Patented Feb. 26, 1952 2,587,064

UNITED STATES PATENT OFFICE

2,587,064

METHOD OF BLEACHING WOOD PULP

William Howard Rapson, Hawkesbury, Ontario, Canada, assignor to Canadian International Paper Company, Montreal, Quebec, Canada, a corporation of Canada

No Drawing. Application March 9, 1949, Serial No. 80,560

3 Claims. (Cl. 8—105)

This invention relates to new and useful improvements in bleaching processes generally, and particularly seeks to provide a novel process for the bleaching of chemical woodpulp to a very high brightness and whiteness through the use of chlorine dioxide and a hypochlorite.

Many efforts have been made in the past to develop processes for the bleaching of woodpulp which would result in a pulp of high brightness and whiteness. Thus bleaching systems having a single stage, two stages or multiple stages have been tried, and these several general types of bleaching systems have used many different bleaching chemicals or combinations of them. Probably the most satisfactory of the prior known bleaching systems may be described as a multistage system in which the pulp is exposed to the action of chlorine or a hypochlorite in one or more stages, followed by a caustic extraction stage in which the soda solubles are removed, finally followed by one or more bleaching stages using a hypochlorite as the bleaching chemical. Even under such a modern system the brightness of a fully bleached sulphite pulp seldom exceeds 90% as measured on the G. E. brightness meter without undue degradation of the pulp, and the brightness of a kraft (sulphate) pulp is usually considerably less.

It is well known that chlorine dioxide under suitable conditions will bleach pulp without appreciable degradation of the cellulose. It is also known that a solution containing a hypochlorite of an alkali or an alkaline earth metal will bleach the same pulp to higher brightness and whiteness than is obtainable with chlorine dioxide alone, but at the same time hypochlorite will degrade the cellulose, lowering its viscosity, decreasing its alpha-cellulose content, and lowering the strength of paper made from such pulp.

I have found that when chemical pulps such as sulphite or kraft pulps are bleached first with chlorine dioxide and then with a small amount of a hypochlorite, the brightness, whiteness and color stability are higher than can be obtained with either bleaching agent alone or with hypochlorite followed by chlorine dioxide, and the degradation of the pulp is much less than that obtained when a hypochlorite is used to develop the maximum brightness it will produce. It is therefore an object of this invention to provide a novel process for the bleaching of chemical woodpulps in which the fully bleached pulps are of extremely high brightness and whiteness (i. e. low color).

Another object of this invention is to provide a novel process in which wood pulp is bleached by chlorine dioxide followed by a hypochlorite.

Another object of this invention is to provide a process of the character described in which wood pulp is bleached by chlorine dioxide, followed by a hypochlorite without an interstage washing.

Another object of this invention is to provide a process of the character described which is adaptable for use in bleach plants employing equipment which is not resistant to normally acid chlorine dioxide, by suitable adjustment of the pH through addition of alkali, without appreciable variation in the ultimate brightness, whiteness, color stability, or fibre strength of the pulp.

Another object of this invention is to provide a process of the character stated in which the bleaching stages can be operated on a predetermined and set routine in so far as retention times, temperatures and proportions of bleaching agents are concerned without regard to variations in viscosity and bleachability of the unbleached pulp and still produce pulp of the highest whiteness and brightness within the limits of a relatively narrow viscosity range.

In the preparation of chemical woodpulps to be used for regenerated cellulose or cellulose derivatives or as fillers for certain types of plastics such as the urea- or melamine-formaldehydes, close attention must be paid to the final viscosity of the pulp as it is an indication of how much the pulp has become degraded. Generally speaking, it is desirable to produce a high white pulp having a relatively high viscosity since a relatively high viscosity indicates that there has been a minimum of degradation of the pulp. It is also important that the pulp retain its high whiteness and not become yellow with age or exposure to high temperatures. These objectives can be readily met with the proper practice of the present invention.

Other workers in the art of pulp bleaching have tried various combinations of bleaching chemicals such as chlorine dioxide alone, a hypochlorite alone, or a hypochlorite followed by chlorine dioxide or even a mixture of chlorine dioxide and a hypochlorite. Certain of these earlier efforts have met with considerable success, but none of them were able to produce the novel results which can be consistently produced through the process described herein. I have for the first time created a compound bleaching stage in which chlorine dioxide is first used to treat the pulp and then a hypochlorite is used, preferably without washing the chlorine dioxide treated pulp. Surprisingly, I have found that the pulp so bleached is of a much higher brightness and whiteness than has heretofore been obtained by any other system of bleaching.

