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METHOD OF BLEACHING MECHANICALLY DISINTEGRATED WOOD PULP

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The present invention relates to an improved process for bleaching wood pulp, and more particularly it relates to an improved process for bleaching mechanically-disintegrated wood pulp involving the use of a water-soluble hydrosulphite in conjunction with an agent providing a markedly-improved bleach.

The bleaching of wood pulp, particularly mechanically-disintegrated wood pulp, is well known. One of the bleaching agents which have been suggested for this purpose is a water-soluble hydrosulphite. By the use of a hydrosulphite, the brightness of mechanically-disintegrated wood pulp, which is normally in the neighborhood of about 60% when measured by the General Electric Reflectance Meter, can be increased a few points at the most. Attempts have been made to increase this bleaching effect through the use of pH control, temperature control, buffering agents, whitening agents, and the like. However, no substantial improvement resulted from these attempts.

It is a principal object of the present invention to provide an improved process for bleaching mechanically-disintegrated wood pulp wherein the brightness increase is markedly greater than that obtained by the above-stated prior methods.

Another object of the present invention is to provide an improved method for bleaching mechanically-disintegrated wood pulp involving the use of a water-soluble hydrosulphite wherein the brightness increase realized is markedly greater than that obtained through the above-stated prior methods involving the use of a hydrosulphite.

Still another object of the present invention is to provide a simple method for bleaching mechanically-disintegrated wood pulp involving the use of a water-soluble hydrosulphite in conjunction with another agent, whereby the brightness increase obtained is substantially greater than that obtained through the use of a water-soluble hydrosulphite alone.

Further objects will be apparent from a consideration of the following specification and claims.

In co-pending application Serial No. 240,982, filed August 8, 1951, is disclosed and claimed a method of bleaching mechanically-disintegrated wood pulp involving the use of a water-soluble polyphosphate in conjunction with a water-soluble hydrosulfite whereby an improved brightness increase is obtained. The brightness increase obtained by the present process is on the same order as that obtained in accordance with the process of the stated co-pending application.

The bleaching process of the present invention comprises intimately mixing, with mechanically-disintegrated wood pulp at an elevated temperature, a water-soluble hydrosulphite and ethylene diamine tetra acetic acid or a salt thereof as hereinafter described. For simplicity herein the term "ethylene diamine tetra acetic acid" will refer to the herein-described salts of the free acid as well as to the free acid itself. The ethylene diamine tetra acetic acid will be mixed with the pulp at a time not substantially later than that at which the hydrosulphite is mixed with the pulp, and preferably the hydrosulphite and ethylene diamine tetra acetic acid are mixed substantially simultaneously with the wood pulp. The hydrosulphite and ethylene diamine tetra acetic acid are left in contact with the pulp until the desired bleaching is obtained.

By the use of the ethylene diamine tetra acetic acid in conjunction with a water-soluble hydrosulphite in accordance with the present invention, a substantial increase in brightness in the treated wood pulp is obtained, and this increase is substantially greater than the increase obtained when a hydrosulphite alone is employed. While the exact reason for this is not fully understood, the following theory is advanced by way of explanation. Mechanically-disintegrated wood pulp contains metal ions including iron, manganese, copper, nickel and cobalt, the iron predominating. Water-soluble hydrosulphites are relatively unstable in solution particularly at elevated temperatures, and this instability appears to be aggravated to a very great extent in the presence of wood pulp. It is, therefore, believed that the stated metal ions catalyze the decomposition of the hydrosulphite. This rapid decomposition of the hydrosulphite prevents that material from exerting its fullest bleaching effect. Since experiments have shown that, in mechanically-disintegrated wood pulp, the hydrosulphite is about five times more stable when ethylene diamine tetra acetic acid is present, it is believed that the ethylene diamine tetra acetic acid combines with the stated metal ions forming complexes therewith, thus preventing their adverse effect on the hydrosulphite. This belief is further strengthened by the fact that if the ethylene diamine tetra acetic acid is added to the wood pulp some time after the hydrosulphite is added thereto, the advantages of the present invention are not realized. Thus, as indicated above, the ethylene diamine tetra acetic acid must be incorporated in the wood pulp not substantially later than the time at which the hydrosulphite is mixed with the wood pulp. Regardless of the theory, it is a fact that the incorporation of the ethylene diamine tetra acetic acid with the hydrosulphite in the wood pulp results in a marked improvement in the bleaching effect realized from the hydrosulphite.

