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PRODUCTION OF WOOD PULPS INCLUDING TREATMENT OF CELLULOSIC FIBERS WITH BISULFITE ION FOLLOWED BY ALKALI METAL BOROHYDRIDE

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This application is a continuation-in-part of co-pending U.S. patent application Serial No. 263,424, filed March 7, 1963, by the present inventors and assigned to the assignee of record and now abandoned.

This invention relates to the production of cellulosic pulps, and particularly to the production of cellulosic pulps having an initially high brightness and the ability to be bleached to a higher final brightness.

Cellulosic pulps, particularly wood fibers used in the manufacture of paper, paperboard and the like, are commonly bleached or brightened with any of a variety of agents, notably peroxygen chemicals such as hydrogen peroxide or sodium peroxide, or with chlorine chemicals such as hypochlorites. Useful processes employing agents from each of these classes have been developed which meet many of the needs of processors. The great volume of materials to be bleached, and the critical demands of end users such as paper makers, however, has necessitated continuing research to develop additional agents for bleaching the fibers.

An important consideration has been the desire to provide bleaching agents applicable in a variety of bleaching operations, for example in bleaching wood fibers which are introduced into the operation in any condition from oriented, that is, aligned, form as wood chips or the like through pulps in which the fibers are randomly associated or disoriented.

An example of an area which has long been under investigation is the sulfite pulping process. This is a chemical pulping process in which wood chips are treated with aqueous solutions containing bisulfite ions and free SO_2 for the production of cellulose fibers useful in paper making. Pulp produced by this process has a good initial brightness and can be bleached to a higher brightness level with the usual bleaching agents, for example hydrogen peroxide, hypochlorites and the like, following its preparation. The sulfite process has a serious drawback, however. The yield of pulp produced by this process is usually low, being only on the order of 40 to 50% of usable pulp from a given quantity of wood.

Numerous variations of the sulfite process have been developed to increase this pulp yield. Typical variations are the chemi-mechanical processes such as the chip-groundwood, neutral sulfite and the like methods in which mechanical fiber-separation is employed along with the fiber-separating effect of the pulping liquor. These chemi-mechanical methods provide substantially increased yields, converting 50 to 90% of the wood to usable fibers. However, pulps produced by these partially-mechanical and partially-chemical methods have lower initial brightnesses than do pulps obtained with the sulfite chemical method and are difficult to bleach to acceptable final levels, even when sulfite liquors are used in their production.

It therefore has been desired to provide a process and agents therefor for increasing the brightness of unbleached

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or partially bleached cellulosic pulps by treatments suitable for use with wood fibers at varying stages of pulping, that is, at any point from wood chips to pulp.

It also has been desired to provide a process and agents therefor which produces cellulosic pulp from wood at an increased yield, and at the same time provides in such pulp a good initial brightness and the ability to be bleached readily to a higher eventual brightness.

It has now been found, quite surprisingly, that a cellulosic pulp having high initial brightness can be produced in a high yield and in a form in which it can be bleached to a higher eventual brightness, by impregnating cellulosic fibers which are in either oriented or disoriented form with an aqueous solution containing bisulfite ion and having a pH of about 2 to 7 to provide at least about 0.04% by weight of the bisulfite ion (about 0.05% expressed as the sodium bisulfite) on the fibers, contacting the bisulfite ion-impregnated fibers with about 0.01 to 0.5% by weight of the fibers of an alkali metal borohydride, and permitting the reagents to act on the fibers to increase their brightness.

In a preferred embodiment of this invention, the cellulosic fibers treated with the aqueous solution containing bisulfite ion are oriented in the form of wood chips, and the chips containing the bisulfite ion are introduced together with the alkali metal borohydride into a mechanical fiber-separating device where they are subdivided into fibers at a temperature of about 140-210° F.

The bisulfite ion is used in the amount of at least about four times the amount of borohydride, or about five times the amount of borohydride when the bisulfite is expressed as sodium bisulfite. Use of substantially more than that amount does not confer added advantages in bleaching, although it may be desirable for pulping, and accordingly no limitation is intended to be set on the maximum amount of bisulfite ion which may be used.

