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BLEACHING OF GROUND WOOD PULP

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This invention relates to the bleaching of paper pulp and, more particularly, to the bleaching of ground wood pulp. In present commercial practice ground wood pulp, either alone or together with other paper pulps, is employed extensively in the manufacture of paper. It is widely used in the manufacture of paper of the grade employed for printing newspapers, and in fact, most newsprint paper consists almost entirely of ground wood pulp. In many papers intended for printing purposes a high content of ground wood pulp is very desirable.

However, owing to the difficulty of bleaching ground wood pulp commercially by an economical and efficient bleaching method a large part, if in fact not all, of the ground wood pulp as usually utilized in paper manufacture is not subjected to any bleaching treatment. In some instances it has been usual to subject the ground wood pulp to a bleaching process wherein a reducing agent is employed, this bleaching treatment being ordinarily of very short duration. Unfortunately any increase in brightness attained in the ground wood pulp when that pulp is bleached by the action of reducing agents such as hydrosulfites is not carried over, generally speaking, into the paper manufactured therefrom. Moreover, any increase in brightness is not a permanent characteristic of the pulp since there is a tendency to revert to the original darker color when the pulp or paper produced therefrom is subjected to the action of light and air. This tendency to develop a yellowish coloration upon standing has constituted a serious detriment to the commercial utilization of papers prepared from ground wood pulp or containing substantial quantities of ground wood pulp in the manufacture of the higher qualities of paper. In general, the use of ground wood pulp is restricted principally to the manufacture of relatively cheap papers, such as paper used for printing purposes including newsprint, and for book papers of the cheaper grades.

Ground wood pulp, as distinguished from chemical wood pulp or pulp which has been subjected to a chemical treatment such as in the sulfite pulp process, soda pulp process, or sulfate pulp process (kraft), is inherently a less expensive raw material for paper manufacture. If the pulp could be bleached in such a manner that paper prepared therefrom or paper containing relatively large quantities of the ground wood pulp would possess good permanent whiteness, ground wood pulp would undoubtedly be of much greater commercial importance in the paper manufacturing industry. Generally speaking, ground wood pulp and soda pulp have many characteristics in common and, if ground wood pulp could be satisfactorily bleached to yield a paper of satisfactory whiteness and satisfactory whiteness retentivity, the resulting product would be competitive with bleached soda pulp and would be utilized commercially to a far greater extent in the manufacture of papers generally than under the present circumstances. Ground wood pulp is, however, a difficult material to bleach, and it is especially difficult to bleach this product in such a manner that the tendency to yellow upon standing, in both the resulting pulp and the paper produced therefrom, is reduced to a satisfactory degree. The previous attempts to bleach pulps, consisting of finely comminuted wood, as used in the paper manufacturing industry, have generally proven unsuccessful, except that in some instances single-stage bleaches wherein the pulp is treated for relatively short periods with a reducing agent have secured a partial though generally unsatisfactory degree of brightening.

We have carefully investigated the problem of color removal in the ground wood pulp industry and have reached the conclusion that previous attempts to bleach this product under conditions wherein reversion to original yellowish color upon standing was avoided have been uniformly unsuccessful for the reason that the necessity for controlling the conditions of bleaching within relatively narrow limits has not been generally appreciated. The critical nature of the conditions to which the ground wood pulp is ordinarily subjected during treatment with an oxidizing bleach, for example, the necessity for controlling such conditions as pH maintained, temperature, time, percentages of active agents, etc., within relatively narrow limits, has not been fully appreciated by those engaged in attempts to develop a satisfactory ground wood pulp bleaching process. Moreover, there has been no appreciation in commercial ground wood pulp bleaching and paper manufacturing operations of the close nature of the inter-relation between the various factors involved. Neither has there been any appreciation of the fact that various conditions maintained are dependent upon other conditions, and this lack of complete knowledge has been instrumental in preventing the attainment of successful bleaching.