Moreover, mechanically-disintegrated wood pulp contains a relatively high concentration of lignins which often react with certain of the metal ions, particularly iron, to form highly coloring products. The combining of the ethylene diamine tetra acetic acid with the stated metal ions thus also prevents the metal ions from combining with the lignin accounting for a further increase in brightness.

As stated, the compound employed in conjunction with the hydrosulphite in accordance with the present invention may be the free ethylene diamine tetra acetic acid or a salt thereof. The acid contains four carboxyl groups the hydrogen of any one or more of which may be substituted by a metal or ammonium ion. In other words, the salts may range from the mono salt to the tetra salt. Suitable salts are those of the alkali metals such as sodium, potassium, lithium, and the like; the alkaline earth metals, such as calcium, magnesium, and the like; and the ammonium salts. Mixed salts may be used if desired. Of the free acid and salts mentioned, the alkali metal salts, particularly the sodium salts, are preferred. Since the salts supply the ethylene diamine tetra acetic acid radical and, therefore, function substantially the same as when the free acid is employed, the term "ethylene diamine tetra acetic acid" is employed, for the sake of simplicity, throughout this specification to refer both to the free acid and to the described salts unless otherwise noted.

Referring to the wood pulp treated in accordance with the present invention, it is, as stated, mechanically-disintegrated wood pulp. There are two types of such wood pulp: (1) ground wood pulp and (2) semi-chemical wood pulp. Ground wood pulp, as is well-known, is obtained merely by grinding logs to reduce the logs to fibers. Semi-chemical wood pulp is obtained by first reducing the log to chips, treating the chips briefly with chemicals, such as sodium sulphite and sodium bicarbonate, at elevated temperature and pressure preliminarily to soften the chips somewhat, and grinding the chips to fibers. Both ground wood pulp and semi-chemical wood pulp are relatively high in lignin content, and accordingly, present a particularly difficult problem, from the standpoint of bleaching, as compared to normal chemical pulp.

The pulp treated in accordance with the present invention may be obtained from several different sources. That is to say it may be ground wood pulp or semi-chem-

ical pulp coming directly from the grinder, or from a point in the pulp-processing procedure remote from the grinder. On the other hand, the pulp coming from the grinder may be first dried and baled, and the bales shipped to a distant point where they are broken up and repulped. The pulp treated in accordance with the present invention may be such repulped material. The source of the pulp treated in accordance with the present invention is relatively immaterial so long as during the bleaching process it has the proper consistency. Generally, the consistency of the pulp treated in accordance with the present process will be at least about 0.5% by weight, and the consistency thereof may range up to the point where satisfactory mixing begins to be no longer feasible, for example up to 10%, or even 15%, by weight, if desired. Preferably, however, the consistency of pulp is between about 2% and about 5%, by weight. Generally, both the pulp coming directly from the grinder and the repulped material will have a consistency within these ranges. The consistency of pulp obtained from other points in the pulp-processing treatment may require adjustment, and, if such be the case, the consistency of the pulp can be adjusted to the desired level by simply adding or removing water.

As stated previously, the treatment in accordance with the present invention is at an elevated temperature. That is to say, the temperature of the pulp during the treatment will be above normal room temperature, and generally will be above about 120° F., more generally above about 135° F. While the temperature of the pulp may range as high as 212° F., no advantage is to be gained by operating at such temperatures, and a preferred operating range is between about 160 and about 190° F. The provision of the stated temperature will offer no problem to those skilled in the art. In the event fresh ground wood pulp, that is slurry coming directly from the grinder, is being treated, such pulp will generally be at a satisfactory temperature due to the heat generated during the grinding operation.

