, adding elemental chlorine, for instance chlorine gas to an aqueous suspension of the unbleached ligneous cellulosic material such as unbleached wood pulp containing a substantial amount of ligneous and other non-cellulosic color-forming impurities in a first stage to chlorinate at a pH value not greater than pH 6, preferably within the range of pH 1.5–3.5, a major portion of the ligneous and color-forming impurities. The chlorinating is carried out in the first stage for a time of not in excess of about 90 minutes, preferably about 30–75 minutes. An alkaline hypochlorite, for instance an alkali metal or alkaline earth metal hypochlorite, for example sodium or calcium hypochlorite, is then added to the cellulosic material in a second stage at a cellulosic material consistency of about 9–17%, preferably about 12–17% to oxidize a portion of the residual ligneous and non-cellulosic color-forming impurities to considerably brighten the pulp. The pH is maintained in the second stage at a value greater than pH 8, preferably at a value within the range of about pH 9–10.5, and the time of treatment in the second stage is not in excess of 240 minutes, preferably about 30–180 minutes. Chlorine dioxide is added to the thus-treated cellulosic material at a cellulosic material consistency of about 9–17%, preferably about 12–17% in a third stage to oxidize an additional portion of the remaining ligneous and non-cellulosic color-forming impurities. The oxidizing is carried out with chlorine dioxide in the third stage for a time not in excess of 300 minutes, preferably about 60–300 minutes, and at a pH value not greater than pH 6.5, preferably within the range of about 2–6.5 to brighten the pulp to a greater unit of brightness than in the second stage. An alkali, for instance caustic soda, is then added to an aqueous suspension of the cellulosic material at a cellulosic material consistency of about 9–17%, preferably about 12–17%, in amount sufficient to increase the pH of the mixture to an alkaline pH above 10, preferably above 11, to bring about dissolution of the oxidized ligneous and non-cellulosic color-forming impurities. The mixture containing the added alkali is maintained at an elevated temperature in the fourth stage, preferably at a temperature of about 100–175° F., more preferably about 100–150° F. for a period sufficient to accomplish dissolution of the oxidized color-forming impurities. Time of such treatment in the fourth stage is preferably about 45–100 minutes, more preferably about 55–65 minutes. The alkali is added in the fourth stage preferably as a dilute aqueous caustic solution in

amount to provide about 1% of caustic soda (based on the dry weight of the cellulosic material). Chlorine dioxide is then added to the cellulosic material at a cellulosic material consistency of about 9–17%, preferably about 12–17% in a fifth stage to oxidize remaining ligneous and color-forming impurities. The pH in the fifth stage during the oxidizing is at a pH value not greater than pH 5.5, preferably within the range of pH 2–5.5 and the time of treatment with chlorine dioxide in the fifth stage is not in excess of 300 minutes, preferably within the range of about 120–300 minutes. The product cellulosic material from the fifth stage is characterized by having a minimum G.E. brightness of about 91, high strength characteristics substantially unchanged from those of the unbleached cellulosic material including very favorable tear, bursting and tensile strengths, and improved color stability.

A General Electric reflectometer was used for measuring the brightness of the present invention. Brightness measurements were obtained of the various pulps in the form of pulp pads. Bursting strengths were measured by the Mullen test, tear strength by the Elmendorf test, tensile strengths by the Schopper test and fold by the M.I.T. Double Fold test, these tests being well known in the paper and pulp industry.

The process is a considerable improvement over prior art processes for bleaching ligneous cellulosic material by virtue of (1) achieving very high brightness with a minimum G.E. brightness of typically about 91; (2) retention of high strength characteristics (in addition to the very high brightnesses) substantially unchanged from those of the unbleached wood pulp including favorable tear, bursting and tensile strengths (the raising of the brightness even one unit at such high brightness levels in itself being a considerable achievement); (3) production of superbleached high strength wood pulp having materially higher brightness, whiteness and purity than bleached pulps obtained by methods currently practiced in the pulp and paper industry; (4) production of very high brightness wood pulp having color stability and retention of unbleached paper making characteristics which are an improvement over bleached pulps currently produced in the pulp and paper industry; and (5) by being an efficient and economical process not requiring processing times of more than one day or of several days. It was surprising and unexpected that the oxidizing could be carried out in the oxidative brightening stages of the processes without substantial oxidation and degradation of the cellulose.