While attempts to utilize various bleaching agents such as hydrogen peroxide, various hypochlorites, sodium peroxide, etc. are reported in the literature, it is significant that such attempts have proven completely unsuccessful. Ground

wood pulp is today not being bleached in commercial practice, other than by means of the short reducing treatment yielding indifferent results which has been briefly referred to above.

After careful investigation of the bleaching of this material, which is inherently difficult to bleach by means of the usual oxidizing agents such as sodium peroxide, per compounds, alkaline solutions of hydrogen peroxide, etc., we have reached the conclusion that those engaged in the earlier attempts to bleach the product failed in that they did not carefully regulate the conditions under which the bleaching was carried out. It is accordingly one of the objects of this invention to develop a process for the commercial bleaching of ground wood pulp wherein the conditions under which the bleaching is carried out are carefully controlled. A further object is the development of a process which will convert the ground wood pulp to a product having a degree of brightness sufficiently high to permit its more extensive and more varied use in the commercial manufacture of paper. Another object of this invention involves the development of a process wherein the degree of brightness secured in the pulp is actually carried over into the paper, resulting in a paper of a high degree of whiteness, to an extent greater than now possible.

Still another object of this invention is the development of a process for the treatment of ground wood pulp which will yield a product of a high degree of brightness and one in which the tendency of both the pulp and the paper produced therefrom to revert to original color upon standing (yellowing) will be reduced to a very substantial degree. All these objects may be summarized by stating that a primary and essential object of this invention is the development of a process for the bleaching of the pulp in question which will convert that pulp to a product which will be competitive with some grades of chemical wood pulp, such as soda wood pulp, in the paper manufacturing industries. This improvement in the character of wood pulp and paper produced therefrom is to be attained, of course, without uneconomical costs. This will permit, to a substantial extent, the utilization of ground wood pulp without considerable admixture with other pulps in the manufacture of even the more expensive types of paper.

The essential keynote of our improved process is the critical control of the conditions maintained during the bleaching process wherein the ground wood pulp is subjected to the bleaching action of an oxidizing bleaching agent such as sodium peroxide or an alkaline solution of hydrogen peroxide. By careful control of the essential conditions the consumption of chemical agents may be regulated in such a manner as to reduce the cost of the chemical treatment of the ground wood pulp to a minimum acceptable in commercial paper manufacturing operations.

We have found that ground wood pulp can be satisfactorily bleached in an economical and efficient manner under conditions wherein the whiteness retentivity is increased to a remarkable extent by the use of sodium peroxide (Na_2O_2) as the bleaching agent. In place of sodium peroxide, equivalent agents, such as an alkaline solution of hydrogen peroxide, or a solution of a per compound such as sodium perborate, may also be utilized. In view of its relative cheapness, however, and in view of the ease in which it is employed in our process for the bleaching of ground wood pulp, we prefer to utilize sodium peroxide as our active bleaching agent. The following description of our preferred procedure will therefore refer specifically to sodium peroxide as the bleaching agent. This is not intended to convey the idea that its equivalent agents, such as those specified above or others, may not be substituted therefor. In utilizing an agent such as an alkaline solution of hydrogen peroxide or a solution of sodium perborate in place of the sodium peroxide, in addition to adjusting the pH of the bleaching bath within the limits specified, it will be necessary to utilize such quantities of those other active oxygen-yielding materials as necessary to yield an active oxygen concentration substantially equivalent to the active oxygen concentration resulting from the use in our process of sodium peroxide.

Our extensive experiments in the bleaching of ground wood pulp have been carried out principally with the commercial aqueous suspensions of ground wood which are usually of from 4 to 7% pulp concentration. In the description of our process which follows we have in mind pulps of approximately this concentration. It should be understood, however, that there is nothing inherent in our process which restricts it to treatment of ground wood slurries falling within the specified consistencies. Any consistency of ground wood pulp suspension may be utilized in our process, and we specify consistencies of from 4 to 7% merely because of the general prevalence of consistencies approximating these figures in the paper pulp and paper industries.

