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METHOD OF BLEACHING PULP

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This invention relates to a process of bleaching ligneous cellulosic materials, and more particularly to a process that is especially adapted to obtain an improved color or brightness of more lasting permanence without deleteriously affecting the strength of the cellulosic material.

In the bleaching of naturally occurring cellulosic materials the primary object is to remove color-imparting non-cellulosic impurities from the cellulose, or modify them so as to be permanently colorless, without attacking or harming the cellulose. This is generally done by treating the cellulosic materials with chlorine, active chlorine-containing compounds, certain oxidizing agents, etc.; some of the more conventional prior art methods will be described hereinafter.

The nature and efficiency of such bleaching processes can be considered primarily in relation to their effect on the properties of the final cellulose product made from the bleached naturally occurring cellulosic material, particularly the strength of the cellulose product, the color of brightness thereof, and the permanence of the color. These three factors will be considered in the order mentioned.

The attack of a bleaching agent on the cellulose results in a depolymerization thereof and a weakening of the strength of the cellulosic fiber. This has commonly been measured in terms of the strength of the resulting cellulose product and common tests in the paper industry include bursting strength (Mullen test), tearing strength (Elmendorf test) and tensile strength (Schopper test). We prefer, however, to express any attack on the cellulose in terms of depolymerization as measured by viscosity of a standard dispersion of the cellulose. A correlation exists between such a viscosity test and the strength properties of the fiber as reflected in the finished cellulose product. In general there can be a material lowering of viscosity indicating some attack on the cellulose before the effect is demonstrable by means of strength tests such as referred to. Thus by viscosity measurements it is possible to ascertain the extent of the early attacks of a bleaching operation upon cellulose when it would not be possible to detect this in the final product. Measurement of viscosity as a determination of the depolymerization of cellulose is a satisfactory test provided it is kept in mind that there is a critical viscosity, above which it would not appear that reduction in viscosity would have much effect on the final product, but below which a reduction in viscosity produces more or less corresponding reductions in product strength. The

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process of the invention can be used so as to achieve a viscosity not substantially below this critical figure so as not to reduce the strength of the product undesirably.

The color of a cellulosic material, such as paper made from various pulps, can be determined by a procedure which is recognized as standard in the industry, namely, with a General Electric Reflectometer which measures brightness on a scale between 0 for minimum reflectance and 100 for maximum reflectance. Merely as illustrative, kraft pulp before bleaching has a color of about 20 to 30 and can be bleached to a color as high as about 70 to 75 by conventional practices with chlorine and hypochlorite without any material loss in the strength properties of the cellulose. When the brightness is to be increased to within the range of 80 to 85 it is exceedingly difficult to achieve this without a substantial loss in the strength properties of the cellulose material. As will be seen hereinafter it is possible, according to our invention, to obtain a brightness in the range of 85 to 90 without any significant attack on the cellulose.

The permanence of the color or brightness is a factor which has not been emphasized in evaluating prior art processes. For example, there have been many proposals to obtain a high degree of brightness in paper made from kraft pulp, such as around 80 to 85, but these measurements were made shortly after the bleaching operation and fail to take into account the fact that the cellulosic material upon ageing for some months does not retain this brightness, but rather reverts to a darker, yellower color, depending upon the particular character of the pulp and manner of the treatment. Furthermore, this neglect of the factor of permanence of color may be attributed, at least in part, to the fact that it takes considerable time to run ageing tests under ordinary ageing conditions, and standard tests under accelerated conditions have not been set up by the industry.

It is not difficult to obtain a good permanence at a low brightness, but it has always been hard to obtain good permanence at high brightness. Heretofore, for example, it has been necessary to use caustic soda extraction at a high temperature for fairly satisfactory permanence at high brightness. This requires an extra stage in the process as well as the steam for heating and the caustic.

In accordance with our invention it is not only possible to obtain a higher initial brightness, but also a substantially higher permanence of this

brightness when the cellulose products are subjected to ordinary ageing tests as well as accelerated ageing conditions, than heretofore, and to obtain this without an extra stage or high expense such as in caustic extraction.