There would be no reason to expect use of the herein small amount of borohydride to effect the observed marked increase in brightness of the pulp. When the borohydride is employed in the herein amounts alone, either in a wood impregnation stage or as an additive to a pulp substantially no brightness increase is obtained. This is despite the fact that the typical borohydride, sodium borohydride, is known as a bleaching agent and likely is due to the small amount of the agent employed in the present operation. Furthermore, the non-borohydride impregnation liquors employed in the first step of the process of this invention do not achieve adequate brightening of the pulp without the addition of the borohydride.

An additional point is that although it may be theorized that sodium borohydride and bisulfite react to form the bleaching agent sodium hydrosulfite, direct introduction of sodium hydrosulfite as a bleach requires, for satisfactory bleaching, much more of this chemical than would be formed by reaction of the herein sodium borohydride and bisulfite.

The bleaching liquors employed in the first step of this process have a concentration of bisulfite ion of from about 0.25% by weight to the maximum amount soluble in the impregnation liquor. It is important only that the bisulfite ion be in solution in the liquor so that it may be absorbed properly by the fibers.

The bisulfite ion is introduced into the process as the alkali metal, the alkaline earth metal or ammonium bi-

sulfites, particularly the sodium, potassium, magnesium, calcium and ammonium bisulfites or as sulfur dioxide or sulfurous acid. The step one liquors preferably include substantial amounts of an alkali sulfite or other alkaline material along with the bisulfite ion in order to adjust the liquor pH to about 5 to 7, the preferred pH for the bisulfite liquors in the present process. The pH of these liquors in the absence of an alkaline additive normally is about 4.5 to 5 or less; with added alkali the pH is about 5 to 7. If the pH of the liquor as it is employed in the initial treatment is substantially above 7, the extent of brightening of the pulp by the second treatment with borohydride is reduced. Additional ingredients commonly used in sulfite liquors, such as sodium carbonate, sodium bicarbonate, sodium hydroxide, magnesium hydroxide and the like, may be incorporated in the bisulfite pulping liquor.

The alkali metal borohydride is a solid, and normally is introduced in the form of its aqueous solutions. It tends to decompose at a pH below about 7, and accordingly it is desirable for optimum stability to maintain the pH of the borohydride solution prior to use slightly alkaline by addition of inert alkaline materials such as sodium hydroxide, sodium carbonate and the like. The preferred alkali metal borohydrides for use herein are the sodium and potassium borohydrides.

The alkali metal borohydride is employed in the pulp in the amount of about 0.01 to 0.5 part by weight. Normally not more than about 1 part by weight of the borohydride is used for each four parts by weight of bisulfite ion, or 5 parts by weight of bisulfite when it is expressed as sodium bisulfite, retained by the wood chips. The bisulfite ion is present after the first treatment in the wood in the amount of at least about 0.04 to 2.0% by weight as the ion and of at least about 0.05 to 2.5% by weight as, for example, the sodium bisulfite, with more often being used to aid in pulping. Despite the frequent use of more than 2.5% of sodium bisulfite, for example in typical wood and pulp treatments, use of more than about 0.5 weight percent of borohydride is not necessary even with such large amounts of bisulfite and is wasteful, since excellent brightness levels are obtained with up to 0.5% of borohydride. As indicated above, this amount of 0.01% to 0.5% of borohydride in the absence of the bisulfite ion is ineffective to accomplish useful brightening of the pulp.

The present pulping method is applicable to essentially any of the woods which are employed to make wood pulps. Such woods preferably are the softwoods such as pines, spruces, firs, hemlocks and the like, although hardwoods such as the beeches, maples, oaks, birches and the like may be treated by the herein process. This process is particularly useful where it is desired for economy to retain substantially all of the wood, including the non-cellulosic lignin and other materials present in the wood, in the pulp since these non-cellulosic materials in the absence of the present treatment substantially darken the wood.