When utilizing sodium peroxide as the bleaching agent we have found that it is desirable to utilize an amount of sodium peroxide equivalent approximately to 5% of the weight of the dry ground wood being treated. In specifying the amounts of chemical agents utilized ordinarily the practice of the paper pulp industry is followed, the amounts being expressed as the percentage based on the weight of the dry ground wood pulp being treated. For example, bleaching with 5% sodium peroxide means that there will be present in the bleach five pounds of sodium peroxide for every one hundred pounds of ground wood being treated. Similarly, bleaching with 2% sodium peroxide means that the bleach liquor contains two pounds of sodium peroxide per one hundred pounds of dry ground wood present in the slurry being treated. This method of expression is customary in the industries utilizing the various paper pulps and will be followed here.

While ordinarily we prefer to use about 3% sodium peroxide or three pounds of sodium peroxide per one hundred pounds of the dry weight of the ground wood present in the pulp being treated, it is possible to utilize higher percentages of sodium peroxide to give generally a greater degree of whiteness. Similarly, lower percentages of sodium peroxide may be employed but result, generally, in a less increase in brightness. For securing improvements in brightness satisfactory for commercial operations we have found it inadvisable to utilize less than 0.25% sodium peroxide (one-quarter pound of sodium peroxide per one hundred pounds of ground wood present in the pulp being treated). Amounts of 0.50 pound of sodium peroxide per one hundred pounds of ground wood (0.50%) have been found in many instances to yield a satisfactory bleached pulp. The prior art has in general failed to appreciate the necessity for utilizing amounts of sodium peroxide at least of this order to secure adequate whiteness and adequate whiteness re-

tentivity. While the higher concentrations of sodium peroxide, concentrations up to 7.5% sodium peroxide based on the dry weight of the pulp or even higher as, for example, 10% sodium peroxide, will generally result in greater whiteness and to some extent a higher degree of whiteness retentivity, we have generally found it inadvisable to exceed the figure of 7.5% sodium peroxide concentration, i. e. 7.5 pounds of sodium peroxide per one hundred pounds of dry ground wood. Percentages in excess of 10.0% will practically always result in but slight increase in whiteness and will tend to increase the cost of the bleaching treatment to one which will no longer render the process attractive from the commercial viewpoint.

We have found that the temperature at which the ground wood pulp is treated is of the utmost importance. We prefer to carry out our bleaching process with a ground wood pulp suspension having a temperature of approximately 100° F. Temperatures as low as 80° F. have, however, been utilized and temperatures as high as 120° F. are also practical. The temperature range that we have found necessary, 80 to 120° F., does not differ materially from ordinary room temperatures and the use of such relatively low temperatures in bleaching the ground wood pulp constitutes a distinct departure in the art. It has previously been considered necessary to maintain relatively high temperatures in attempts to bleach ground wood pulp, and the maintenance of these high temperatures has not only increased the losses due to decomposition of the bleaching agent but has also resulted in uncertain and unsatisfactory bleaching. In view of the inherently difficultly bleachable characteristics of ground wood pulp, we have found that the maintenance of the temperature preferably in the neighborhood of 100° F. and in any event within the range 80 to 120° F. is essential.

Another essential factor which must be strictly regulated in order to secure the desired degree of bleaching and the desired whiteness retentivity is the pH of the mixture of ground wood pulp suspension and bleaching agent. The regulation of this pH during the bleaching operation within a very narrow range is essential if a product of commercial value is to be secured. We have found that the pH must fall strictly within the range 10.0 to 11.0 if results of commercial acceptability are to be obtained. Generally speaking, at the lower temperatures, such as temperatures of 80° F., or thereabouts, relatively higher pH values such as a pH value up to 11.0 can be maintained without the danger of excessive injury to the pulp. For temperatures of 120° F. we have, however, found that a pH of 10.5 is the upper limit and that if the pH exceeds 10.5 there will practically always result unsatisfactory bleaching.