In the conventional process of bleaching cellulosic materials the bleaching agents more commonly used are chlorine and hypochlorite. Many of such bleaching processes are based upon the purification of the cellulosic material by the removal of ligneous or other non-cellulosic materials before a final bleaching with a hypochlorite, generally calcium hypochlorite. Such processes usually involve one or more treatments with elemental chlorine which acts primarily to modify the non-cellulosic materials or impurities which are more readily attacked by the chlorine than the cellulose under the conditions used. A substantial amount of the impurities can be removed in this way with consequent improvement in color without unduly attacking or weakening the cellulose. After the chlorine treatment or treatments the impurities are washed out with water or more frequently with an alkaline solution in view of the more ready solubility of modified impurities in alkaline solution, such as one of caustic or lime. In some cases the alkaline material is added while there is still a substantial amount of chlorine so as to form a hypochlorite by reaction of the alkaline material and the chlorine. This formation of a hypochlorite in situ is generally carried out under conditions so that the bleaching is not sufficiently harsh to attack the cellulose. The art has developed many combinations of the steps of treating with chlorine, extracting with alkaline materials, the formation of a hypochlorite in situ, preliminary partial bleaching with hypochlorite, washing, etc. After these steps, the final bleach is obtained with a hypochlorite, and in all of these processes the last operation is a bleach with hypochlorite of such strength as to exert a pronounced final bleaching action.

While hypochlorite is a good bleaching agent and satisfactory brightness can be obtained if enough is used, it has the undesirable property of attacking cellulose with the result that it is weakened. This is particularly significant in paper making processes when the pulp is bleached with hypochlorite, because the paper made from the pulp is of poorer strength. Many efforts have been made to minimize this attack, but the oxidizing action of the hypochlorite appears to be so vigorous that it cannot effectively attack the residual impurities to the extent required for bleaching without attacking the cellulose itself. While calcium hypochlorite may be used with care under conditions which achieve a reduction in impurities in the preliminary purifying process, it has not been possible to use it as the sole bleach so as, for example, to obtain papers of high brightness without undesirable attack on the cellulose and, therefore, a loss of strength in the paper product.

Because of these considerations, the art contains many proposals, most of which are aimed at processes that are less harmful on the pulp than hypochlorite. Another proposal is to purify the pulp so completely that it is possible to use something other than hypochlorite as the final bleach.

One such bleaching material that has been proposed for use on the cellulose materials is chlorine dioxide (ClO_2). This bleach does not attack

the cellulose to as great an extent as does calcium hypochlorite, and while it can be used to produce cellulosic materials of a high brightness, this color is not permanent. Cellulosic materials which have been bleached by chlorine dioxide will revert to a darker or less bright color upon ageing. This disadvantage is a material limitation on the use of chlorine dioxide and renders it unsatisfactory for making high grade cellulosic products, such as paper of a high permanent brightness.

Another bleach that has been proposed is peroxide, such as hydrogen peroxide or sodium peroxide. This bleach is relatively satisfactory in some respects, particularly as compared with a hypochlorite. However, peroxide does attack the cellulose to an appreciable extent if high bleaching is obtained, although not as much as the hypochlorite. Another serious disadvantage of peroxide is the relatively high cost of an amount of peroxide to achieve satisfactory bleaching if it is used to replace hypochlorite entirely. This makes its use prohibitive in the required amounts.

With these considerations in mind the process of the invention, viewed in its broadest aspects, comprises three steps:

(1) Partial purification of the cellulosic material by means of known procedures involving the use of one or more purifying agents, such as chlorine, hypochlorous acid and alkali metal and alkaline earth hypochlorites, other oxidizing agents, together with various alkaline extractions and washing steps which may be practiced in various combinations to the extent of removing a major portion of the non-cellulosic impurities, but short of the point of materially affecting the strength of the cellulose product. This is viewed more as purification than bleaching.

(2) Bleaching the partially purified cellulosic material by means of chlorine dioxide in any form such as gaseous chlorine dioxide dissolved in water, chlorine dioxide solutions prepared from solutions of chlorites either by acidification or by introduction of hypochlorite ion, or any solution containing both chlorine dioxide and chlorous acid in varying proportions to obtain preferably at least 50% of the desired additional increase in brightness without undue attack on the cellulose to obtain a bleached material of impermanent color.