The borohydride may be added to the bisulfite-containing cellulosic fibers either before or after the fibers have been disoriented, that is, pulped. For example, the bisulfite ion may be introduced while the fibers are associated in the form of wood chips, and the borohydride suitably may be added either in the fiber-separation stage or after the wood has been subdivided into fibers. It is necessary only that the fibers being treated with the borohydride have bisulfite ion present on them. Thus the wood may be impregnated with bisulfite ion in a grinder and the fibers produced thereafter treated with borohydride, or the fibers resulting from other fiber-separating processes which provide a bisulfite ion-containing fiber product may be treated with borohydride. Alternatively the fibers may be pulped without bisulfite and the bisulfite ion added to preformed pulp; the borohydride may then be added to the pulp containing bisulfite ion.

A further useful application of the process is borohydride after-treatment of bleached fibers. Following a hydrogen peroxide bleach, for example, a metal bisulfite frequently is produced in-situ on the fibers by acidification with sulfurous acid, often introduced as sulfur dioxide. Addition of borohydride following this specification is effective in increasing the brightness level of the pulp.

In the preferred embodiment of this invention, the wood preferably is pulped after having been cut into chips to facilitate absorption of impregnation liquor. The chips are first impregnated with the pulping liquor, namely the bisulfite-containing liquor, and thereafter are drained and introduced into a fiber-separation device such as a disc refiner, a hammer mill, a rod mill or similar equipment. As they are introduced into the fiber-separation operation, the fibers are in aligned or oriented form in the wood chips. As they flow from the fiber separation equipment, the fibers are randomly associated as pulp.

The temperature employed in the fiber-separating device is about 140° to 210° F. It is neither necessary nor desirable to increase this temperature substantially above about 210° F., while operating below about 140° F. increases the time required for the operation. The chips preferably are fed to the fiber separating device at the usual refining densities of about 4% to 20% solids. After they are removed from the fiber separating device they may be treated for removal of water or may be processed further at the concentration at which they are obtained.

The temperature at which the herein process is carried out may be varied over wide limits, as is demonstrated in the examples which follow. As noted above, when the borohydride is added in the fiber-separation stage in a process which operates in wood chips, the temperature normally will be about 140° to 210° F. However, it is possible and even desirable for varying modes of operating, to carry out the process of this invention at temperatures ranging from about 60° to 240° F.

The following examples are presented only by way of illustration of various modes of carrying out the herein process, and are not intended to limit the scope of the present process in any way.

*Example 1.—Preferred embodiment of this invention—
Includes a comparative run with hydrosulfite*

Northern pine chips were impregnated with an aqueous solution containing 5% of sodium bisulfite and 10% of sodium sulfite on an oven dry wood basis and having a pH of 7, at a liquor to wood ratio of 5.2 to 1. The impregnation was carried out at 200 p.s.i.g. for 15 minutes at room temperature, and the pH of the residual liquor following impregnation was 6.7. The wood chips retained 2.6% of their weight of sodium bisulfite and 5.2% of sodium sulfite.

These chips were fed simultaneously with aqueous solutions as shown in the following table to a disc refiner at a pulp density of 5.0%. The temperature in the disc refiner was 160° to 210° F., and the pulp produced was retained at a temperature of 140° F. for one hour, after which the brightness values reported in Table 1 were determined.

TABLE 1

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1.....	No impregnant.....	0	55.5
2.....	Sodium Borohydride ²	0.05	59.2
3.....	do. ²	0.10	63.4
4.....	do. ²	0.20	63.7
5.....	Sodium Hydrosulfite ³	1.0	59.3

¹ Oven dry wood basis.

² Introduced as a 0.1% aqueous solution.

³ Equivalent to 0.22% of sodium borohydride reacted with 1.2% of sodium bisulfite.

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Example 2.—Process of Example 1 without bisulfite

The process of Example 1 was repeated with the exception that the impregnation liquor employed for the first treatment of the wood chips was water whose initial and final pH (after impregnation) was 6.7.

TABLE 2

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	49.3
2-----	Sodium Borohydride ² -----	0.20	51.5
3-----	do. ² -----	0.40	51.8

¹ Oven dry wood basis.² Introduced as a 0.1% aqueous solution.*Example 3.—Process of this invention*

Northern pine chips were impregnated with an aqueous solution containing 9.5% of sodium bisulfite and 19% of sodium sulfite (oven dry wood basis) at a liquor to wood ratio of 9.1 to 1. The pH of this impregnating solution before impregnation was 7.0 and following impregnation was 6.6. Impregnation was carried out at 150 p.s.i.g. for 20 minutes at room temperature. The chips absorbed 5.0% of their weight of sodium bisulfite and 6.5% of sodium sulfite.