Ordinarily we prefer to maintain the pH value at not over 10.5 although at temperatures as low as 80° F., as previously stated, the pH may go up as high as 11.0 without interfering with the desired bleaching. If the pH value is allowed to go too high, not only is the bleaching not satisfactory but there is a tendency to cause a distinct yellowing in the color of the pulp, which yellow color is very difficult to bleach out or remove therefrom. We have observed, on the other hand, that pH values below 9.5 will result in inconsequential and unsatisfactory bleaching and will not produce a pulp of the desired brightness. For most purposes, therefore, it is essential to maintain a pH of not below about 10.0 in order to secure satisfactory bleaching, although pH values within the range 9.5 to 10.0, while generally not the proper values to attain the highest degree of bleaching, may sometimes be utilized in commercial practice if only a very slight degree of lightening in color is required, especially under those circumstances where the higher temperatures or temperatures of close to 120° F. are utilized.

We have also found that the presence of sodium silicate in the slurry of ground wood pulp and bleaching agent is very desirable if not essential as it provides the necessary alkalining agent and moreover acts to some extent as a buffering material to maintain the pH value within the narrow range 10.0 to 10.5. Surprisingly enough, we have found that the amount of sodium silicate which should be present for satisfactory bleaching depends largely on the concentration of sodium peroxide utilized. Thus, when utilizing 1 or 2% sodium peroxide, i. e. one to two pounds of sodium peroxide per one hundred pounds dry weight of the ground wood, it is desirable to have present at least 6% of sodium silicate. The sodium silicate concentration is specified in the same manner as the sodium peroxide concentration, and a 6% concentration means six pounds of sodium silicate per one hundred pounds dry weight of the ground wood being treated in the pulp. If amounts of sodium silicate less than 6% are present, when the sodium peroxide concentration is 1 to 2% sodium peroxide, the degree of brightness of the pulp will be definitely lowered. For example, when utilizing 1% sodium peroxide, the bleaching being carried out at 100° F., and the bath containing 6% sodium silicate (42° Bé.) a brightness of 63% has been obtained. If the sodium silicate content is cut in half and if there is present only three pounds of sodium silicate per one hundred pounds of ground wood, the brightness is reduced to approximately 61.5%. When utilizing 2% sodium peroxide and a 6% sodium silicate concentration (42° Bé. Grasselli No. 30 grade) we have observed that the percentage brightness is approximately 65%. When, however, there is present only 2% sodium silicate the brightness is 61% or below. Should the sodium silicate concentration be approximately 4% the brightness is somewhat less than 64%. It is thus evident that there is a definite relationship between sodium silicate content present in the bleach bath and the amount of sodium peroxide present. When 1 or 2% sodium peroxide concentration is employed there should be present at least 6% sodium silicate.

When the sodium peroxide concentrations are higher than 2% we have found that there is also a definite minimum percentage of sodium silicate which should be present if maximum brightness is to be secured. For 3% sodium peroxide or 4% sodium peroxide bleaching solutions, i. e. three or four pounds of sodium peroxide per one hundred pounds dry weight ground wood, the sodium silicate concentration should be about 10% or ten pounds per one hundred pounds of ground wood. For example, when treating ground wood at 100° F. in a 3% sodium peroxide bleach bath, the presence of 10% sodium silicate results in a brightness of 68% while with 2% sodium silicate concentration the brightness is only 62.5%. Intermediate values of sodium silicate produce intermediate brightness with the 3% sodium peroxide concentration; for example, 4% sodium silicate produces a brightness of

slightly less than 65%, 6% sodium silicate results in a brightness of 66%, while 8% sodium silicate results in a brightness of 67%. It may be stated that these tests are all based on a standard commercial sodium silicate (42° Bé. Grasselli No. 30) but of course our invention is not in any sense restricted to the use of this silicate or to silicate of this particular gravity. Similarly, the precentages of whiteness are given for convenience in values as determined by the "Brightness Meter" sold for this purpose by the General Electric Company.

The sodium silicate concentration in the bleach bath will ordinarily not exceed 10%, even for the higher concentrations of peroxide, i. e. concentrations up to 10.0% Na_2O_2. We have also found that concentrations of at least 6% sodium silicate are essential, even for very low concentrations of sodium peroxide, concentrations as low, for example, as 0.50% or 0.25%. The sodium silicate range extends from 6% sodium silicate to 10% sodium silicate, the particular amount selected being chosen, as previously specified, in accordance with the concentration of sodium peroxide or equivalent agent utilized.