In accordance with the process of the present invention there is added to the stated wood pulp, a water-soluble hydrosulphite as the main bleaching agent. Water-soluble hydrosulphites employed for bleaching wood pulp are well-known and include zinc hydrosulphite, the alkali metal hydrosulphites, such as sodium hydrosulphite and potassium hydrosulphite, ammonium hydrosulphite, and the like. Of the various water-soluble hydrosulphites, sodium hydrosulphite and zinc hydrosulphite, particularly the former, are preferred. The hydrosulphite may be added to the pulp in solid form or as a solution in water. However, in order to insure intimate mixing of the hydrosulphite with the pulp, it is preferred that the hydrosulphite first be dissolved in water and the resulting solution then mixed with the pulp. The amount of hydrosulphite incorporated in the pulp may vary somewhat depending upon the type of pulp treated, the degree of brightness increase desired, and other factors known to those skilled in the bleaching art. Generally, the amount of hydrosulphite mixed with the pulp will be at least about 0.25%, by weight, based on the weight of the dry pulp. While amounts of hydrosulphite as high as about 5% or even higher, may be employed, no significant advantage is to be gained by using amounts substantially in excess of about 3%, by weight. Preferably, the amount of hydrosulphite employed will be between about 0.5% and about 1.5%, by weight, based on the dry weight of the pulp.

As in the case with the hydrosulphite, the ethylene diamine tetra acetic acid may be added to the wood pulp as a solid or as an aqueous solution or dispersion thereof, preferably in the form of a solution. The amount of ethylene diamine tetra acetic acid employed may vary somewhat depending upon the type of pulp treated and the degree of brightness increase desired. The amount of ethylene diamine tetra acetic acid employed may be as low as about 0.01%, by weight, based on the weight of the dry pulp, particularly if the compound is used in conjunction with a water-soluble polyphosphate in accordance with co-pending application Serial No. 240,982. While amounts of the compound as high as about 2% or even higher, may be employed, no significant advantage is to be gained by the use of amounts thereof substantially in excess of about 1%. Preferably, the amount of ethylene diamine tetra acetic acid employed is between about 0.05% and about 0.5%, by weight, based on the weight of the dry pulp.

As stated previously, the ethylene diamine tetra acetic acid will be added to the pulp not substantially later than the time when the hydrosulphite is added to the pulp. This means, of course, that ethylene diamine tetra acetic acid may be added to the pulp at any time before, or at the same time as the hydrosulphite is added thereto, or may even be added directly after the hydrosulphite is added to the pulp. Thus, the term "not substantially later" when used in connection with the time of addition of the ethylene diamine tetra acetic acid to the pulp in relation to the time of addition of the hydrosulphite, means that any delay between the addition of the hydrosulphite to the pulp and the addition of the ethylene diamine tetra acetic acid to the pulp will not be such as will permit a substantial amount of the hydrosulphite to be decomposed before the ethylene diamine tetra acetic acid is mixed therewith. As stated previously, the ethylene diamine tetra acetic acid and the hydrosulphite are preferably mixed substantially simultaneously with the wood pulp. Thus, the hydrosulphite and the ethylene diamine tetra acetic acid may be added separately but substantially simultaneously, or the hydrosulphite and the ethylene diamine tetra acetic acid may be premixed, for example, in water, and the resulting mixture added to the pulp. This latter means is the preferred way of incorporating and mixing the hydrosulphite and ethylene diamine tetra acetic acid with the wood pulp.

The hydrosulphite and ethylene diamine tetra acetic acid, as stated, must be intimately mixed with the wood pulp. This intimate mixture may be obtained through a wide variety of means, such as the use of conventional mixing blades, and the like. Following mixing, the hydrosulphite and ethylene diamine tetra acetic acid are permitted to remain in contact with the pulp until the desired bleaching has taken place. This time of contact may be varied depending upon the amounts of hydrosulphite and of ethylene diamine tetra acetic acid employed, the temperature conditions employed, the type of pulp treated, the degree of brightness desired, as well as the other considerations known to those skilled in the bleaching art. However, in general, the time may range from as little as a few minutes, for example three minutes, up to an hour and a half or even longer. Under the preferred operating conditions referred to above, satisfactory bleaching may be obtained in from about 10 to about 30 minutes.