(3) Finally subjecting the bleached cellulosic material to the action of a peroxide such as hydrogen peroxide or compounds derived therefrom, for example, alkali and alkaline earth peroxides, or organic peracids or salts thereof such as sodium peracetate, and mixtures of the aforesaid compounds, without undue attack on the cellulose, to obtain the final bleached product of permanent color.

We are aware of the fact that each of the steps mentioned above in their broadest forms have been used in bleaching cellulosic materials and that there have been proposals to combine a large variety of bleaching steps in many ways. We are not aware, however, that the particular steps enumerated in the process have been used in the order mentioned under the conditions that are specified more fully to achieve the outstanding results to be described. As far as we are aware any other way of achieving the high degree brightness obtained in accordance with the invention also results either in less permanence of the color or less strength in the product, or both.

In considering our process it is emphasized that although we use chlorine dioxide to achieve

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a large portion of the bleaching, and this bleach ordinarily results in relative impermanence of color, nevertheless a marked permanence of color is obtained in accordance with the invention despite the fact that the amount of peroxide used in the process is markedly less than that which would give a corresponding brightness if the peroxide were used without a chlorine dioxide treatment in step 2. Furthermore, although peroxide ordinarily causes an attack on the cellulose when used to obtain a very high brightness, there is no substantial reduction in strength of the product when the peroxide is used in accordance with the process following a bleach with chlorine dioxide, and there is a higher degree of permanence than can otherwise be obtained. These two considerations are novel in the process as far as we are aware. They may warrant the conclusion that an amount of chlorine dioxide may be used under the proper conditions to achieve preferably at least 50% of the desired additional improvement in brightness so as to convert the residual impurities to forms which would revert to color bodies upon ageing; but which, nevertheless, can be readily further modified so as to be permanently colorless by peroxide treatment carried out under conditions and with an amount of peroxide to yield the desired final brightness without attacking the cellulose. There appears to be a peculiar or synergistic action which achieves a high color, permanence and strength that cannot be obtained with either agent alone or predicted from their known separate actions. Thus an unusually high degree of initial brightness is obtained in the product without the presence of impurities which would revert to color bodies upon ageing and without any substantial attack on the cellulose. These considerations will be apparent from the data given in the specific examples hereinafter, and are entirely novel and unobvious from the prior art in so far as we are aware.

The invention makes it economical and feasible to use peroxide in obtaining high brightness without an attack on the cellulose, and to make a pulp having all three requirements, namely, strength, brightness and permanence, in an economical and practical manner.

The process of the invention is peculiarly adapted for the bleaching of cellulosic fibers and materials that are derived from ligneous-containing materials by any of the processes that are generally practiced for fiber liberation. The invention finds special application in the bleaching of wood pulp, such as the chemical and semi-chemical pulps used in making paper, it being more particularly adapted for the treatment of pulp produced by the kraft (sulfate) process which is normally darker in color and requires more extensive bleaching. Although it may not be as economical, the invention may be applied to other cellulosic materials such as fibers and pulps derived otherwise from wood, flax, jute, etc. Economic, rather than operative considerations will control largely the cellulosic materials to which our process may be applied on a commercial scale.

Kraft pulp is one of the strongest and least expensive of the paper pulps. However, it is one of the most difficult to bleach to a high brightness which is permanent. Prior art drastic bleaching operations which achieve a good color materially reduce this strength of the paper and many of the extremes to which it has been necessary to go heretofore to achieve satisfactory

bleaching have a profound effect on cellulose with a resulting lowering of strength. If kraft pulp could be bleached so as to have a high permanent brightness with a high strength, the pulp would be an exceptionally fine paper making material. The process of the invention accomplishes this outstanding result.

Because of the great difficulty involved in bleaching kraft pulp to a high permanent brightness without affecting the strength of the cellulosic material and the paper made therefrom, the invention will be described hereinafter as applied to kraft pulp. It will be understood that in view of the excellent results obtained on such a pulp the process can be all the more readily applied for the treatment of other cellulosic materials which are easier to bleach.