Another unusual feature of my process is the practicability of elimination of washing between the chlorine dioxide and hypochlorite phases of the bleaching, contrary to the usual practice in multi-stage bleaching, with no deleterious effects on the properties of the final pulp. This feature has many important advantages. There is a saving in capital equipment required for bleaching, such as washers, storage chests, thickening equipment, and conveyors. Operating costs with respect to heat, water, electricity and labor are lower, and the usual loss of small fibres in the washing stage is eliminated. I have found that not only does the elimination of this washing edge have no harmful effects, but on the contrary the reaction products formed when chlorine dioxide acts on pulp have a highly desired inhibiting effect on the degradation of the pulp normally caused by hypochlorite, without detracting from its bleaching activity. This feature of my process makes it possible to bleach some types of pulp, for example, those used with urea-formaldehyde or melamine-formaldehyde resins for very light colored plastics, with a fixed cycle of times, temperature and proportions of bleaching agents without regard to variations in viscosity and bleachability of the unbleached pulp, and still produce pulp of the highest brightness, whiteness and color stability, within the limits of a relatively narrow viscosity range.

I have also found the chlorine dioxide phase of my process can be practiced under either acid or alkaline conditions with similar beneficial results. Under acid conditions the bleaching reaction is slower, but less chlorine dioxide is required due to the elimination of its reaction with alkali, and also to the activation of any chlorite produced. As long as the pH is low (say pH3-5) the temperature can be raised to about 80° to 90° C. without appreciable degradation of the pulp, thereby shortening the time required. As the pH is raised, the rate of bleaching increases, but the loss of chlorine dioxide by reaction with alkali also increases. One advantage of operating at pH 8 to 9 is that bleaching temperature can be lowered, and the time of bleaching can be shortened, as will be more fully explained hereinbelow. Another advantage is that the corrosive action of the chlorine dioxide is greatly decreased so that less resistant materials can be used for the construction of bleaching equipment. This would enable my process to be employed in any multi-stage bleach plant which has equipment normally resistant to hypochlorite solutions.

Although the reactions taking place during chlorine dioxide bleaching are not fully understood, and my invention is not predicated upon any particular hypothesis, a possible interpretation of the phenomena involved in my compound bleaching process is offered.

When chlorine dioxide is mixed with pulp, it reacts with some of the colored contaminants, thereby bleaching them and at the same time being reduced to chlorite, without appreciably degrading cellulose. At low pH the chlorite is also an active bleaching agent, and therefore somewhat less chlorine dioxide is required to accomplish the same degree of bleaching, although the rate of reaction is slow and the temperature must be raised to speed up the bleaching. As the pH is increased by adding alkali, the bleaching activity of the chlorite ions is diminished, but the rate of reaction between the chlorine dioxide and contaminants is increased, and lower temperatures may be used. The amount of chlorine dioxide required increases, and the residual chlorite at the end of the bleaching increases. Also as the pH rises an increasing part of the chlorine dioxide reacts with alkali, equal portions being simultaneously oxidized to chlorate and reduce to chlorite, respectively, according to the following equation:

$$2ClO_2+2NaOH \rightarrow NaClO_3+NaClO_2+H_2O$$

As mentioned before there is a limit above which chlorine dioxide will not increase the brightness of a given sample of pulp, no matter how long the treatment is continued. Similarly, there is such a limit for hypochlorite, but in attempting to reach this limit with hypochlorite the cellulose is severely degraded. If, however, the pulp which has been bleached with chlorine dioxide is then bleached with a little hypochlorite, a higher level of brightness can be reached with relatively little degradation of the pulp. The same level of brightness is not obtained if chlorine dioxide is used after hypochlorite bleaching.

A possible explanation of this may be that chlorine dioxide bleaches some of the colored matter in the pulp, but has not sufficient oxidizing power to bleach certain colored substances present, but it does activate these substances so that they are readily bleached by the subsequent hypochlorite treatment.