Refining was carried out in a disc refiner with the pulp at a density of 5.0% on an oven dry basis, and at a temperature of 160° to 200° F. with addition of the solution referred to in Table 3.

TABLE 3

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	54.5
2-----	Sodium Borohydride ² -----	0.05	59.3

¹ Oven dry wood basis.² Introduced as a 0.1% aqueous solution.*Example 4.—Process of this invention—Followed by a post-bleach*

Mixed spruce-fir-hemlock chips were impregnated with an aqueous solution containing 9.2% of sodium bisulfite and having a pH of 4.5 at an impregnation liquor to wood ratio of 8 to 1, at 190 p.s.i.g. for 15 minutes at room temperature. The residual liquor removed from the impregnator had a pH of 4.9. The chips absorbed 2.8% of their weight of sodium bisulfite. The chips were then refined at a pulp density of 5.5% at a temperature of 160° to 200° F. in a disc refiner with simultaneous addition of the ingredients noted in Table 4.

TABLE 4

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	58.8
2-----	Sodium Borohydride ² -----	0.025	62.3
3-----	do. ² -----	0.050	64.2
4-----	do. ² -----	0.20	63.3
5-----	do. ² -----	1.0	62.5
6-----	Sodium Hydrosulfite ³ -----	1.0	60.6

¹ Oven dry wood basis.² Introduced as 0.1% aqueous solution.³ Equivalent to 0.22% of sodium borohydride reacted with 1.2% of sodium bisulfite.

The samples of this example were given a final bleach with hydrogen peroxide, employing a standard aqueous hydrogen peroxide solution containing 1.0% H₂O₂ (100%), 5.0% of sodium silicate 41° Bé. and 1.0% of sodium hydroxide (oven dry pulp basis). The bleach was carried out by impregnating the refined pulp at a pulp density of 12% and holding it at 140° F. for 3 hours. The results of this bleaching are shown in Table 5.

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TABLE 5

Sample No.	Pre-Bleaching Brightness	Post-Bleaching Brightness
1-----	58.8	70.2
2-----	62.3	72.6
3-----	64.2	72.7
4-----	63.3	74.5
5-----	62.5	73.8
6-----	60.6	71.8

Example 5.—Process of Example 4 without bisulfite

Wood chips similar to those treated in Example 4 were impregnated with water having a pH of 6.8 at a liquor to wood ratio of 8 to 1. Impregnation was carried out at 190 p.s.i.g. for 15 minutes at room temperature and following impregnation the residual water had a pH of 6.3.

The impregnated chips were then refined in a disc refiner at a density of 5.5% and a temperature of 160° to 200° F. The ingredient noted in following Table 6 was added as indicated.

TABLE 6

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	51.9
2-----	Sodium Borohydride ² -----	0.05	53.4

¹ Oven dry wood basis.² Introduced as a 0.1% aqueous solution.*Example 6.—Process of this invention—Spruce, fir and hemlock—Includes a comparative run with hydrosulfite*

Mixed spruce-fir-hemlock chips were impregnated with an aqueous solution containing 9.3% of sodium bisulfite and 18.6% sodium sulfite at a liquor to wood ratio of 8.2:1. The impregnation liquor had an initial pH of 7.0 and following impregnation the residual liquor had a pH of 6.8. The impregnation was carried out at 190 p.s.i.g. for 15 minutes at room temperature and the chips absorbed 2.25% of their weight of sodium bisulfite and 6.5% of sodium sulfite.

The impregnated chips were then treated in a disc refiner at a pulp density of 5.0% and a temperature of 160° to 200° F. with simultaneous addition of the agents noted in Table 7.