The pH of the mixture during the process should not be permitted to become substantially alkaline, that is to say, the pH of the medium during the bleaching treatment should not be substantially in excess of about 8.5 A pH on the acid side of neutrality may be, and preferably is, employed, and a pH as low as about 3 is satisfactory. The precise pH employed will depend somewhat upon the nature of the hydrosulphite and the form of the ethylene diamine tetra acetic acid selected. In most cases, the pH will range between about 4 and about 6.5, with pHs between about 5 and about 6 being preferred. The adjustment of the pH, if after the addition of the hydrosulphite and ethylene diamine tetra acetic acid such adjustment is desired, will offer no problem to those skilled in the art, and conventional alkaline or acidic materials may be employed.

An advantageous method of mixing the hydrosulphite and ethylene diamine tetra acetic acid with the wood pulp, and carrying out the bleaching treatment in general, is the process described and claimed in co-pending application Serial No. 240,897 filed August 8, 1951. In accordance with that process, the bleaching material, in aqueous solution, is continuously fed to a continuously-moving stream of the wood pulp. Thereafter, the mixture of bleaching material and pulp is subjected to combined vigorous agitation whereby the solution of bleaching material is intimately mixed with the pulp, and propulsion forcing the mixture of pulp and bleaching material as continuously-moving stream, preferably characterized by streamlined plug flow, along a confined, air-tight path. The flow mixture of pulp and bleaching material will substantially fill the cross-section of the confined path. The mixture is flowed continuously in the closed circuit until the desired bleaching is obtained. In accordance with the preferred embodiment of that process, the confined, air-tight path comprises a vertical fluid way, particularly an alternately vertically ascending

and vertically descending fluid way, such as a series of upright columns through which the mixture of pulp and bleaching material flows in series. The pulp-consistency, concentration of hydrosulphite and ethylene diamine tetra acetic acid, temperature and pH, are as mentioned above.

After the desired bleaching has been obtained, the pulp suspension may be treated to de-water it, in accordance with the usual practice, or may be made directly into paper. For example, the suspension may be diluted and sent to a bull screen where any chunks of wood not previously removed are removed, following which the suspension may be diluted further, for example to about 0.3–0.4% consistency. After the diluted, bleached pulp is run through a fine screen, if desired, the pulp may be de-watered on a wet lap machine, for example, to a consistency of about 25%, and then pressed to a consistency of about 50%.

While the foregoing description has dealt primarily with a hydrosulphite as the bleaching agent, it will be realized that the process is not limited to a hydrosulphite as the sole bleaching agent and that other bleaching agents may be employed in conjunction with the hydrosulphite. Likewise, the process is not limited to the use of ethylene diamine tetra acetic acid as the sole supplemental agent, and it will be understood that other agents may be included for whatever effect desired.

The process of the present invention will be more readily understood from a consideration of the following specific example which is given for the purpose of illustration only and is not intended to limit the scope of the invention in any way.

Example

To ground wood pulp, at a temperature of about 176° F. and at a consistency of about 3%, is added the tri sodium salt of ethylene diamine tetra acetic acid followed by an aqueous solution of sodium hydrosulphite. The amounts of those materials added are .1% and 1%, by weight, respectively, based on the weight of the dry pulp. During the addition of these materials, the pulp is agitated vigorously and for about 15 seconds thereafter. The pulp is then held without agitating for about 10 minutes. The resulting pulp has a brightness of 72.4% (as measured on the General Electric Reflectance Meter) as compared to the unbleached pulp which has a brightness of 61.1%.

Considerable modification is possible in the selection of the various ingredients and in the amounts thereof as well as in the particular technique followed in carrying out the process without departing from the scope of the invention.

We claim:

1. In the bleaching of mechanically-disintegrated wood pulp by the use of a water-soluble hydrosulphite, the improvement which comprises mixing with said wood pulp, at a time not substantially later than that at which the hydrosulphite is mixed with the pulp, a compound selected from the group consisting of ethylene diamine tetra acetic acid and the alkali metal, alkaline earth metal and ammonium salts thereof, whereby the hydrosulphite and compound are in admixture with said wood pulp during bleaching.

2. In a bleaching of mechanically-disintegrated wood pulp wherein a water-soluble hydrosulphite is mixed with the wood pulp at elevated temperature, the improvement which comprises mixing with said wood pulp, at a time not substantially later than that at which the hydrosulphite is mixed with the pulp, a compound selected from the group consisting of ethylene diamine tetra acetic acid and the alkali metal, alkaline earth metal and ammonium salts thereof, whereby the hydrosulphite and compound are in admixture with said wood pulp during bleaching.