It might furthermore be stated that the sodium silicate is valuable in the bleach bath for protecting metallic equipment against corrosion by alkaline compounds present in that bath. Similarly the silicate is effective in maintaining the pH within the range given and to some extent serves both as alkalining agent and buffering agent.

We have found that a period of contact between the ground wood pulp and the bleaching solution of from two to four hours is necessary in order to secure satisfactory bleaching results. While the pH should fall during the greater portion of the bleaching process at some value within the range 10.0 to 11.0, it is not detrimental to the quality of the bleached pulp if the pH drops as low as 9.5, and in some instances as low as 9.0, toward the end of the bleaching step, as the major portion of the bleaching will have been substantially completed by this time.

Ordinarily, after the ground wood suspension is permitted to flow into the vessel wherein it is to be contacted with the bleaching agent it is desirable to stir the resulting suspension to an extent sufficient to insure thorough mixing. Continuous stirring is not essential but agitation in some manner sufficient to secure thorough mixing at the start of the bleaching process may be regarded as a desirable element in our process. In place of stirring by means of an actual mechanical stirrer, thorough contact between bleaching agent and wood pulp may of course be secured by some other equivalent means such as discharge of gas bubbles in the solution, by shaking the container, or by some other procedure.

As examples of our improved process for the bleaching of ground wood pulp, the following may be given:

Example I

A solution of sodium peroxide of 1.5% concentration, i. e. 1.5 pounds of sodium peroxide per one hundred pounds dry weight of ground wood pulp being treated, was prepared. This solution was neutralized by the addition of sulfuric acid until the pH fell within the range 10.0 to 10.5.

This stock solution was then mixed with the pulp slurry and sodium silicate in amounts equivalent to approximately 6%, or six pounds of sodium silicate per one hundred pounds dry weight of ground wood, was added to the solution. The pH was carefully adjusted so that it fell within the range 10.0 to 10.5. The consistency of the pulp was maintained within the range 5 to 10%.

The temperature of the mixture of pulp and bleach liquor was maintained at approximately 100° F. for approximately four hours. Care was taken to insure the maintenance at all times of a temperature above 80° F., and the temperature was also carefully regulated so that it did not exceed 120° F. at any time. At the end of four hours the pulp was removed, washed with water, and used subsequently in the manufacture of paper. The ground wood pulp had been bleached to a very satisfactory degree of brightness and the paper resulting therefrom was of a high whiteness and high degree of whiteness retentivity.

It may be stated that washing at the conclusion of the bleaching process is not always necessary but may be carried out with advantage in some cases.

Example II

A solution of sodium peroxide of approximately 4.0% concentration, i. e. 4.0 pounds of sodium peroxide per hundred pounds dry weight of the ground wood to be treated, was prepared. The ground wood pulp of approximately 4% consistency was introduced into this solution of sodium peroxide. The pH of the mixture was carefully adjusted by the addition of sulfuric acid so that a pH of 10.5 was secured. To the solution sodium silicate in amount approximately 10%, i. e. ten pounds of silicate per hundred pounds of ground wood, was added. The resulting pH was approximately 10.5.

At the end of five hours' treatment at 100° F. the brightness of the pulp as determined by the General Electric Company's "Brightness Meter" was found to be 69.0. As the original pulp had a brightness of 59.5, it is evident that there was an increase of 9.5 points in brightness.

Example III

The same ground wood pulp treated in Example II was bleached in a 2.0% sodium peroxide solution which contained approximately 6% sodium silicate. The bleaching was carried out at 90° F. and required five hours. The pH of the mixture of bleach bath and ground wood pulp during the greater portion of this bleaching process was approximately 10.2.

At the end of five hours the brightness of the wood pulp had increased from 59.5 to 65.0, an increase of 5.5 points. Paper made from the resulting pulp was of excellent whiteness and possessed a high degree of brightness retentivity.

