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PROCESS OF BLEACHING CHEMICAL WOOD PULP WITH NITROGEN TRICHLORIDE

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This invention relates to a method of bleaching chemical wood pulp, and in particular to a bleaching process employing a nitrogen trichloride treatment.

The bleaching of wood pulp, and other cellulosic fibers to a high brightness, with the common chlorine bleaching agents, such as chlorine water or hypochlorite, is almost always accompanied by a degradation of the cellulose; consequently, the increase in brightness is secured at the expense of loss in strength of the pulp. Numerous proposals have been made relating to means of avoiding this degradation during bleaching. But in spite of the large amount of work that has been done in the field of pulp bleaching, and of the development of multi-stage bleaching and its various modifications, no completely satisfactory answer to bleaching without degradation has been found. The chlorites and chlorine dioxide do have the property of bleaching without degradation but their high cost is a serious drawback.

Some of the proposals to avoid degradation involve the use of nitrogen compounds. One such proposal (Dodson, U.S. Patent No. 2,478,379) teaches that the presence of a small amount of an ammonium compound in a chlorine bleaching step serves to inhibit degradation of the cellulose; it is said that the amount of ammonium compound present can be only a very small fraction of that necessary to react with all chlorine; otherwise, the beneficial effects of the presence of the ammonium compound are no longer obtained. This particular proposal is essentially a chlorine bleaching step carried out at a low pH in the presence of a very small amount of an ammonium compound inhibitor.

Chloramines, which are formed by reacting ammonia and chlorine, are said to be inferior bleaching agents and, according to the literature, their presence in any substantial quantity in a bleaching operation is undesirable. Also the technical literature teaches that in bleaching with a chlorine solution, it is necessary to raise the pH of the chlorine solution to above 4.5 by the addition of one of the alkalies, including ammonia, in order to prevent weakening of the fibers.

However, I have found that there is a certain critical range in proportions of nitrogen compound and chlorine, combined with a particular pH range, not previously disclosed, wherein very desirable bleaching results are obtained.

In contrast to these prior proposals I have discovered that the reaction product (or products), formed when all of the chlorine in an aqueous chlorine solution is reacted with an ammonium compound at a pH below 4.5, is an effective bleaching agent, and that little or no weakening of the fiber accompanies the bleaching. That is, I have discovered that a very substantial increase in brightness can be secured in a chemical wood pulp by treating it with nitrogen trichloride in the presence of water at a pH below 4.5, and that the increase in brightness is accomplished with very much less degradation of the cellulose than with the common bleaching agents. The values for the disperse-viscosity and the

bursting and tear strengths of the pulp will be substantially the same after bleaching as before, where nitrogen trichloride is used, whereas where chlorine water or a hypochlorite is employed there is usually a substantial loss in strength. The treatment can be carried out by immersing the pulp in an aqueous solution of nitrogen trichloride or by exposing a suitably water-wetted pulp in permeable form to nitrogen trichloride vapors.

My bleaching agent is conveniently prepared by adding a sufficient amount of an ammonium compound to an aqueous chlorine solution at a pH below 4.5 to react with all of the chlorine to form nitrogen trichloride. The reaction is believed to proceed as follows, taking ammonium sulfate as a typical ammonium compound:

$$3Cl_2+(NH_4)_2SO_4\rightarrow NCl_3+3HCl+NH_4HSO_4$$

One part by weight of chlorine is equivalent to approximately 0.62 part by weight of ammonium sulfate. I have found that the presence of free chlorine with the nitrogen trichloride is detrimental, in that degradation of the cellulose is pronounced. Consequently, it is necessary to have present at least one reacting weight of ammonium compound for each reacting weight of chlorine; in fact, it is desirable to use a slight excess of ammonium compound over the theoretical amount required to react with all of the chlorine present. Various ammonium compounds have been found suitable, particularly ammonia itself and the salts such as the sulfate, chloride, phosphate, and persulfate; salts of polyvalent acids are preferred.

While it is most practical to form the nitrogen trichloride in situ thereby avoiding the hazards of handling nitrogen trichloride, and to form it most economically from chlorine and an ammonium salt the invention also applies where the nitrogen trichloride is otherwise derived. For example, the bleaching solution can be prepared by reacting at a pH below 4.5, hypochlorous acid and ammonium sulfate, or sodium hypochlorite and ammonium chloride. Also, the nitrogen trichloride as the isolated compound can be added to water to form a bleach solution or it can be vaporized and the gas mixed with wetted cellulose at a pH below 4.5.

The pH during the nitrogen trichloride bleaching operation is maintained below 4.5. If necessary, the mixture of chlorine and ammonium compound is adjusted to a pH below 4.5 by the addition of an acid; if the pulp is alkaline the suspension thereof should be acidified to a pH below 4.5 before the nitrogen trichloride solution is added. At higher pH's apparently the compound tends to be converted into dichloramine with less increase in brightness and the fiber is attacked with a loss in disperse-viscosity. Good bleaching is obtained at pH values as low as 1 but a pH range of 1.5 to 3.0 gives optimum results. Any of the non-oxidizing acids can be used to secure the desired pH value, for example, hydrochloric acid, sulfuric acid, phosphoric acid, oxalic acid, etc.