The pH values are brought or maintained within the ranges specified for the various stages to avoid certain undesirable disadvantageous results. For instance, at pH values much below pH 8 in the second stage, more than 80% of the available chlorine present has a tendency to react as hypochlorous acid (HOCl) with less than 20% acting as the desired hypochlorite ion (OCl^-). With such high concentrations of hypochlorous acid and low concentrations of hypochlorite ion, there is a marked increase in oxycellulose formation with attendant decrease in pulp strength. At pH values substantially higher than pH 6.5 in the third and 5.5 in the fifth stage, there is considerable weakening of the cellulose due to oxidation and degradation due to depolymerization of the cellulose. At pH values much below pH 10 in the fourth stage, difficulty is encountered in effecting dissolution of the oxidized color-forming impurities in the liquor. However, with the higher alkaline pH's above 10 and preferably above 11, the color bodies formed in the oxidative stage are very soluble in hot dilute alkali and can therefore be readily removed from the pulp fiber bodies. The specific sequence of stages is also of utmost importance for the reason that other procedures including single-, two- and multi-stage procedures involving different sequences of stages were tried and found not successful.

In co-filed application Serial No. 47,619, filed Aug. 5, 1960, entitled "Method for Production of High Brightness High Strength Wood Pulps" there is disclosed and claimed a process for bleaching ligneous cellulosic material involving generally the steps of chlorination, oxidation with an alkaline hypochlorite, oxidation with chlorine dioxide, oxidation with an alkaline peroxide and again oxidation with chlorine dioxide in that sequence.

In a specific embodiment of the invention the unbleached wood pulp, for instance unbleached soda, kraft, sulfite or dissolving grades of pulp containing a substantial amount of ligneous and non-cellulosic color-forming impurities is mixed with water to form a suspension having a low pulp consistency of typically about 2–4%, preferably 3%. Chlorine gas is then passed into the aqueous pulp suspension in a first stage to chlorinate at a pH value within the range of pH 1.5–3.5. In this manner a major portion, typically about 40–60% of the ligneous and color-forming impurities are removed. The amount of chlorine added in the first stage will generally range from about 40%–70% of the chlorine demand of the pulp as determined by the permanganate number (T.A.P.P.I. standard method T214M42). Amounts of chlorine substantially higher than 70% and much below 40% of the chlorine demand should be avoided as amounts substantially higher than 70% of the chlorine demand will degrade the cellulose while amounts much lower than 40% will produce a shivy "hard to bleach" pulp for the oxidative stages. The time of chlorination in the first stage is that which is sufficient for the exhaustion of the chlorine with a maximum time of 90 minutes and the temperature of chlorination is about 65°–95° F., preferably about 70°–80° F. After chlorination in the first stage, the pulp is separated from the liquor, for instance by filtration, and then thoroughly washed with water to remove reaction products including water-soluble, chlorinated ligneous and non-cellulosic color-forming impurities, unreacted chlorine and hydrochloric acid.

An alkali metal or alkaline earth metal hypochlorite, for instance sodium or calcium hypochlorite, is then added to the partially purified pulp having a pulp consistency of about 12–17% from the first stage in a second stage, an oxidative brightening stage to oxidize residual ligneous and non-cellulosic color-forming impurities. If desired, potassium or magnesium hypochlorites could be used instead of the sodium or calcium hypochlorite. The oxidizing with the alkaline hypochlorite in the second stage is carried out for a time of about 30–240 minutes, at a pH value within the range of about pH 8–10 and at a temperature of about 90°–125° F. Excess alkali usually is added to the pulp in this second stage to insure maintenance of high pH within the range of about 8–10.5 during the reaction. With pH values much below pH 8, for instance at pH 6–7, more than 80% of the available chlorine present tends to react as hypochlorous acid (HOCl), with less than 20% acting as the desired hypochlorite ion (OCl^-). With these high concentrations of hypochlorous acid and low concentrations of hypochlorite ion at the pH values substantially below pH 8 there is a marked increase in oxycellulose formation and a resultant decrease in pulp strength. Temperatures of about 95°–125° F. are preferably employed in the second stage with pulp consistencies of about 12–17% for purposes of increasing the reaction rate in the second stage. After the oxidative treatment in the second stage, the pulp fibers are separated from the liquor by, for instance filtration, and then thoroughly washed with water.