3. The method of claim 2 wherein the temperature of the pulp is between about 120° F. and about 212° F., and wherein the compound selected is an alkali metal salt of ethylene diamine tetra acetic acid.

4. The method of claim 3 wherein the temperature of the wood pulp is above about 135° F., and wherein the compound selected is a sodium salt of ethylene diamine tetra acetic acid.

5. In the bleaching of mechanically-disintegrated wood pulp wherein a water-soluble hydrosulphite is mixed with the pulp, the improvement which comprises mixing with the wood pulp, substantially simultaneously with the hydrosulphite, a compound selected from the group consisting of ethylene diamine tetra acetic acid and the alkali metal, alkaline earth metal and ammonium salts thereof.

6. The method of claim 5 wherein the temperature of the wood pulp is between about 120° F. and about 212° F., and wherein the compound selected is an alkali metal salt of ethylene diamine tetra acetic acid.

7. The method of claim 6 wherein the alkali metal salt is a sodium salt of ethylene diamine tetra acetic acid.

8. The method of bleaching mechanically-disintegrated wood pulp which comprises intimately mixing with said wood pulp at a consistency of between about 0.5% and about 10% and at a temperature between about 120° F. and about 212° F., a water-soluble hydrosulphite and a compound selected from the group consisting of ethylene diamine tetra acetic acid and the alkali metal, alkaline earth metal and ammonium salts thereof, said ethylene diamine tetra acetic acid compound being mixed with said pulp at a time not substantially later than that at which said hydrosulphite is mixed with the pulp, whereby the hydrosulphite and compound are in admixture with said wood pulp during bleaching.

9. The method of claim 8 wherein the consistency of the pulp is between about 2% and about 5%; wherein the temperature of the pulp is above about 135° F., and wherein the compound selected is an alkali metal salt of ethylene diamine tetra acetic acid.

10. The method of bleaching mechanically-disintegrated wood pulp which comprises intimately mixing with said pulp at a temperature between about 120° F. and about 212° F., a water-soluble hydrosulphite and a compound selected from the group consisting of ethylene diamine tetra acetic acid and the alkali metal, alkaline earth metal and ammonium salts thereof, said ethylene diamine tetra acetic acid compound being mixed with said pulp at a time not substantially later than that at which said hydrosulphite is mixed with said pulp whereby the hydrosulphite and compound are in admixture with said wood pulp during bleaching, and said mixture of pulp, hydrosulphite and ethylene diamine tetra acetic acid compound having a pH between about 3 and about 8.5.

11. The method of claim 10 wherein the pH of the mixture is between about 4 and about 6.5, and wherein the compound selected is a sodium salt of ethylene diamine tetra acetic acid.

12. The method of bleaching mechanically-disintegrated wood pulp which comprises mixing with said pulp, at a consistency of between about 0.5% and about 10% and at a temperature between about 120° F. and about 212° F., a water-soluble hydrosulphite and an alkali metal salt of ethylene diamine tetra acetic acid, said ethylene diamine tetra acetic acid salt being mixed with said pulp at a time not substantially later than that at which said hydrosulphite is mixed with said pulp whereby the hydrosulphite and the salt are in admixture with said wood pulp during bleaching, and said mixture of pulp, hydrosulphite and ethylene diamine tetra acetic acid salt having a pH between about 3 and about 8.5

13. The method of claim 12 wherein the consistency of said pulp is between about 2% and about 5%; wherein the temperature of said pulp is above about 135° F.; wherein the alkali metal salt is a sodium salt of ethylene diamine tetra acetic acid; wherein said ethylene diamine tetra acetic acid salt is mixed with said pulp substantially simultaneously with said hydrosulphite, and wherein the pH of the mixture of pulp, hydrosulphite and ethylene diamine tetra acetic salt is between about 4 and about 6.5.

14. The method of claim 13 wherein the temperature of said pulp is between about 160 and about 190° F.; and wherein the pH of said mixture is between about 5 and about 6.

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