In carrying out the invention on a preferred commercial scale the process will be generally applicable to existing installations in which the preliminary steps of treating with chlorine and/or hypochlorite, alkaline extractions, washing, etc., may be largely the same. These bleaching or purification operations will act on the color imparting impurities included in the cellulosic material. If they were carried to a point where maximum bleaching were obtained by means of them, the cellulose would be degenerated by their action. This bleaching or purification is carried on until there is a substantial modification of the color imparting impurities, but is not carried to the point where there is any substantial destructive activity on the cellulose. It is immaterial how this preliminary purification is carried out so long as there is a minimum of degradation of the cellulose. In the treatment of kraft pulp which has an initial brightness of about 20 to 30, the pulp may be partially purified by one or more stages of chlorine treatment, washing, alkaline extractions, mild hypochlorite treatment, etc. until the pulp has a brightness of about 60 to 78.

Following this the pulp is treated with chlorine dioxide in an amount to achieve preferably at least 50% of the desired additional increase in brightness. For example, if the partially purified pulp has a brightness of 70, and a final brightness of 85 is desired, the chlorine dioxide treatment preferably should achieve a brightness of between 77.5 and 85. The chlorine dioxide bleaching step is carried out under substantially neutral or under acidic conditions. It may be used in an aqueous solution formed by adding the chlorine dioxide gas to water, in which case the pH will normally be between 5 and 8. The gas may be added to the pulp or a solution of the gas may be added. Alternatively chlorite may be added, such as sodium chlorite ($NaClO_2$), or calcium chlorite ($Ca(ClO_2)_2$) to an acidic solution, chlorine dioxide thereby being released in situ, or a chlorite may be added to the acidified pulp. If a chlorite is used in this manner, a pH value of about 3 to 5 or slightly lower is preferred in order to generate the chlorine dioxide with ease. There is no point in using a lower pH than necessary because too much acid will cause corrosion of equipment and increases the chemical cost. If hypochlorite ion (added either as elemental chlorine or as a solution of a hypochlorite) is employed to generate chlorine dioxide in the chlorite solution, the pH will normally fall in the range of 5–8. A reference to the treatment with chlorine dioxide contemplates any of the above processes.

The treatment with peroxide is preferably carried out on the alkaline side, that is, at a pH

above 8, preferably above 9. This can be obtained by means of hydrogen peroxide added under the above stated alkaline conditions or by the addition of sodium peroxide which in itself generates the desired alkalinity. Still higher pH values can be used as long as there is no harm to the cellulose, but the cost of an increased amount of alkali more than offsets any advantage. The amount of the peroxide used can be exceedingly small and far less than that which would be required for a corresponding increase in brightness with the pulp not previously treated with chlorine dioxide so as to place it in the peculiar condition which renders it susceptible to action by the peroxide.

The temperature, length of treatment and other conditions in these treatments are those commonly prevailing in the treatment of pulp and these conditions are not critical, provided the above conditions are met. Additional agents conventionally used with peroxide can be employed if desired, such as buffering or stabilizing agents, but they are not essential to the operation of the process.

The following illustrative examples are included for the purpose of demonstrating the results that may be obtained in accordance with the invention:

Example I

(1) A sample of typical southern pine unbleached sulfate (kraft) pulp was employed as a starting material. The preliminary purification treatment is as follows: The pulp was treated with an amount of calcium hypochlorite to provide 4.9% of available chlorine, at a consistency of 3.5%, and at a temperature of 75° F. After treatment for 85 minutes, the residual chlorine was 0.12%. In this example and in the following examples, all of the percentage figures are based on the air-dry weight of the fibrous material. During the treatment the pH was maintained in the range of 8.8 to 10.6 by the addition of 0.9% of caustic soda. As a result of this treatment the brightness of the pulp was increased from 23.2 to 41.7 and the viscosity dropped from 73.9 to 60.9.