Chlorine dioxide is then added to the partially brightened pulp at a pulp consistency of about 12–17% in a third stage, also an oxidative brightening stage, to oxidize an additional portion of the residual ligneous and color-forming impurities present in the pulp from the second stage. Treatment with chlorine dioxide is carried out in the third stage for a time of about 60–300 minutes and at a pH value within the range of about pH 2–6.5. At pH values substantially higher than 6.5 there is con-

siderable weakening of the cellulose due to oxidation and degradation due to depolymerization of the cellulose. Temperature is about 120–180° F., preferably about 155°–165° F. in the third stage. The chlorine dioxide is added either as an aqueous solution or as a gas diluted with an inert gas, for instance nitrogen. The pulp is then separated from the liquor, for instance by filtration, and again thoroughly washed with water to remove the oxidized ligneous and non-cellulosic color-forming impurities.

Alkali, for instance caustic, preferably caustic soda in the form of a dilute aqueous caustic soda solution is then added to the further purified and brightened pulp in a fourth stage, which is an impurity extraction stage, at a pulp consistency of about 12–17% in amount to provide about 1% of caustic soda based on dry weight of pulp and to increase the pH value of the mixture above 11. If desired, a small amount of about 0.5–2.5 wt. percent, preferably from about 0.5–1.0 wt. percent (based on dry weight of pulp) of an alkali metal or alkaline earth metal hypochlorite, for instance sodium or calcium hypochlorite can be added to the fourth stage in addition to the alkali. Such alkaline hypochlorite when employed in the fourth stage will achieve oxidation brightening of the pulp simultaneous with the extraction of the color-forming impurities by the alkali. The mixture containing the caustic is maintained in the fourth stage at a temperature of about 100–150° F., preferably about 100–130° F. by heating for a time of about 45–100 minutes, preferably about 55–65 minutes whereby dissolution occurs in the liquor of the oxidized ligneous and non-cellulosic color-forming impurities. The oxidized color-forming impurities are very soluble in the hot dilute alkali but are considerably less soluble or only slightly soluble in the dilute alkali at room temperature. The pulp is then separated from the liquor and washed with water to remove substantially all caustic and impurities from the bodies of the pulp fibers. Examples of other alkali that may be employed in this fourth stage in place of caustic soda include caustic potash and sodium carbonate. The pulp is then treated in a fifth stage with chlorine dioxide at a pulp consistency of about 12–17% to oxidize remaining ligneous and color-forming impurities, typically oxidizing a major portion or substantially all of the remaining impurities. The treatment with chlorine dioxide is carried out for a time of preferably about 60–300 minutes at a pH value of about pH 2–5.5, and at a temperature of about 140°–180° F., preferably about 155°–165° F. pH values considerably above 5.5 should be avoided as they result in degradation of the cellulose due to depolymerization with attendant considerable weakening of the cellulose. The pulp is separated from the liquor, for instance by filtration and again washed with water to remove oxidized impurities. The product pulp from the fifth stage has a typical minimum G.E. brightness in the case of soda pulp of about 91.

The following examples illustrate the invention. Parts and percentages are by weight unless otherwise specified.

Example 1

Unbleached soda pulp obtained from the blow tank and after washing with hot water of temperature of 180° F. had G.E. brightness of 28.4%, a $KMnO_4$ number of 9.4 and a Cl_2 demand of 4.4%. The following are slowness and strength characteristics:

Time (minutes)	Slowness	Burst	Tear	Tensile	Fold
0	15.0	40	1.38	5.1	10
5	16.5	55	1.53	6.0	10
25	21.0	103	1.44	8.8	190
45	27.5	131	1.31	11.1	780
65	36.5	136	1.27	10.8	1,700
85	48.0	146	1.23	11.3	1,410
105	56.5	139	1.17	11.8	3,070

Chlorine gas was added to an aqueous suspension of the unbleached soda pulp at a pulp consistency of about 3% in a first stage at a temperature of 73° F. The amount of chlorine added was 2.64% and the amount of chlorine consumed was 2.64%. The chlorination was carried out for a time of 60 minutes and the final pH was 1.9. After separating the pulp from the liquor by filtration and washing with water the pulp had a G.E. brightness of 37.6%. Sodium hypochlorite was then added to the pulp in a second stage at a pulp consistency of 12% and a temperature of 95° F. Sodium hydroxide was also added in the amount of 0.5% for maintaining the pH. The amount of available Cl_2 added as sodium hypochlorite was 1.75% and the amount of this Cl_2 consumed was 1.57%. The second stage bleaching was carried out for 220 minutes, and the final pH was 9.4. After separation of the pulp from the liquor by filtration and washing with water, the pulp had a G.E. brightness of 70.2%.