TABLE 7

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	55.6
2-----	Sodium Borohydride ² -----	0.05	65.4
3-----	Sodium Hydrosulfite ³ -----	1.0	61.3

¹ Oven dry wood basis.² Introduced as a 0.1% aqueous solution.³ Equivalent to 0.22% of sodium borohydride reacted with 1.2% of sodium bisulfite.*Example 7.—Process of Example 6 modified by adding the bisulfite and borohydride together during impregnation*

The process of the preceding example was modified by introducing the sodium borohydride during the impregnation of the wood chips with the sodium bisulfite-sodium sulfite impregnation liquor rather than during the refining stage. The impregnation and refining otherwise were carried out in the same fashion as described in the preceding example.

TABLE 8

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	55.6
2-----	Sodium Borohydride ² -----	0.05	54.5

¹ Oven dry wood basis.² Introduced as a 0.1% aqueous solution.

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Example 8.—Process of this invention—Western pine

Western pine chips were impregnated with an aqueous solution containing 7% of sodium bisulfite and 14% of sodium sulfite at a liquor to wood ratio of 7.6 to 1 and at 190 p.s.i.g. for 15 minutes at room temperature. The liquor pH before and after impregnation was 6.8. The chips absorbed 1.53% of sodium bisulfite and 2.8% of sodium sulfite.

The chips were then refined with simultaneous addition of ingredients as noted in Table 9 at a pulp density of 5.5% and a temperature of 160° to 200° F.

TABLE 9

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	58.6
2-----	Sodium Borohydride ² -----	0.05	63.3
3-----	do. ² -----	0.20	67.9

¹ Oven dry wood basis.

² Introduced as a 0.1% aqueous solution.

Example 9.—Process of this invention—Hardwood

A mixture of beech, birch, maple and oak chips (hardwoods) was impregnated with an aqueous solution containing 6.5% of sodium bisulfite and 13% of sodium sulfite (oven dry wood basis) at a liquor to wood ratio of 7:1 and at 150 p.s.i.g. for 15 minutes at room temperature. The pH of the impregnation liquor was 7 before impregnation and of the residual liquor after impregnation was 6.8. The chips absorbed 1.57% of sodium bisulfite and 2.7% of sodium sulfite.

The wood chips so impregnated were refined with the addition of added ingredients as noted in Table 10 at a pulp density of 5.5% and at a temperature of 160° to 200° F.

TABLE 10

Sample No.	Refiner Additive	Percent Additive ¹	GE Brightness
1-----	None-----	0	46.7
2-----	Sodium Borohydride ² -----	0.05	52.4
3-----	do. ² -----	0.20	56.6

¹ Oven dry wood basis.

² Introduced as a 0.1% aqueous solution.

Example 10.—Process of this invention—Bleaching of groundwood

Two hundred grams of mixed spruce-fir-hemlock groundwood pulp having an initial brightness of 59.8, was slurried in an aqueous solution of sodium bisulfite to provide a pulp slurry having a consistency of 6% pulp and 2% sodium bisulfite on an oven dry pulp basis. The pH of this slurry was 6.3 and the pulp resulting from the bisulfite addition had a brightness of 60.6%.

Fifty gram samples of the above pulp were treated by addition of the chemicals noted in Table 11, in the amounts indicated there, and diluted to a 3% oven dry pulp consistency. These samples were then held for one hour at 140° F. The brightnesses of the resulting pulps are shown in Table 11.

TABLE 11

Sample No.	Additive	Percent Additive ¹	pH	GE Brightness
1-----	NaBH ₄ ² -----	0.05	6.5	68.3
2-----	NaBH ₄ ² -----	0.22	7.0	69.1
3-----	Na ₂ S ₂ O ₄ ³ -----	1.0	5.9	68.3

¹ Oven dry pulp basis.

² Introduced in 200 ml of aqueous solution containing the amount of borohydride required and sufficient sodium hydroxide to adjust the pH to 9.5.

³ Equivalent to 0.22% sodium borohydride reacted with 1.2% of sodium bisulfite. 0.5% sodium triphosphosphate (oven dry pulp basis) was applied with the Na₂S₂O₄.