While the hypochlorite does simultaneously degrade the cellulose to some extent, the small amount required to accomplish the additional bleaching action does not bring about severe degradation. Furthermore, when the hypochlorite is added without washing after the chlorine dioxide treatment, it reacts with the chlorite present to activate it in some manner, possibly by formation of chlorine dioxide in a "nascent" or reactive state, such that a further bleaching action ensues. At the same time the hypochlorite loses some of its cellulose-degrading power, thereby minimizing the drop in viscosity usually encountered when bleaching to high whiteness with hypochlorite.

For a more detailed knowledge of the manner in which my new process may be carried out reference is made to the several specific examples set forth hereinbelow. It should be clearly understood that these examples are given for illustrative purposes only and the values given therein should not be construed as limitations on the ways in which this invention may be carried out.

In the following examples of various methods of applying my bleaching process all oxidizing agents are expressed in terms of the equivalent amount of available chlorine as a percentage by weight on the bone-dry pulp. Other chemicals are expressed as percentage of the chemical by weight on the bone-dry pulp.

Viscosity is expressed in centipoises of a 1% cuprammonium solution of the pulp according to the TAPPI standard method T 206 m.

Brightness was determined by measuring the reflectance at 458 millimicrons wavelength on General Electric recording spectrophotometer, catalog number 5962004G19, serial number 727120, using a magnesium carbonate standard.

Example 1

Chlorinated and caustic extracted sulphite pulp was treated with 0.7% chlorine dioxide, at 12%

consistency, at 80° C., for 30 minutes. After washing, the pulp was treated with 0.44% soda bleach and 0.25% sodium hydroxide, at 6% consistency, at 60° C. for 6 hours. Pulp brightness was 97.4% and viscosity 22.7 centipoises.

Example 2

Chlorinated and caustic extracted sulphite pulp was treated with 0.7% chlorine dioxide, at 6% consistency, at 60° C., for 5 hours. Without washing, 0.33% sodium hydroxide and 0.44% sodium hypochlorite were mixed in, and heating was continued at 60° C., for 4 hours. Pulp brightness was 97.8% and viscosity 21.0 centipoises.

Example 3

Sulphite pulp which had been previously treated with chlorine in aqueous solution and extracted with hot aqueous alkali, was treated with 1.4% chlorine dioxide, at 6% consistency, at 45° C. Sodium hydroxide was added periodically to maintain the pH between 9 and 7. After 4 hours, 0.35% sodium hypochlorite and 0.15% sodium hydroxide were mixed in and heating was continued at 45° C., for 4 hours. The pulp brightness was 98.5% and viscosity was 28.5 centipoises.

Example 4

Chlorinated and caustic extracted sulphite pulp was treated with 1.4% chlorine dioxide, at 6% consistency, at 45° C., with 0.835% sodium carbonate added to maintain the pH in the range 9.4 to 7.9. After 4 hours, 0.35% sodium hypochlorite and 0.15% sodium hydroxide were mixed in, and the temperature was raised to 55° C. for 3 hours. The pulp brightness was 98.4 and viscosity 24.3 centipoises.

Example 5

Unbleached kraft paper pulp was chlorinated with 5.1% chlorine, at 3% consistency, at 20° C., for 1 hour, and washed. Then it was extracted with 2% sodium hydroxide at 15% consistency, at 60° C., for 1.5 hours, and washed. Next it was treated with 0.7% calcium hypochlorite, and 0.3% calcium hydroxide, at 6% consistency, at 45° C. for 3 hours. Finally it was treated with 2.1% chlorine dioxide, at 6% consistency at 45° C. After 2 hours the pH was raised to between 8 and 9 for 2 hours more. Without washing, 0.35% sodium hypochlorite and 0.15% sodium hydroxide were mixed in, and heating was continued at 45° C., for 3 hours. Pulp brightness was 90.0% and viscosity 30.3 centipoises.

Example 6

Unbleached kraft dissolving pulp was chlorinated, extracted with dilute caustic soda solution, and treated with 2.1% chlorine dioxide, at 6% consistency, at 45° C. The pH was raised to 9.0 by adding sodium bydroxide solution after ½, 2 and 4 hours. After 4 hours, without washing, 0.7% sodium hypochlorite and 0.3% sodium hydroxide, were mixed in, and the temperature was raised to 60° C., for 3 hours. Pulp brightness was 94.6% and viscosity 7.8 centipoises.