The brightness was measured with a General Electric Reflectometer using the No. 1 filter, and all brightness figures given hereinafter were similarly measured. The pulp handsheets, for all of the brightness tests in this example and in the following examples, were prepared in accordance with T. A. P. P. I. Standard Method T218M–45.

The viscosity determination was made by the cuprammonium procedure, according to T. A. P. P. I. Standard Method T206M–44. All references to viscosity hereinafter were similarly measured.

The pulp mixture was then acidified by the addition of 0.85% sulfuric acid to provide a pH of 6.0, following which 3.0% of chlorine gas was added over a period of 20 minutes. After treatment for an additional 25 minutes, the residual chlorine was 0.15% and the pH value 2.1. The pulp was then washed thoroughly with water. The brightness of the pulp was 42.1 and the viscosity was 47.8.

The pulp was then subjected to a second treatment with calcium hypochlorite in an amount to provide 1% available chlorine. The treatment was carried out at a temperature of 95° F. for 45 minutes with a consistency of 5%. A final pH of 8.9 was obtained by the initial addition of 0.6% caustic soda. At the end of the treatment the residual chlorine was 0.15%. The pulp was then thoroughly washed with water and found to have a brightness of 71.0 and a viscosity of 44.2. The average strength of the pulp was 1.89 as compared with 1.80 for the original untreated pulp, indicating the removal of undesirable impurities without such reduction in the viscosity as is reflected in a lowering of the strength of the cellulose. The average strength value was obtained by averaging the values of the bursting strength and the tearing resistance. Since these tests were the same for all samples they are comparative and need not be described in detail.

(2) The preliminary purified pulp described above was next treated with a solution of chlorine dioxide (prepared by absorbing chlorine dioxide gas in water) in an amount to furnish 0.70% available chlorine. The treatment was carried out with a consistency of 5% and at a temperature of 125° F. for a period of 3 hours. The pH range during the treatment was 6.2 to 6.7. At the end of the treatment the residual chlorine was 0.23%. The pulp was then thoroughly washed with water, the brightness was now 81.5 and the viscosity was 43.9.

(3) The partially bleached pulp was next treated with 0.12% of H_2O_2 at a consistency of 15%, and at a temperature of 150° F. An average pH value of 10.75 was obtained by the addition of 0.4% caustic soda. After treatment for 4 hours, the residual H_2O_2 was 0.022%, and the pulp was given a final thorough wash with water. The brightness of the pulp was 84.5, the viscosity was 42.4, and the average strength was 1.91.

The various pulps were tested for color stability by three tests; the results are tabulated hereinafter in the table. In the lamp test, pulp handsheets were exposed to ultraviolet light for 1 hour at a distance of 16 inches to the light from a General Electric 250-watt type H–5 mercury vapor lamp. In the heat test the handsheets which had been subjected to the lamp test were placed in an oven at 100° C. for 1 hour, and the additional loss in brightness was then determined. In the storage test the handsheets were stored in the dark at a temperature of 72° F. and at a relative humidity of 50% for a period of exactly 8 weeks and were then tested again for brightness.

Example II

(1) The pulp was prepared in the manner identical with that described under (1) in Example I.

(2) The pulp was next treated with a chlorine dioxide solution (prepared in situ by acidifying a solution of sodium chlorite to a pH value of 4.0), the amount of available chlorine furnished being 0.7%. The treatment was carried out with a consistency of 5%, for 2 hours, at a temperature of 150° F., after which the residual chlorine was 0.10%. The pulp was washed and found to have a brightness of 81.0 and a viscosity of 46.4.

(3) The pulp was next treated with 0.12% of H_2O_2 exactly as described under (3) of Example I, and after 4 hours treatment the residual H_2O_2 was 0.026%. After the pulp was washed the brightness was 86.4, the viscosity was 47.7, and the average strength value was 1.90. These samples were also tested for stability with the results given in the table hereinafter.

Example III

(1) The pulp was preliminarily purified in the same manner as described under (1) of Example I.

(2) The pulp was next treated in exactly the

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same manner as described in (2) in Example II.