While the nitrogen trichloride bleaching can be carried out in various ways and in place of conventional agents, it is preferably carried out as one of the steps of a conventional multi-stage bleaching process. This agent produces a bleaching effect no matter at what stage in the bleaching process it is applied, and without any material impairment of the viscosity. But the non-degrading properties of nitrogen trichloride can be used to best advantage by employing it in one of the final steps of a multi-stage process since at that point the cellulose is in a more highly refined condition and is more susceptible to degradation. Moreover, the nitrogen trichloride is more effective in removing color bodies after the pulp has been partially bleached, that is, when the pulp has previously been bleached to at least a brightness of 55 or 60. Particularly good gain in brightness is obtained

when it is used in place of hydrochlorite in the final stages. While nitrogen trichloride can be used in place of other bleaching agents, it works to best advantage when used in only one or two of the stages of a multi-stage bleaching and other conventional bleaching agents, such as chlorine, hypochlorite, chlorine dioxide, and peroxide, are employed in the other stages.

My invention is particularly suitable for production of high strength pulp.

Nitrogen trichloride bleaching is aided somewhat by elevated temperatures; temperatures of 120° to 160° F. speed the reaction. However, the nitrogen trichloride tends to vaporize so that a closed vessel is advantageous. Conventional bleaching times are adequate. Pulp consistency does not appear to be critical.

Usually a solution containing from 0.5% to 1% of available-chlorine, based on the dry weight of the pulp, and converted into nitrogen trichloride with an ammonium compound at a pH below 4.5, will produce a substantial increase in brightness of the pulp. In some stages as much as 2.5% (calculated as available-chlorine on the dry weight of pulp) is applied. Larger amounts can be used but the gain is brightness is not commensurate with the added cost.

The pulp viscosities given herein were determined by the pipet-version of Testing Method T 230 sm-46 of the Technical Association of the Pulp and Paper Industry, entitled Cupriethylenediamine Disperse Viscosity of Pulp. The viscosity results secured by this, as well as by other viscosity methods, are accepted as being indicative of the strength and particularly the change in strength occurring during a bleaching process or other chemical treatment. As the viscosity of a given pulp drops in the bleaching process, its strength properties such as tear, tensile, and bursting strength generally will be found to be reduced.

My invention is further illustrated by the following examples:

Example I

Thirty grams of semi-bleached southern pine sulfate pulp having a brightness of 73.9, and having a viscosity of 8.3 centipoises were suspended in water and to this was added a previously formed mixture of 1.87 cc. of a 10% solution of ammonium sulfate and 76 cc. of chlorine water containing 0.3 gram of available-chlorine (1% on the dry weight of the pulp). Sufficient water was then added to form a pulp suspension of 10% consistency and this was thoroughly mixed. The pH was 2.1. The slurry was gradually heated to 120° F. and after 2 hours contact with the nitrogen trichloride solution the pulp was water washed. Brightness was 82.4 and the viscosity was 7.9 centipoises.

A second portion of the same pulp was bleached with chlorine water containing 1% of available-chlorine on the dry weight of the pulp under substantially the same conditions of 10% consistency, pH of 2.6, temperature raised to 120° F., and total bleaching time of 2 hours. Its brightness was 82.3 but the viscosity had been reduced to 4.9 centipoises.

Example II

Unbleached pine kraft pulp, having a permanganate number of 17.9 (Tappi Method T214M–42) and a viscosity of 25.4 centipoises, was pre-bleached by conventional chlorination, caustic extraction, and calcium hypochlorite steps. Thereafter the bleaching was completed by three steps consisting in (1) applying 1% of available-chlorine as calcium hypochlorite at 10% consistency and a temperature of 105° F. for 60 minutes, (2) extracting with caustic, and (3) applying 0.6% of available-chlorine as calcium hypochlorite. The bleached pulp had a brightness of 82.7, a viscosity of 9.9 centipoises, an average bursting strength of 181, and an average tear strength of 564.

A second portion of the same unbleached pulp was bleached by exactly the same steps, using the same total amount of available-chlorine except that the next to the last hypochlorite step, i.e. (1), was replaced by a nitrogen trichloride step. The nitrogen trichloride solution was prepared by forming a chlorine solution containing 1% available-chlorine (based on the weight of oven dry pulp to be bleached), then adding ammonium sulfate in the proportion of 0.62 pound for each pound of available-chlorine present. The bleaching with this solution was then carried out at 10% consistency, a pH of 2.0 to 2.1, and a temperature of 140° F., for 60 minutes; the process was then completed by a caustic extraction and a final hypochlorite bleach carried out under the same conditions as used on the sample in the preceding paragraph. The bleached pulp had a brightness of 82.9, a viscosity of 11.2 centipoises, an average bursting strength of 189, and an average tear strength of 604.