To those skilled in the art many modifications and widely different embodiments and applications of our invention in the general field of bleaching ground wood pulp will be readily apparent. It should be understood that the details of our preferred process as described, including the concentrations, conditions under which the bleaching is carried out and other factors involved, may be subjected to some change without departing from either the spirit or scope of our invention. It is intended that our invention is not to be restricted to specific preferred embodiments, minor details, or specific modes of operation, other than as necessitated by the prior art and appended claims.

We claim:

1. A process of bleaching ground wood pulp which comprises contacting said pulp with an

alkaline solution containing a peroxide at a temperature within the range 80 to 120° F., the pH of the mixture during the major portion of the bleaching process being maintained within the range 10.0 to 11.0.

2. A process of bleaching ground wood pulp which comprises contacting said pulp with a solution of an alkali metal peroxide, said mixture being maintained throughout the bleaching at a temperature within the range 80 to 120° F. and the pH during the major portion of said bleaching being maintained within the range 10.0 to 11.0.

3. A process of bleaching ground wood pulp which comprises contacting said pulp with a solution of sodium peroxide, there being present from 0.25 pound to 10 pounds of sodium peroxide per 100 pounds of ground wood present in said pulp being treated, the temperature being at all times maintained within the range 80 to 120° F., and the pH of said bleaching liquor during the major portion of the bleaching step being maintained within the range 10.0 to 11.0.

4. A process of bleaching ground wood pulp which comprises subjecting a pulp of 4 to 10% consistency to the action of sodium peroxide, said sodium peroxide being present in amounts ranging from 0.25 pound to 10 pounds per 100 pounds dry weight of ground wood, the temperature of the bleaching liquor during the bleaching process being maintained within the range 80 to 120° F., and the pH of said bleach bath being adjusted to fall within the range 10.0 to 11.0 during the major portion of said bleaching.

5. A process of bleaching ground wood pulp which comprises subjecting said pulp to the action of sodium peroxide in a bleach bath containing sodium silicate, there being present from 0.25 to 10.0 pounds of sodium peroxide per 100 pounds dry weight of the ground wood pulp being bleached, the pH of said bleach liquor being maintained during the major portion of the bleaching operation within the range 10.0 to 11.0, and the temperature at which said bleaching is carried out being maintained between the range 80 to 120° F.

6. A process of bleaching ground wood pulp which comprises subjecting said pulp to the action of an alkaline solution of a peroxide in a bleach bath containing sodium silicate, the temperature of said bleach bath being maintained within the range 80 to 120° F., and the pH of said bath being regulated so as to fall within the range 10.0 to 11.0 during the major portion of said bleaching process.

7. A process of bleaching ground wood pulp which comprises subjecting said pulp to the action of an alkali metal peroxide in a solution containing sodium silicate, the alkali metal peroxide concentration ranging from 0.25 pound to 10 pounds per 100 pounds dry weight of the ground wood being treated, said sodium silicate concentration ranging from approximately 6 pounds per 100 pounds dry weight of ground wood, to 10 pounds per 100 pounds dry weight of ground wood, the pH value of said bleach bath being maintained within the range 10.0 to 11.0 during the major portion of the bleaching process and the temperature at which said bleaching is carried out being regulated so that it falls within the range 80 to 120° F. during the major portion of said bleaching.

8. A process of bleaching ground wood pulp which comprises subjecting said pulp to the action of a solution of sodium peroxide, said solution of sodium peroxide having a pH during the major portion of the bleaching operation falling within the range 10.0 to 11.0 and containing sodium silicate, said sodium peroxide being present in amounts ranging from 0.25 pound to 10 pounds per hundred pounds dry weight of the ground wood being treated, said sodium silicate concentration ranging from approximately 6 pounds per 100 pounds dry weight of ground wood to 10 pounds per 100 pounds dry weight of ground wood, and the temperature at which said bleaching is carried out being regulated so that it falls within the range 80 to 120° F. during the major portion of said bleaching.

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