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Example 11.—Process of this invention—Sulfur dioxide treatment of peroxide-bleached pulp followed by borohydride

Four hundred grams of mixed spruce-fir-hemlock groundwood pulp from the same source as that treated in Example 10 was bleached with a hydrogen peroxide bleach formulation in an aqueous slurry having a 12% oven dry pulp consistency. The bleach formulation comprised 2% of 50% hydrogen peroxide, 5% of sodium silicate (41° Bé.) and 1% of sodium hydroxide. The pulp was treated with these chemicals for 3 hours at 120° F.; the initial pH of the bleaching slurry was 10.2 and its final pH was 8.3 to 9. The pulp then was treated with sulfur dioxide to provide a pH of 5.5. The brightness of the pulp so treated was 71.4%.

This product was divided into eight samples, each containing 50 g. of pulp. Tests 1 through 4 in Table 12 which follows were conducted by providing 3% oven dry basis aqueous slurries of the pulp containing the chemicals indicated in the table and holding the slurries for one hour at room temperature (65° F.). Test 5 through 8 were the same except that the temperature at which the pulp was held for the hour period was 140° F. The sodium hydrosulfite and sodium borohydride additives were introduced in the same fashion as shown in the footnotes to Table 11 above. Brightnesses of the resulting pulp samples are shown in Table 12.

TABLE 12

Sample No.	Additive	Percent Additive ¹	pH	GE Brightness
1-----	NaBH ₄ -----	0.025	6.0	72.8
2-----	NaBH ₄ -----	0.05	6.4	73.6
3-----	NaBH ₄ -----	0.22	6.9	73.8
4-----	Na ₂ S ₂ O ₄ -----	1.0	5.8	73.7
5-----	NaBH ₄ -----	0.025	6.4	72.6
6-----	NaBH ₄ -----	0.05	6.6	73.8
7-----	NaBH ₄ -----	0.22	7.4	75.1
8-----	Na ₂ S ₂ O ₄ -----	1.0	6.1	74.4

Example 12.—Process of this invention—Cold steep bleaching of groundwood pulp

Groundwood pulp pads each containing 25 g. of pulp on an oven dry basis, were formed on a 25 centimeter diameter Büchner funnel. The pulp was from the same source as the spruce-fir-hemlock groundwood employed in Examples 10 and 11, and had a brightness before treatment of 59.8.

The additives referred to in Table 13A which follows were applied by spraying from aqueous solutions, the solutions being those referred to in the footnotes to Table 11. Where sodium bisulfite and sodium borohydride both were applied to the pad, the bisulfite was sprayed on first and the borohydride followed. After the bleached chemicals had been applied to the pads the pads were broken up and stored at 65° F. in sealed containers. The consistency of these pulps was 25% on an oven dry basis. Brightness determinations were made on the stored, treated pulp at intervals over a period of 11 days; the results are shown in Table 13B.

TABLE 13A

Sample	Percent Additive Applied		
	NaHSO ₃	Na ₂ S ₂ O ₄	NaBH ₄
1-----	2.0	-----	0.025
2-----	2.0	-----	0.050
3-----	2.0	-----	0.220
4-----	-----	-----	0.220
5-----	-----	1.0	-----

TABLE 13B

Sample	GE Brightness (Days)					
	pH	1	4	7	pH	11
1-----	6.3	67.3	67.4	68.7	6.0	68.9
2-----	6.4	68.1	69.1	69.0	5.8	69.2
3-----	6.8	67.1	68.3	69.5	6.4	67.7
4-----	8.2	65.4	65.2	64.5	7.8	62.7
5-----	6.4	66.5	67.4	68.0	6.0	68.0

Example 13.—Process of this invention—Cold steep bleaching of semi-bleached sulfite

The procedure of Example 12 was followed with the exception that the pulp treated was a northern semi-bleached softwood sulfite which had been bleached prior to receipt by an outside source. The method employed for the bleach was a typical single stage hypochlorite treatment. The brightness of this pulp was 80.7% prior to the following treatment. The additive chemicals were introduced from solutions of the kind identified in the footnotes to Table 11 above.

The resulting pulps were broken up as described in Example 12 and held in sealed containers at room temperature, in this case for 7 days.