The foregoing examples illustrate many of the possible ways in which my process may be practiced with perfectly satisfactory commercial results.

Example 1 is illustrative of the relatively high density bleaching of sulphite pulp which had been cooked and pre-bleached (chlorination and caustic extraction) to produce a relatively high viscosity pulp. In this example the reaction of chlorine dioxide on the pulp was carried out under acid conditions and the pulp was washed before treating with hypochlorite.

It will be noted that Example 2 is generally similar to Example 1 but the pulp was bleached at a lower consistency and the example shows a somewhat lower temperature in the chlorine dioxide phase of the compound final bleaching stage. Furthermore, the hypochlorite treatment followed the chlorine dioxide treatment without interstage washing.

Example 3 is illustrative of the treatment of a moderate consistency, high viscosity sulphite pulp under alkaline conditions which are necessary where less resistant bleaching equipment is used. It will be noted that in this example sodium hydroxide is used to maintain the pH between 9 and 7.

Example 4 is similar to Example 3 but shows the use of sodium carbonate to maintain the pH in the desired range.

Example 5 is illustrative of how this process can be applied to kraft paper pulp to produce extremely high brightness for that type of pulp without substantial degradation.

Example 6 clearly illustrates how my process can be applied to a kraft pulp that has been expressly cooked and pre-bleached (chlorination and caustic extraction) to produce a low viscosity dissolving pulp to which my process can be applied in the final compound bleaching stage to produce a dissolving pulp of extremely high brightness.

In all the foregoing examples it should be remembered that the final viscosity of the fully bleached pulp is primarily dependent on the nature of the cooking and the pre-bleaching steps up to and including the caustic extraction stage. My process is particularly applicable in the cases where it is desired to minimize viscosity reduction in the final bleaching operations by comparison with the reductions normally effected by prior known processes and yet produce a pulp of superior brightness.

Another advantage which is derived through the use of my process comes from the production of a finally bleached pulp which is resistant to degradation which may be caused by the application of heat. Many of the pulps heretofore produced while having a relatively high brightness and acceptable viscosity have not been heat stable in nature.

To illustrate the effect of my bleaching process on the heat stability of the pulp the results of another series of experiments on partly bleached sulphite pulp are presented hereinbelow. In these experiments an attempt was made to reach the highest possible brightness with sodium hypochlorite alone, and with chlorine dioxide alone, and then with chlorine dioxide followed without washing by hypochlorite. After measuring brightness in the usual manner the samples were pressed between hot plates at 149° C., at 200 lbs. per sq. in., for 2 minutes, and the brightness was measured again. As the amount of sodium hypochlorite used alone increased, the brightness after heating decreased, showing decreased resistance to degradation. With chlorine dioxide alone the level of brightness after heating was higher, and increased as the amount of chlorine dioxide increased, showing increased stability. When the chlorine dioxide was followed without washing by a small amount of sodium hypochlorite, the level of brightness after heating was still higher, showing still higher stability.

Percent Sodium Hypochlorite	Percent Chlorine Dioxide	Percent Sodium Hypochlorite after Chlorine Dioxide	Percent Brightness	Percent Brighness After Heating	Viscosity Centipoises
1.05	0	0	97.0	84.7	16.2
1.40	0	0	97.4	82.3	11.9
1.75	0	0	97.6	82.2	11.3
2.10	0	0	97.8	80.3	10.3
2.45	0	0	97.6	77.8	10.3
0	0.70	0	94.4	86.3	35.0
0	1.05	0	95.3	87.5	32.8
0	1.40	0	96.3	87.1	31.6
0	1.75	0	96.5	87.9	31.4
0	2.10	0	96.5	88.1	31.7
0	1.05	0.35	97.4	89.6	23.0
0	1.40	0.35	97.8	89.6	21.2
0	1.75	0.35	97.6	88.7	21.6
0	1.40	0.09	97.1	88.2	31.2
0	1.40	0.18	97.4	88.7	28.0
0	1.40	0.35	98.1	89.6	24.5
0	1.40	0.53	98.7	88.5	21.8
0	1.40	0.70	98.5	88.7	19.3

It will be apparent from a perusal of the above table that pulps bleached in accordance with my process are not only of higher initial brightness than those produced by other processes, but the brightness after heating is substantially higher than that of the other pulps. This clearly indicates that pulps produced in accordance with my process are heat stable and that subsequent processing steps in converting operations involving heat will not result in any abnormal decrease in brightness of the finished product.

