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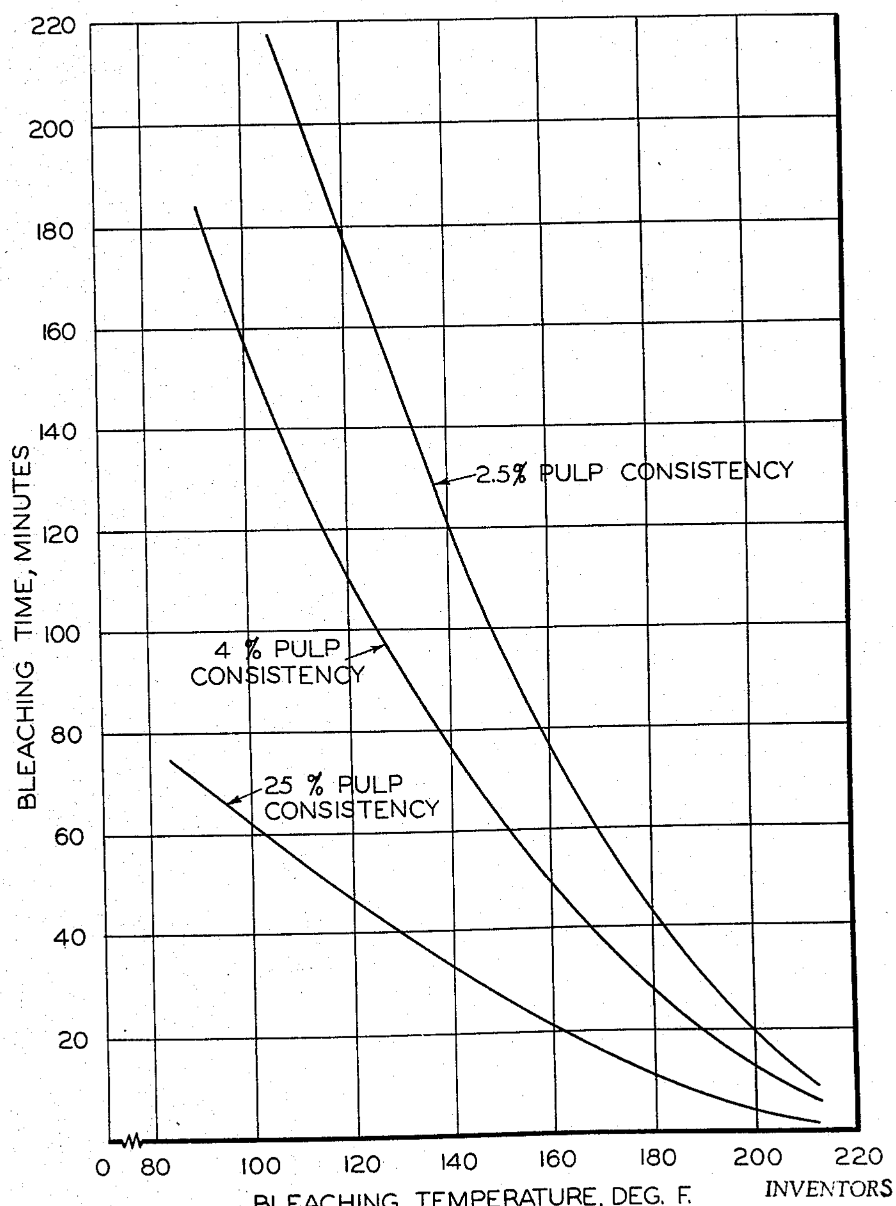

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PROCESS OF BLEACHING LIGNOCELLULOSIC PULPS

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This invention relates to a process of bleaching lignocellulosic pulps. More specifically, it relates to bleaching fibrous lignocellulosic pulps using a water-soluble hydrosulfite as the essential bleaching agent.

The bleaching of wood pulp, particularly groundwood, with either sodium or zinc hydrosulfite is well known in the pulp and paper industry. The procedures suggested or employed commercially in the industry involve the use of pulp to be bleached in a slush form, usually at a low consistency of from about 0.5% to about 6%. Aqueous pulp suspensions having a relatively low dry fiber content, as indicated above, contain a large amount of water and consequently require large size bleaching equipment, require a relatively long bleaching time to attain a high degree of brightness, consume large quantities of heat, have a tendency of contaminating pulp with undesirable ions generally present in water, and produce a considerable quantity of effluent from the bleaching operation which contributes to the stream pollution.