Thus, it will be seen that nitrogen trichloride can be used in place of hypochlorite in a multi-stage bleaching process. An equal or better brightness is produced with the nitrogen trichloride employing the same amount of available-chlorine; in addition the pulp is less degraded, exhibiting a higher viscosity and higher bursting strength and tear throughout the beating curve.

Example III

Southern pine sulfate pulp partially bleached by conventional bleaching methods and having a brightness of 68.7 and a viscosity of 11.2 centipoises was further bleached by means of 0.5% of available-chlorine on the weight of the dry pulp applied as nitrogen trichloride. The nitrogen trichloride solution was prepared by adding to chlorine water 0.62 pound of ammonium sulfate for each pound of available-chlorine present and adjusting the pH to 2.4 with sulfuric acid. The nitrogen trichloride bleaching was carried out at 5% consistency and a temperature of 160° F. for 180 minutes, followed by a water wash. The pulp was found to have a brightness of 78.3 and a viscosity of 11.1 centipoises.

Example IV

A portion of the same partially bleached pulp used in Example III was exposed to nitrogen trichloride vapors. The pulp was first dispersed in water acidified with sulfuric acid to a pH of 2.2, then filtered, and pressed to a cake having 21.2% solids. This wet cake was broken up and placed upon a porous support over an aqueous solution evolving nitrogen trichloride vapors in a closed chamber. After an hour's exposure, the pulp was washed with water; its final brightness was 76.8 as compared to 68.7 before treatment with nitrogen trichloride.

The time of exposure to nitrogen trichloride vapors is dependent upon the degree of bleaching desired and the concentration of vapor. Normally a substantial degree of whitening is obtained in the first hour of exposure to vapors which are predominantly nitrogen trichloride, but several hours may be needed to secure sufficient absorption if diluted vapors are employed. No apparent injury is incurred if the pulp remains in contact with the nitrogen trichloride for several hours. The amount of water need be only enough to moisten the fibers thoroughly and uniformly. A pulp mass containing 50% moisture can be bleached by means of the vapor. However, since nitrogen trichloride has a somewhat limited solubility in water, a higher moisture content, in the range of at least 60% to 70%, facilitates absorption of the vapors.

Although in the examples softwood pulps have been employed, the invention is not limited to coniferous pulps. Nitrogen trichloride is also adapted to bleaching of hardwood pulps, and can be used in place of chlorine or hypochlorite, particularly in multistage bleaching. Hardwood pulps of high brightness can be produced with less degradation utilizing nitrogen trichloride than when using conventional chlorine bleaching agents.

Cellulosic materials other than wood pulp, for example,

cotton and flax, suitably pretreated with alkaline liquors to remove waxy impurities, can also be bleached by the herein described process.

Brightness values given herein were measured on a General Electric brightness meter.

Bursting strength values given were determined by measuring the bursting strength on a standard Mullen tester on hand-sheets made from samples of pulp taken after 0, 25, 50, 75, 100 and 125 minutes' ball milling, multiplying the Mullen reading in each case by 100 and dividing by the basis weight (17 x 22—500), and averaging the results. Values given are as percent points per pound.

Tear strength values given were determined by measuring tear strength on a standard Elmendorf tester on hand-sheets made from samples of pulp taken after 0, 25, 50, 75, 100 and 125 minutes ball milling, multiplying each tear reading by 100 and dividing by the basis weight (17 x 22—500), and averaging the results. Values are given as percent points per pound.

I claim:

1. In the process of bleaching chemical wood pulp, the improvement which comprises applying nitrogen trichloride to chemical wood pulp in the presence of a quantity of water at least equal in weight to the dry weight of the pulp, in the absence of free chlorine and at a pH in the range of 1.0 to 4.5 obtained by the addition of a non-oxidizing acid, the period of contact between the nitrogen trichloride and the pulp being sufficient to permit bleaching to be effected.

2. In a multistage process of bleaching chemical wood pulp, the step which comprises applying nitrogen trichloride to partially bleached chemical wood pulp in the presence of a quantity of water at least equal in weight to the dry weight of the pulp, in the absence of free chlorine and at a pH in the range of 1.0 to 4.5 obtained by the addition of a non-oxidizing acid, the period of contact between the nitrogen trichloride and the pulp being sufficient to permit bleaching to be effected.

3. Process of bleaching chemical wood pulp which comprises exposing chemical wool pulp mixed with at least an equal weight of water to nitrogen trichloride vapors in the absence of free chlorine for a period sufficient to permit bleaching to be effected, said mixture of pulp and water having a pH in the range of 1.0 to 4.5 obtained by the addition of a non-oxidizing acid.

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