(3) The pulp was next treated with H_2O_2 in an amount of 0.06%. Otherwise the conditions were the same as described under (3) of Example I. The residual H_2O_2 was 0.019% after 1 hour treatment, and the pulp was then washed. The brightness of the pulp was 82.0, and the viscosity was 49.4.

In all of the above three examples the particular sequence of treatments in the first step of the process is the same. However, this step may be accomplished in many other ways. For example, the pulp may be chlorinated, washed, chlorinated with an excess of chlorine for a short time, then neutralized with an alkali to provide a limited amount of hypochlorite bleaching, washed, bleached further with hypochlorite, and again washed. Alternatively the pulp may be chlorinated, washed, made alkaline, and bleached with hypochlorite in one or more stages, with washing after each stage. It may be preferable in the case of some pulps to employ an alkaline extraction stage as a part of the preliminary purification procedure. Any such processes can be used, provided they are terminated before there is any attack on the cellulose which reflects itself in a lowering of the strength value.

The results in the three preceding examples are tabulated in the table in columns 1, 2 and 3. Columns 4, 5 and 6 are also included in order that the results obtained in accordance with the invention may be compared with other processes.

Table

Column No.	1	2	3	4	5	6
Example No.	I	II	III			
Treatment:						
Step (2)	ClO_2 Sol.	Chlorite Sol.	Chlorite Sol.	Hypochlorite Bl.	Hypochlorite Bl.	0.12% H_2O_2
Step (3)	0.12% H_2O_2	0.12% H_2O_2	0.06% H_2O_2	0.12% H_2O_2	0.24% H_2O_2	ClO_2 Sol.
Brightness:						
before Step (2)	71.0	71.0	71.0	71.0	71.0	71.0
after Step (2)	81.5	81.0	81.0	81.1	81.1	74.6
after Step (3)	84.5	86.4	82.0	82.2	84.7	87.1
Increase due to peroxide	3.0	5.4	1.0	1.1	3.6	
Loss in brightness:						
Lamp test after Step (2)	8.3	7.1	7.1	8.1	8.1	3.0
Lamp test after Step (3)	3.5	3.7	3.2	4.4	5.3	6.8
Heat test after Step (2)	4.3	3.9	3.9	4.0	4.0	1.7
Heat test after Step (3)	2.3	2.3	2.2	2.8	2.8	2.5
8-weeks' storage after Step (2)	6.4	5.8	5.8	5.5	5.5	1.8
8-weeks' storage after Step (3)	1.9	2.1	1.8	2.0	2.4	4.4
Viscosity:						
before Step (2)	44.2	44.2	44.2	44.2	44.2	44.2
after Step (2)	43.9	46.4	46.4	36.8	36.8	43.4
after Step (3)	42.4	47.7	49.4	33.0	31.6	41.4
Per cent change due to peroxide	−3.4	+2.8	+6.5	−10.3	−14.1	
Total per cent change	−4.1	+7.9	+11.7	−25.3	−28.5	−6.4
Average strength:						
before Step (2)	1.89	1.89	1.89	1.89	1.89	1.89
after Step (3)	1.91	1.90		1.82		

A consideration of the results shown in columns 1 and 2 will show that the process of Examples I and II achieves a final high brightness of 84.5 and 86.4, respectively. Despite this high brightness the permanence after step (3) in the lamp test, heat test and 8 weeks' storage test were markedly superior to the permanence of the lower brightness after the chlorine dioxide treatment (step 2). This is surprising since generally good permanence is associated with lower brightness and poor permanence is associated with high brightness. The viscosity changes show that there is substantially no attack on the cellulose, despite the final high brightness and permanence obtained and the use of hydrogen peroxide which is normally known to attack cellulose. This is confirmed by the strength figures.

Example III in column 3 shows that although the amount of peroxide used has been reduced to half of that used in Example II so as not to obtain as much improvement in brightness due to the use of peroxide, the permanence has nevertheless been greatly improved, as shown by the lamp test, heat test and storage test. The invention contemplates the use of peroxide in the final step to achieve permanence even though there is very little or no improvement in brightness attributable to the peroxide. The viscosity change and the strength value in column 3 confirms the absence of attack on the cellulose.