Accordingly, it is the general object of the present invention to overcome such disadvantages by providing an improved process of bleaching lignocellulosic pulps with a water-soluble hydrosulfite at a high pulp consistency, i.e. containing an insufficient amount of water to produce a free-flowing slurry but rather forming a semi-solid, non-flowable, moist mass of pulp containing more than 15% by weight of oven-dry fiber.

It is also an object of the invention to provide a process of bleaching pulps with a stabilized water-soluble hydrosulfite at high pulp consistency and in an atmosphere substantially free of oxygen in order to obtain maximum bleaching efficiency of the hydrosulfite upon the pulp.

Still another object of this invention is to provide an improved process of bleaching pulps at high consistency with a reducing bleaching agent under controlled operating conditions, whereby pulps of maximum brightness are produced with a highly efficient use of the hydrosulfite in a relatively short time, while a uniform distribution of the bleaching solution throughout the moist pulp mass is achieved.

Other objects and advantages of this invention will be apparent from the following description.

Briefly stated, bleached lignocellulosic pulp according to the present invention is produced by first providing a moist mass of pulp having a dry fiber content higher than 15% but not exceeding 50%, by weight, removing a substantial proportion of air from the pulp, admixing the pulp with an aqueous solution comprising essentially a hydrosulfite bleaching agent and a stabilizer therefor, and subjecting the pulp to the action of said bleaching agent in an atmosphere substantially free of oxygen at a temperature between about 100° F. and 230° F., while maintaining the pulp consistency throughout the bleaching in the range of 15–50%, and a pH of about 4 to 8 for a period of time sufficient to produce a substantial increase in brightness of said pulp.

After the desired degree of pulp brightness has been attained, the bleached pulp is discharged from the oxygen-

free zone. It then may be diluted with water to low consistency normally used in the conversion of pulps to paper.

The lignocellulosic pulps suitable in the practice of the present invention may comprise mechanical pulps derived from wood or non-woody lignocellulose, semi-chemical pulps, and pulps derived from chemical digestion of wood or other lignocellulosic materials. Such pulps still contain a certain proportion of lignin materials, depending on the pulping procedure employed.

The pulp coming directly from either mechanical, semi-chemical or chemical pulping operations is usually of low consistency. In accordance with the present invention, the pulp consistency must be, therefore, increased to a value of from above 15% to 50% by weight, oven-dry pulp basis. This may be effectuated in any suitable dewatering equipment, such as a vacuum thickener, screw-press and the like. The moist, high-consistency pulp is then shredded or otherwise comminuted in particulate form, if necessary, in order to facilitate removal of air therefrom and its subsequent mixing with the bleaching solution.

The comminuted pulp in form of a semi-solid, discontinuous moist mass, having voids therein and containing an appreciable quantity of air, may be carried by any suitable conveying means, such as a screw conveyor, to a mixing chamber. Such chamber may be equipped with suitable agitating means, such as a double shaft mixer, which is generally satisfactory for pulps having a consistency between 15 and 20%. The chamber should be provided with an inlet for steam or gas and with an outlet for purging oxygen therefrom. If an excess of steam is present in the chamber, such excess may be released through such outlet and recovered for heating purposes. The pulp mass, substantially free of oxygen, may be transferred through an air-tight conduit to another mixing chamber where it is mixed mechanically with the solution of the hydrosulfite bleaching agent.

For pulps having a consistency in the range of from about 20% to 50%, the removal of air and the subsequent mixing with the bleaching agent may be carried out in a screw press or in a pulper of refiner-type, such as a roto-pulper. Good results may be also obtained by first removing air from the pulp in a screw press, feeding the substantially oxygen-free pulp into a pulper into which the bleach solution is incorporated and thoroughly mixed with the pulp. The resulting bleached pulp may be discharged onto a screw conveyor and transported thereby to a dilution tank.

It is important that after oxygen has been removed from the pulp, the pulp be confined in an air-tight mixing equipment so as to prevent the access of air from the outside, and thus maintain a substantially oxygen-free atmosphere until the bleaching of the pulp is complete.

The removal of a substantial proportion of oxygen contained in the moist, comminuted pulp, which constitutes an integral step in the present process, may be carried out by purging with live steam or with inert gases, such as nitrogen, flue gas from furnaces operating under reducing conditions, or by means of vacuum. The preferred procedure is to inject live steam into the mixing chamber, while subjecting the pulp to vigorous agitation. This produces an atmosphere substantially free of oxygen. If desired, steam purging may be effectuated countercurrently in a suitable mixing apparatus.