Chlorine dioxide was then added to the pulp in a third stage at a pulp consistency of about 12% to oxidize remaining ligneous and non-cellulosic color-forming impurities. The amount of chlorine dioxide added was 0.50% and the amount consumed was 0.49%. The treatment with chlorine dioxide was effected in the third stage for about 240 minutes and at a temperature of about 160° F. The final pH was 3.6. The pulp was separated from the liquor by filtration and washed with water. It had a G.E. brightness of 84.0%. An aqueous caustic soda solution was then added to an aqueous suspension of the pulp at a pulp consistency of about 12% in a fourth stage in amount to provide about 1% of caustic soda (based on dry weight of the pulp) and to increase the pH value to above pH 11. The temperature of the mixture was maintained at 160° F. in the fourth stage for a time of 60 minutes. The final pH of the mixture was 11.8. The pulp was then filtered from the liquor and washed with water to remove the caustic soda and the impurities from the bodies of the pulp fibers. This pulp had a G.E. brightness of 78.3%.

Chlorine dioxide was then added to the pulp in a fifth stage at a pulp consistency of about 12%, the amount of chlorine dioxide added being about 0.5% and the amount consumed being about 0.4%. Treatment with chlorine dioxide was carried out in the fifth stage for 300 minutes at a temperature of 160° F. to oxidize remaining ligneous and non-cellulosic color-forming impurities. The final pH in the fifth stage was 5.0. The pulp was then filtered from the liquor and again washed with water. A product bleached soda pulp having a G.E. brightness of 90.7 and of improved color stability was obtained. This high brightness soda pulp had the following slowness and strength characteristics:

Time (minutes)	Slowness	Burst	Tear	Tensile	Fold
0	15.0	42	1.40	4.8	10
5	16.0	63	1.29	6.1	20
25	22.5	112	1.26	8.9	200
45	31.0	129	1.16	10.7	920
65	45.5	144	1.08	10.6	1,730
85	55.5	144	1.11	12.3	2,160

Example 2

An unbleached kraft pulp (mixture of hardwood and softwood) had a G.E. brightness of 29.4%, a $KMnO_4$ number of 11.4, a Cl_2 demand of 5.5%, and the following freeness and strength characteristics:

Time (minutes)	Slowness	Burst	Tear	Tensile	Fold
0	13.5	33	1.67	3.8	10
5	14.5	56	1.98	5.0	30
20	21.5	113	1.84	8.9	510
35	39.0	138	1.51	10.2	960
50	64.0	141	1.35	10.5	1,180

Chlorine gas was introduced into an aqueous suspension of the unbleached pulp at a pulp consistency of 3.0% in

a first stage at a temperature of 86° F. The amount of chlorine added was about 3.30% and the amount consumed was about 2.96%. The chlorination was carried out for a time of about 41 minutes. The final pH was 2.2.

Sodium hypochlorite was added to the pulp from the first stage in a second stage at a pulp consistency of 12%. Treatment with sodium hypochlorite was carried out in the second stage for 34 minutes and at a temperature of 110° F. Sodium hydroxide was added to the mixture to maintain the pH. The final pH was 10.8. After separation of the pulp from the liquor by filtration and again water washing the pulp, the pulp had a G.E. brightness of 64.6%.

Chlorine dioxide was added to the pulp from the second stage in a third stage at a pulp consistency of about 12%. The amount of chlorine dioxide added was 0.65% and the amount consumed was 0.56%. The chlorine dioxide treatment was carried out in the third stage for 100 minutes and at a temperature of 160° F. to oxidize remaining ligneous and color-forming impurities. The final pH was 4.0. The pulp was then filtered from the liquor and washed with water. It has a G.E. brightness of 84.5%.