In column 4 there is described, for comparative purpose, an example in which hypochlorite bleach was used in place of chlorine dioxide in an amount to obtain a brightness of 81.1, which is about the same brightness as was obtained with the chlorine dioxide in Examples I, II and III. Following this, 0.12% peroxide was used to obtain a final brightness of 82.2.

A comparison of column 4 with column 3 will show that double the amount of peroxide is required for about the same final brightness when hypochlorite is first used, that the permanence by any of the tests is not as good for this brightness, and that there has been a substantial attack on the cellulose, as is shown by both the large decrease in the viscosity and the lower average strength figure.

A comparison of column 4 with columns 1 and 2 shows that when the same amount of peroxide is to be used, the process of the invention using chlorine dioxide gives a much higher final brightness than when a hypochlorite is used and that the permanence by all three stability tests is substantially better when the pulp is treated in accordance with the invention, despite the fact that the final brightness is much higher and therefore ordinarily associated with poorer permanence. In addition, the viscosity and strength figures of the pulp treated in accordance with the invention are much better. In a process in which a given amount of peroxide is to be used as the final bleach, substantially better final brightness, permanence, and strength can be obtained in accordance with the invention. On the other hand, if one is interested in using as small an amount of peroxide as possible, and this often is the case because it is the most expensive of the

various bleaching agents, a smaller amount of peroxide gives an equally good brightness, better permanence and better strength in accordance with the invention.

Column 5 is similar to column 4, except that the amount of peroxide is increased to 0.24% in order to obtain a final brightness of 84.7, which is about the final brightness obtained in accordance with Example I. Double the amount of peroxide is required and this is commercially undesirable because of the expense. In addition, the permanence is markedly inferior to that obtained in Example I and there is a profound attack upon the cellulose.

Column 6 demonstrates the critical nature of the order of the steps, and describes an experiment similar to Examples I and II, except that the peroxide treatment preceded the treatment with chlorine dioxide. The final brightness is as good as might be expected, but the permanence is poor. In each of the three tests the permanence of the end product is poorer than after the second step which is just the reverse of Examples I and II. While relatively good permanence was obtained after the hydrogen peroxide treatment, this was at the relatively low brightness of 74.6. It is pointed out earlier that better permanence at such lower brightness is to be expected, and that it is at the high brightnesses of 80 or above that there is difficulty in achieving good permanence. At the high brightness, the permanence is entirely unsatisfactory. Furthermore there is more attack on the cellulose as shown by the greater decrease in viscosity.

No data is included on the use of hypochlorite followed by chlorine dioxide to obtain a final high brightness, but it is obvious from the above data that such a process would give poor stability of color and poor strength.

The above data demonstrates that when chlorine dioxide solutions are used as a bleach preceding hydrogen peroxide bleach for treatment of preliminary purified stock, the following advantages among others are obtained:

1. A method of bleaching ligneous cellulosic considerably less peroxide is required to obtain a given brightness;

2. The treatment does not have any deleterious attack on the cellulose;

3. The final bleached product possesses an unexpectedly high degree of color stability;

4. These results can be achieved with a minimum amount of expensive chemicals and additional stages and without the use of the usual hot caustic extractions.

It will be obvious to one skilled in the art that variations may be made from the best mode of practicing the invention, as described herein, and all such variations are to be included as fall within the scope of the following claims.

We claim:

1. A method of bleaching ligneous cellulosic materials, which comprises subjecting the cellulosic material to a preliminary bleaching by treating with a bleaching agent for cellulosic materials selected from the class consisting of chlorine, hypochlorous acid, and alkali metal and alkaline earth hypochlorites to remove a major portion of the non-cellulosic impurities short of the point of materially affecting the strength of the cellulose; treating said preliminarily bleached cellulosic material with chlorine dioxide to obtain an increased brightness, said bleached material having poor color stability; and then subjecting said bleached cellulosic material to the action of a peroxide bleaching agent which does not unduly attack the cellulosic material and yields a final bleached, strong product of improved color stability.