The lignocellulosic pulp, substantially free of oxygen, is then admixed with a solution of a hydrosulfite which is the essential bleaching agent in accordance with the present invention. Examples of suitable water-soluble hydrosulfites are zinc hydrosulfite, the alkali metal hydrosulfites, such as sodium and potassium hydrosulfite, ammonium hydrosulfite, and the like. These may be used singly or in admixture with each other. Sodium hydrosulfite and zinc hydrosulfite are the preferred members of the group. The aqueous solutions of the hydrosulfite may be prepared at any desired concentration of hydrosulfite depending upon its solubility characteristics. A suitable concentration range for a hydrosulfite solution may be from 2 to 10%, by weight, calculated as sodium hydrosulfite, however it is to be understood that higher or lower concentrations may be employed, if desired. In preparing the hydrosulfite aqueous solution it may be desirable to pretreat the water employed by deaerating it so that incorporation of oxygen into the pulp mixture during bleaching will be reduced to a minimum.

The amount of a hydrosulfite employed in the bleaching of the lignocellulosic pulps may vary according to the degree of brightness increase desired, as well as depending on the type of pulp used. In general, from 0.2% to 5% by weight of hydrosulfite, based on the weight of oven-dry pulp will be sufficient to obtain the desired brightness increase. The preferred range for the use of hydrosulfite is from 0.5% to 2% by weight, based on the oven-dry weight of pulp.

In order to improve the stability of a hydrosulfite in an aqueous solution and to avoid impairment of bleaching response due to possible contamination of pulp with certain metal ions, such as iron, copper, manganese and the like which may be present in the pulp itself or in the water, a certain amount of a stabilizer for the hydrosulfite is incorporated in the hydrosulfite solution, or in the pulp prior to its admixture with the bleaching agent. Examples of suitable stabilizers for hydrosulfite are water-soluble polyphosphates, such as sodium tripolyphosphate, sodium tetraphosphate, sodium pyrophosphate and the like. Other suitable stabilizers for the hydrosulfite comprise commercially available chelating agents such as ethylene-diamine-tetra-acetic acid or the alkali metal, alkaline earth metal and ammonium salts thereof, alkali metal citrates and the like. The amount of the chelating agent employed is generally somewhat lower than that of a polyphosphate-type stabilizer. In general, an amount of from 0.01% to 2%, preferably from 0.05% to 0.5%, by weight, based on the oven-dry weight of the pulp is sufficient. Any of the foregoing types of stabilizers for the hydrosulfite may be used singly or in admixture with each other.

A freshly prepared aqueous solution of a stabilized hydrosulfite should have a pH value in the neighborhood of neutrality. A satisfactory pH range for such solution may range from about 5 to about 12, depending on the type of hydrosulfite employed and the acidity of the pulp to be bleached. If necessary, a small amount of an alkaline material, such as sodium hydroxide, sodium carbonate, and the like, may be added into the bleaching solution for adjustment for its pH within the above indicated range. After the hydrosulfite containing solution having a pH within the above stipulated range has been added to and mixed with the pulp to be bleached in an atmosphere substantially free of oxygen, the pH of the mixture during bleaching is maintained at a value between about 4 and 8, preferably between about 5 and 7.

The lignocellulosic pulp is treated with the hydrosulfite bleaching agent at a temperature which lies broadly between 100° F. and about 230° F., preferably between 140° F. and 215° F. The bleaching treatment is continued for a time sufficient to produce a substantial increase in the pulp brightness.

The duration of the bleaching treatment is determined by such factors as the bleaching temperature, the amount of bleaching agent employed, the pulp consistency, and the identity of the lignocellulosic pulp. In general, however, a reaction time at a temperature of from 100° F. to 230° F. will be from one minute to about sixty minutes, the longer reaction times being employed with the lower temperatures and vice versa.

The accompanying drawing is a graph plotting the bleaching time in minutes against the bleaching temperature in degrees Fahrenheit. The curves shown represent time required for bleaching groundwood at three pulp consistency levels, namely 2.5%, 4% and 25% by weight, respectively, in an atmosphere substantially oxygen-free, using 1% of sodium hydrosulfite and 0.5% of sodium tripolyphosphate, by weight, each based on the weight of oven-dry pulp. The bleaching time, as indicated, was required in each case to increase the original brightness of the pulp from 59% GE to 70% GE, or a brightness increase of 11 points.

As is apparent from the drawing, a considerable reduction in bleaching time at a given temperature level, this being accompanied by other advantages, as explained hereinabove, can be realized by hydrosulfite bleaching of pulp at high consistency.