Aqueous caustic soda solution was then added to an aqueous suspension of the pulp at a pulp consistency of about 12% in a fourth stage in quantity to provide about 1% of caustic soda (based on dry weight of pulp) and to increase the pH value of the mixture to a pH above 11. The mixture containing the caustic soda was maintained at a temperature of about 160° F. by heating for a time of about 98 minutes. The final pH was 11.8. The pulp was then filtered from the liquor and washed with water to remove the caustic soda and color-forming impurities from the bodies of the pulp fibers. The pulp was found to have a G.E. brightness of 78.2%. Chlorine dioxide was then added to the pulp in a fifth stage at a pulp consistency of about 12%. The chlorine dioxide was added in amount of about 0.30% and the amount consumed was about 0.19%. The treatment was chlorine dioxide was carried out in the fifth stage for 116 minutes and at a temperature of about 160° F. After filtration separation of the pulp from the liquor and water washing, the product bleached pulp had a G.E. brightness of 91.1% and was of improved color stability. This high brightness pulp had the following freeness and strength characteristics:

Time (minutes)	Slowness	Burst	Tear	Tensile	Fold
0	13.5	37	1.63	3.6	10
5	14.0	67	1.77	5.7	40
20	20.0	107	1.76	7.9	490
35	35.0	135	1.60	9.5	780
50	53.0	145	1.46	10.5	1,510
60	63.0	141	1.42	10.2	1,300

Example 3

Chlorine gas was bubbled through an aqueous suspension of unbleached kraft pulp at a pulp consistency of 3% in a first stage. The unbleached pulp had substantially identical strength characteristics, G.E. brightness, $KMnO_4$ number and Cl_2 demand as the unbleached kraft pulp treated in Example 2. The amount of chlorine added was about 3.30% and the amount consumed was about 3.13%. Chlorination was effected for a time of about 41 minutes and at a temperature of about 85° F. The final pH was 2.6.

Sodium hypochlorite was then added to the pulp in a second stage at a pulp consistency of about 12%, the amount of available chlorine added as sodium hypochlorite being 2.0% and the amount of the chlorine consumed being 1.71%. Sodium hydroxide was added to the mixture in amount of about 0.5% to maintain the pH. The treatment with hypochlorite was carried out for about 34 minutes and at a temperature of about 120° F. The final pH was 10.7. The pulp was then filtered from the liquor and washed with water. It had a G.E. brightness of 76.1%.

Chlorine dioxide was then added to the pulp in a third stage at a pulp consistency of about 12%. The amount of chlorine dioxide added was about 0.65% and the amount consumed was about 0.57%. The chlorine dioxide treatment was carried out for about 100 minutes and at a temperature of about 160° F. The final pH was 4.5. After filtration separation of the pulp from the liquor and water washing of the pulp, it had a G.E. brightness of 85.8%. Aqueous caustic soda solution was added to the pulp from the third stage in a fourth stage in amount to provide about 1% of caustic soda (based on dry weight of the pulp) and to increase the pH value of the mixture to a pH above 11. The mixture containing the caustic soda was maintained at a temperature of about 160° F. by heating for about 98 minutes. The final pH was 11.3. The pulp was then filtered from the liquor and washed with water to remove the caustic soda and color-forming impurities from the bodies of the fibers. The pulp had a G.E. brightness of 78.7%.

Chlorine dioxide was then added to the pulp at a pulp consistency of about 12% in a fifth stage in amount of about 0.30%. The amount of chlorine dioxide consumed was about 0.19%. The treatment with chlorine dioxide was carried out for about 116 minutes and at a temperature of about 160° F. After filtration separation of the pulp from the liquor and water washing of the pulp, it was found to have a G.E. brightness of 91.3% This product superbleached pulp was found to have the following strength characteristics:

Time (minutes)	Slowness	Burst	Tear	Tensile	Fold
0	13.5	39	1.78	3.8	10
5	14.0	64	1.54	5.8	30
20	21.5	107	1.48	8.6	330
35	40.0	130	1.37	9.9	680
50	60.0	138	1.33	10.5	1,390

Example 4

An unbleached kraft pulp having substantially identical brightness, $KMnO_4$ number, Cl_2 demand and strength characteristics as the unbleached pulp of Example 3 was treated in a substantially identical manner employing the five stage process of Example 3. However, the amount of available Cl_2 added as sodium hypochlorite in the second stage was 1.50% in this example (instead of 2.0% as in Example 3) and the amount of available Cl_2 consumed was 1.39% (instead of 1.71% as in Example 3). The pulp had G.E. brightnesses of 71.4%, 83.5%, 75.9% and 90.6% at the end of the second, third, fourth and fifth stages respectively. The product bleached pulp from the fifth stage had the following strength characteristics. The cupri-ethylene diamine viscosity was 13.2 which is a measurement of no strength loss as compared to the unbleached pulp.