2. A method of bleaching ligneous cellulosic materials, which comprises subjecting the cellulosic material to a preliminary bleaching by treating with a bleaching agent for cellulosic materials selected from the class consisting of chlorine, hypochlorous acid, and alkali metal and alkaline earth hypochlorites to remove a major portion of the non-cellulosic impurities short of the point of materially affecting the strength of the cellulose; treating said preliminarily bleached cellulosic material with chlorine dioxide at a pH of less than 8 to obtain an increased brightness, said bleached material having poor color stability; and then subjecting said bleached cellulosic material to the action of a peroxide bleaching agent at a pH value above 8 which does not unduly attack the cellulosic material and yields a final bleached, strong product of improved color stability.

3. A method of bleaching ligneous cellulosic materials, which comprises subjecting the cellulosic material to a preliminary bleaching by treating with a bleaching agent for cellulosic materials selected from the class consisting of chlorine, hypochlorous acid, and alkali metal and alkaline earth hypochlorites to remove a major portion of the non-cellulosic impurities short of the point of materially affecting the strength of the cellulose, treating said preliminarily bleached cellulosic material with chlorine dioxide to obtain at least 50% of the desired additional increase in brightness, said bleached material having poor color stability; and then subjecting said bleached cellulosic material to the action of a peroxide bleaching agent which does not unduly attack the cellulosic material and yields a product having the remainder of the desired additional increase in brightness and an improved color stability.

4. A method of bleaching kraft pulp, which comprises subjecting the pulp to a preliminary bleaching by treating with a bleaching agent for kraft pulp selected from the class consisting of chlorine, hypochlorous acid, and alkali metal and alkaline earth hypochlorites, to remove a major portion of the non-cellulosic impurities short of the point of materially affecting the strength of the pulp; treating said preliminarily bleached pulp with chlorine dioxide at a pH of less than 8 to otbain at least 50% of the desired additional increase in brightness, said bleached pulp having poor color stability; and then subjecting said bleached pulp to the action of a peroxide bleaching agent at a pH value above 8 which does not unduly attack the pulp and yields a product having the remainder of the desired additional increase in brightness and an improved color stability.

5. A method of bleaching kraft pulp, which comprises subjecting the pulp to a preliminary bleaching by treating with a bleaching agent for kraft pulp selected from the class consisting of chlorine, hypochlorous acid, and alkali metal and alkaline earth hypochlorites to remove a major portion of the non-cellulosic impurities short of the point of materially affecting the strength of the pulp; treating said preliminarily bleached pulp with a chlorite selected from the group consisting of alkali metal and alkaline earth metal chlorites at a pH of less than 5 to obtain at least 50% of the desired additional increase in bright-

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ness, said bleached pulp having poor color stability; and then subjecting said bleached pulp to the action of a peroxide selected from the group consisting of hydrogen peroxide, alkali metal and alkaline earth metal peroxides at a pH value above 9 which does not unduly attack the pulp and yields a product having the remainder of the desired additional increase in brightness and an improved color stability.

6. A method of bleaching kraft pulp having an unbleached brightness of about 20 to 30, which comprises first subjecting the pulp to bleaching by treating with a bleaching agent selected from the group consisting of chlorine, hypochlorous acid, and alkali metal and alkaline earth hypochlorites to remove a major portion of the non-cellulosic impurities and bleach the pulp to a brightness of at least about 70 to 75 but short of the point of materially affecting the strength of the pulp; and subjecting the preliminarily bleached pulp to a finishing bleach to obtain a finished brightness of improved permanence in the range of 80 to 90, comprising the steps of (1) treating the preliminary bleached pulp with a chlorite selected from the group consisting of alkali metal and alkaline earth metal chlorites at a pH of less than 5 to obtain at least 50% of the desired additional increase in brightness, said

bleached pulp having poor color stability; and then (2) subjecting the impermanently brightened pulp to the action of a peroxide selected from the group consisting of hydrogen peroxide, alkali metal and alkaline earth metal peroxides at a pH value above 9 to obtain a permanence of brightness and the remainder of the desired additional increase in brightness, whereby a bleached pulp is obtained of high strength, high finished brightness, and enhanced permanence of brightness.

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