Although a batch process may be used for bleaching the lignocellulosic pulp in accordance with the present invention, it is preferred in commercial practice to carry out this operation continuously. Thus, the pulp which has been thickened to a consistency above 15% and not exceeding 50% by weight may be fed continuously by a suitable conveyor means, such as a screw conveyor, to a suitable air-tight mixing chamber from which oxygen is continuously removed. The stabilized hydrosulfite solution is then continuously fed into the pulp mass at such a rate as to provide a hydrosulfite usage of 0.2–5%, by weight, oven-dry pulp basis, as indicated above. The mixture is subjected to a vigorous agitation in order to obtain a thorough mixing of the bleaching solution with the pulp. The bleaching reaction is continued in an atmosphere substantially oxygen-free for a short period, as may be necessary to obtain a desired pulp brightness increase. The bleached pulp is discharged by dumping or any other suitable means to a dilution tank where it is mixed with water to a consistency level suitable for papermaking operations.

The present invention is further illustrated by the following specific examples which are not intended to limit the scope thereof.

Example 1.—Groundwood pulp derived from west coast softwood species having the brightness of 59% GERS (General Electric Recording Spectrophotometer) is partially dewatered to a consistency of 28.4% and shredded in the form of small particles. It is then placed in a suitable air-tight vessel provided with agitating means. Live steam is injected into the pulp-containing vessel in order to purge out substantially all of the air therefrom. An aqueous bleaching solution containing 2% by weight of sodium hydrosulfite, 1% by weight of sodium tripolyphosphate and 0.16% by weight of sodium hydroxide, is added to the deaerated pulp in an amount sufficient to provide 1% by weight of hydrosulfite, based on the weight of oven-dry pulp. The resulting mixture, having a consistency of about 25%, and a pH 5.5, is vigorously agitated to insure a substantially uniform distribution of the bleaching agent throughout the pulp mass and maintained in an atmosphere substantially free of oxygen at a temperature of about 212° F. for five minutes. It is next discharged from the vessel, further diluted with water and formed into a sheet. The resulting bleached pulp produced by the foregoing procedure has a brightness value of 70% GERS, corresponding to a brightness increase of 11 points.

Example 2.—The same pulp as described in Example 1 is treated in the same manner as in Example 1, except that the pulp consistency during bleaching is 18% and the reaction time is 10 minutes. The resulting bleached pulp has a brightness of 70% GERS, or a brightness increase of 11 points.

Example 3.—Groundwood pulp having 58% GE brightness is bleached in an atmosphere substantially free of oxygen obtained by applying a vacuum of about 24 inches of mercury in the reaction vessel. The pulp is subjected to the action of the same bleaching solution and in the same amount as described in Example 1 for 30 minutes at a temperature of 140° F. at 25% consistency. The pH of the pulp mixture is maintained at 6 during bleaching. At the end of this reaction period the bleached pulp is discharged, diluted with water and formed into a sheet. The resulting pulp has a brightness of 70% GERS, corresponding to a brightness increase of 12 points.

Example 4.—The same pulp as employed in Example 1 is treated in the same manner as described in Example 3 with a reducing bleaching agent consisting of an aqueous solution containing 1% of zinc hydrosulfite and 0.5% of sodium tripolyphosphate by weight. The amount of the hydrosulfite added is 1.11%, by weight, based on the oven-dry weight of pulp. The pulp is bleached at 25% consistency in an atmosphere substantially free of oxygen for 30 minutes at 140° F. The resulting bleached pulp has a brightness of 70% GERS, compared to its initial brightness value of 59% GERS. Hence, an increase in brightness of 11 points is achieved.

Example 5.—Unbleached sulfite pulp produced by cooking western hemlock by the conventional acid sulfite process is admixed with the same groundwood pulp as described in Example 1 in the proportion of 20% and 80%, respectively. The brightness of the pulp is 60% GERS. The pulp at 28% consistency is shredded and placed in a suitable air-tight vessel provided with agitating means. In order to remove air from the vessel, the pulp is heated to 170° F., the pressure is reduced to a value corresponding to the vapor pressure of water at this temperature (a vacuum of about 18 inches of mercury), then nitrogen gas is injected while normal atmospheric pressure is gradually restored in the vessel. The same bleaching solution as employed in Example 1 is added to the pulp in amount sufficient to give 1.5% hydrosulfite and 0.75% polyphosphate by weight, based on the weight of oven-dry pulp. The bleaching is carried out with continuous agitation in the atmosphere of nitrogen at 170° F. for 25 minutes. The consistency of the pulp during bleaching is about 25% and the pH value of 5.5 is maintained throughout the reaction period. The brightness of the resulting bleached pulp is 72% GERS, corresponding to a brightness increase of 12 points.