TABLE 14A

Test	Percent Additive Applied		
	NaHSO ₃	Na ₂ S ₂ O ₄	NaBH ₄
1-----	2.0		
2-----	2.0	1.0	
3-----	2.0		0.025
4-----	2.0		0.050
5-----	2.0		0.220
6-----		1.0	

TABLE 14B

Test	GE Brightness						
	1 Day	pH	2 Days	pH	3 Days	4 Days	7 Days
1-----	83.6	5.0	84.8	4-5	84.3	84.0	83.1
2-----	84.1	5.0	84.5	4-5	85.5	85.1	85.3
3-----	85.1	5.0	85.2	4-5	85.3	85.8	84.8
4-----	84.8	5.0	85.7	4-5	86.4	85.6	85.6
5-----	86.3	5.0	86.5	4-5	87.3	86.4	86.7
6-----	84.6	5.0	84.8	4-5	85.0	85.1	84.1

Example 14.—Process of this invention—Dryer steep bleaching of chemical pulps

The procedure of Example 12 was followed for the preparation of pulp pads from a northern semi-bleached softwood pulp prepared as was the pulp of Example 13 to provide a GE brightness of 80.7%. In this case the pulp pads were provided at a pulp density of 35-40% on an oven dry basis. After application of the chemicals to these pads, they were suspended in an oven, in this case at 110° C., and held at this temperature for approximately 30 minutes. This treatment dried the pulp pads to an oven dry consistency of 75-90%. Brightness and pH determinations of the pulp were made immediately after this so-called dryer steep treatment, and the pulps were permitted to stand at room temperature for 7 days. Brightness readings were made during this 7-day period. Chemicals were added as described in the footnotes to Table 11 above.

TABLE 15A

Test	Percent Additives Applied		
	NaHSO ₃	Na ₂ S ₂ O ₄	NaBH ₄
1-----	2.0		
2-----	2.0	1.0	
3-----	2.0		.025
4-----	2.0		.050
5-----	2.0		.220
6-----		1.0	

TABLE 15B

Test	GE Brightness					
	30 min.	pH	1 Day	pH	2 Days	5 Days
1-----	83.1	4.5	83.6	4.0	83.7	82.6
2-----	84.2	4.5	85.1	4.0	85.3	84.5
3-----	84.4	4.5	84.7	4.0	85.4	84.8
4-----	84.7	4.5	84.9	4.0	85.9	85.6
5-----	84.9	4.5	84.6	4.0	86.2	85.3
6-----	84.6	4.5	85.0	5.0	85.4	85.1

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

We claim:

1. Method of producing cellulosic pulps having high brightness, comprising impregnating cellulosic fibers with an aqueous solution containing bisulfite ion and having a pH of 2 to 7 to provide at least about 0.04% of said

bisulfite ion on the fibers, contacting the resulting bisulfite ion-impregnated fibers containing said at least about 0.04% of bisulfite ion with 0.01 to 0.5% of the weight of the fibers of an alkali metal borohydride, and permitting the reagents to act on the fibers to increase their brightness.

2. Process of claim 1 in which the aqueous bisulfite ion-containing solution for impregnating the cellulosic fibers contains sodium bisulfite and sodium sulfite, the pH of the aqueous pulping solution is 5 to 7 and the alkali metal borohydride employed is sodium borohydride.

3. Method of producing a wood pulp having a high brightness, in which wood chips are impregnated with an aqueous pulping liquor containing bisulfite ion and having a pH of 2 to 7 to provide in said wood chips on the weight thereof at least about 0.04% by weight of said bisulfite ion, feeding the resulting impregnated wood chips containing said at least about 0.04% of bisul-

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fite ion into a fiber-separating device along with an alkali metal borohydride in an amount to provide 0.01 to 0.5% by weight of said borohydride in said wood chips, separating said wood chips into pulp fibers in said fiber-separating device at a temperature of 140° to 210° F. and recovering the resulting pulped fibers from the fiber-separating device.

4. Method of claim 3 in which the aqueous bisulfite-containing solution for impregnating the wood chips contains sodium bisulfite and sodium sulfite, the pH of the aqueous pulping solution is 5 to 7 and the alkali metal borohydride employed is sodium borohydride.

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