Such a high degree of heat stability is particularly desirable, since in order to put the pulp in suitable physical form for shipment and for further processing it must be made into sheet form and dried, usually over a series of steam-heated dryers. Furthermore, in some applications as when used as a acomponent of plastics, pulp is subjected to high temperatures during molding. Pulp bleached in accordance with my process undergoes materially less degradation in such processes than other pulps which have been been heretofore known, resulting in products of better color and appearance.

A further analysis of the above table will indicate that where the final bleaching of the pulp was effected by sodium hypochlorite alone the brightness was at high values, but the viscosity of the pulp had dropped to very low levels by comparison with the viscosities obtained through the practice of my process. Where chlorine dioxide alone was used for the final bleaching the viscosities of the samples stayed at quite high levels but the final brightness was not sufficiently high. However, when the chlorine dioxide was followed by a small amount of sodium hypochlorite in the final bleaching operations the brightness of the pulp samples was higher than the brightness obtained with sodium hypochlorite alone but the decrease in viscosity was not nearly as great as that when sodium hypochlorite alone was used. Thus my process is particularly adaptable to the production of high brightness pulp with relatively close control over the viscosity of the fully bleached pulp, and as mentioned above, the brighness of the pulp samples after heating when bleached by my process is considerably higher than the brightness of samples bleached by either sodium hypochlorite alone or by chlorine dioxide alone.

To my knowledge, pulps having the high levels of brightness, viscosity and heat stability which are regularly obtainable by the practice of my invention have not been made heretofore, and this general type of pulp constitutes a new product. A pulp with a brightness of at least 97.5, whose brightness after heating between hot plates at 149° C. at 200 lbs. per sq. in. pressure for 2 minutes is at least 87.5, and with a TAPPI viscosity of at least 15 would be such a product.

This new product can be used in ways in which it was not possible to use pulp successfully heretofore, for example in the manufacture of pulp-filled plastics with very light color.

I claim:

1. A process for completing the bleaching of partially bleached chemical wood pulp comprising the steps of adding chlorine dioxide to an aqueous suspension of said pulp, maintaining the pH at a numerical value greater than 7, and after substantially exhausing the chlorine dioxide as an active bleachant in the resulting suspension adding to said pulp a quantity of an alkaline hypochlorite and an alkaline hydroxide whereby to produce without substantial degradation a bleached pulp having a brightness of at least 90 and suitable for conversion into cellulose derivatives.

2. A process for completing the bleaching of partially bleached chemical wood pulp comprising the steps of adding chlorine dioxide to an aqueous suspension of said pulp, maintaining the pH within the range of 7 to 10, and after substantially exhausting the chlorine dioxide as an active bleachant in the resulting suspension adding to said pulp a quantity of an alkaline hypochlorite and an alkaline hydroxide whereby to produce without substantial degradation a bleached pulp having a brightness of at least 90 and suitable for conversion into cellulose derivatives.

3. A process for completing the bleaching of partially bleached chemical wood pulp comprising the steps of adding chlorine dioxide to an aqueous suspension of said pulp, permitting said chlorine dioxide to act on said pulp for a substantial length of time, maintaining the pH within the range of 7 to 10 during such action, and after substantially exhausting the chlorine dioxide as an active bleachant in the resulting suspension adding to said pulp a quantity of an alkaline hypochlorite and an alkaline hydroxide whereby to produce without substanital degradation a bleached pulp having a brightness in the range of 90 to 98.7 and suitable for conversion into cellulose derivatives.

WILLIAM HOWARD RAPSON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,580,136	Hamburger	Apr. 13, 1926
2,120,678	Parsons	June 14, 1938
2,129,719	Vincent	Sept. 13, 1938
2,166,330	Vincent	July 18, 1939
2,235,837	Logan	Mar. 25, 1941
2,377,171	Murdock et al.	May 29, 1945
2,494,542	Casciani	Jan. 17, 1950
2,502,410	Cederquist	Apr. 4, 1950

FOREIGN PATENTS

Number	Country	Date
446,444	Belgium	Aug. 31, 1942

OTHER REFERENCES

Taylor et al., "Use of Sodium Chlorite in Bleaching," Technical Association Papers, 1940, pages 251 to 256.