It will be apparent that by the practice of the present invention we have provided an improved process for the manufacture of high quality lignocellulosic pulps, particularly groundwood, or high degree of brightness which process includes bleaching high consistency pulp in form of a non-flowable, semi-solid mass, incapable of forming a continuous stream upon pouring, in an atmosphere substantially free of oxygen using a stabilized, water-soluble hydrosulfite as the essential bleaching agent. It will be also apparent that the bleaching procedure with a hydrosulfite at high consistencies in accordance with the present invention, presents several advantages over that conventionally practiced in the pulp industry wherein low-consistency, flowing streams of slush pulps are employed. These advantages include a more efficient use of the reducing bleaching agent, a considerable reduction in bleaching time, heat economy, use of small size equipment, and reduction of stream pollution due to a smaller volume of effluent produced. The foregoing and other advantages can be achieved without any impairment of other physical or chemical properties of the resulting bleached pulps.

Having thus described our invention in preferred embodiments, we claim:

1. The continuous process of bleaching lignocellulosic pulp which comprises feeding into an air-tight zone a semi-solid, non-flowable, moist mass of pulp in particulate form, removing substantially all of the air therefrom, forming a mixture containing said pulp and a reducing bleaching agent comprising essentially a stabilized aqueous solution of a hydrosulfite selected from the group consisting of zinc, alkali metal and ammonium hydrosulfites, the amount of said hydrosulfite being from 0.2% to 5%, by weight, oven-dry pulp basis, and mixing mechanically said pulp with said hydrosulfite in an atmosphere substantially free of oxygen at a temperature of from 100° F. to 230° F. for a period of time sufficient to produce a substantial increase in the pulp brightness, the pH of said mixture during bleaching being maintained between about 4 and 8.

2. The process of claim 1 wherein the pH of the mixture is maintained between about 5 and 7.

3. The process of claim 1 wherein air is removed from the pulp by purging with live steam and the pulp is bleached at a temperature of about 212° F.

4. The process of claim 1 wherein the hydrosulfite comprises zinc hydrosulfite.

5. The process of claim 1 wherein the hydrosulfite comprises sodium hydrosulfite.

6. The process of claim 1 wherein the amount of the hydrosulfite employed is from 0.5% to 2% by weight.

7. The process of claim 1 wherein the consistency of the pulp and the reducing bleaching agent mixture is from above 15% to 50%.

8. In the bleaching of lignocellulosic pulp with a hydrosulfite reducing bleaching agent in an atmosphere substantially free of oxygen at a temperature between about 100° F. and 230° F. wherein the pH of the pulp is maintained at a value between about 4 and 8, the improvement which comprises feeding a semi-solid, nonflowable, moist mass of pulp in particulate form into an air-tight vessel, removing substantially all of the air from said vessel to provide therein an atmosphere substantially free of oxygen, adding to the pulp a solution containing a hydrosulfite selected from the group consisting of zinc, alkali metal and ammonium hydrosulfites and a stabilizer therefor selected from the group consisting of water-soluble polyphosphates, ethylene-diamine-tetra-acetic acid and the alkali metal, alkaline earth metal and ammonium salts thereof, and alkali metal citrates, and mixing mechanically said pulp with said solution in an atmosphere free of oxygen for a period of time sufficient to produce a substantial increase in brightness of said pulp, the respective amounts of the hydrosulfite and of the stabilizer employed being from 0.2% to 5% and from 0.01% to 2% by weight, based on the weight of oven-dry pulp.

9. The process of claim 8 wherein the moist mass of pulp is at a consistency from above 15% to 50%.

10. The process of claim 8 wherein the pulp comprises groundwood.

11. The process of claim 8 wherein the hydrosulfite comprises sodium hydrosulfite.

12. The process of claim 8 wherein the hydrosulfite comprises zinc hydrosulfite.

13. The process of claim 8 wherein the pH of the pulp during bleaching is maintained at a value between about 5 and 7.

14. The process of claim 8 wherein the temperature of the pulp during bleaching is between about 140° F. and 215° F.

15. The process of claim 8 wherein the amount of the hydrosulfite employed is from 0.5% to 2% by weight based on the weight of oven-dry pulp.

References Cited in the file of this patent

UNITED STATES PATENTS

2,194,956	Taylor	Mar. 26, 1940
2,224,159	Parrett	Dec. 10, 1940
2,707,144	Sparrow et al.	Apr. 26, 1955
2,707,145	Sparrow et al.	Apr. 26, 1955

OTHER REFERENCES

Witham: Modern Pulp and Paper Making, pub. by Reinhold, New York, 1942, p. 283.