In Examples 1–4 slowness is given in Schopper-Riegler degrees; burst strength in percent points/lb./ream—24 x 36–500; tear in grams force/lb./ream—24 x 36–500; tensile strength in kg. force/15 mm./50 lb. ream—24 x 36–500; and fold in M.I.T. double folds/15 mm./50 lb. ream—24 x 36–500.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

I claim:

1. A staged process for the production of superbleached cellulosic material having a brightness in excess of 90 and of high strength characteristics which comprises, in the sequence specified, (A) treating an aqueous suspension of unbleached cellulosic material containing a substantial amount of ligneous and noncellulosic color-

forming impurities in a first stage with elemental chlorine at not greater than pH 6 for not in excess of 90 minutes to chlorinate a major portion of said impurities, water washing the cellulosic material, (B) treating the cellulosic material at a consistency of about 9–17% with an alkaline hypochlorite in a second stage at greater than pH 8 for not in excess of 240 minutes to oxidize a portion of the residual ligneous and color-forming impurities to brighten the pulp without material degradation of the cellulose, water washing the cellulosic material, (C) treating the cellulosic material at a consistency of about 9%–17% in a third stage with chlorine dioxide at not greater than pH 6.5 for not in excess of 300 minutes to oxidize an additional portion of said residual impurities without material degradation of the cellulose, water washing the cellulosic material, (D) then adding alkali to an aqueous suspension of the cellulosic material at a consistency of about 9%–17% in a fourth stage to an alkaline pH above about pH 10 to effect dissolution of said oxidized impurities, water washing the cellulosic material, (E) treating the cellulosic material at a consistency of about 9%–17% in a fifth stage with chlorine dioxide at not greater than pH 5.5 for not in excess of 300 minutes to oxidize remaining ligneous and color-forming impurities without material degradation of the cellulose, water washing the cellulosic material, and recovering superbleached pulp having a G.E. brightness in excess of 90, improved color stability and high strength characteristics substantially unchanged from those of the unbleached cellulosic material.

2. The process of claim 1 in which 0.5–2.5 weight percent based on the dry weight of pulp of an alkaline hypochlorite is added in the fourth stage caustic extraction.

3. A staged process for the production of superbleached cellulosic material having a brightness in excess of about 91 and of high strength characteristics which comprises, in the sequence specified, (A) treating an aqueous suspension of unbleached cellulosic material containing a substantial amount of ligneous and noncellulosic color-forming impurities at a consistency of about 2–4% in a first stage with elemental chlorine at pH 1.5–6 for 30–90 minutes to chlorinate a major portion of said impurities, then separating the cellulosic material from the liquor and water washing, (B) treating the cellulosic material at a consistency of about 12–17% and temperature of about 90–110° F. with sodium hypochlorite in a second stage at pH 9–10.5 for 30–240 minutes to oxidize a portion of the residual ligneous and color-forming impurities to brighten the pulp without material degradation of the cellulose, separating the cellulosic material from the liquor and water washing, (C) treating the cellulosic material at a consistency of about 12–17% in a third stage with chlorine dioxide at pH 2–5.5 for 60–240 minutes to oxidize an additional portion of said residual impurities without material degradation of the cellulose, then separating the cellulosic material from the liquor and water washing, (D) then adding dilute caustic soda solution to an aqueous suspension of the cellulosic material at a consistency of about 12–17% in a fourth stage to provide about 1% of caustic soda based on dry weight of cellulosic material to an alkaline pH above pH 11, maintaining the resulting mixture at about 130–175° F. for 45–75 minutes, then separating the cellulosic material from the liquor and water washing to remove substantially all caustic soda and impurities from the bodies of the cellulosic fibers, (E) treating the cellulosic material at a consistency of about 12–17% in a fifth stage with chlorine dioxide at pH 2–5.5 for 60–300 minutes to oxidize remaining ligneous and color-forming impurities without material degradation of the cellulose, separating the cellulosic material from the liquor and water washing, and recovering superbleached pulp having a minimum G.E. brightness of 91, improved color stability and high strength characteristics substantially unchanged from those of the unbleached cellulosic material, the process sequence of steps being completed within a period not in excess of 24 hours.

4. The process of claim 3 in which the cellulosic material is chemical wood pulp.

5. The process of claim 3 in which the cellulosic material is soda pulp.

6. The process of claim 3 in which the cellulosic material is kraft pulp.

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