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PROCESS FOR BLEACHING WOOD PULP WITH FLUORINE, HYDROFLUORIC ACID, AND OXYGEN DIFLUORIDE

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ABSTRACT OF THE DISCLOSURE

A method of bleaching wood pulp with fluorine, hydrofluoric acid, or oxygen difluoride. The pulp is contacted with from 0.5 to 9% by weight of pulp of one of the above compounds for a period of from 1 to 4 hours and at a temperature of from 60–160° F. Subsequent to the bleaching process the bleach liquor is treated with a calcium compound, such as, lime to precipitate the fluorides in the liquor.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Ser. No. 582,177, filed Aug. 25, 1966.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to processes of bleaching fibrous materials. In one aspect, the invention relates to processes of bleaching wood pulp and natural fibers, such as are used in the processes for making paper, and the like. In a further aspect the invention relates to a process for the combined bleaching and removal of siliceous compounds from the nodes of grasses such as bagasse and the like. In another aspect, the invention relates to a bleaching process in which pollution caused by waste liquors and wash waters can be more readily removed by subsequent treatments.

In a further aspect, my invention relates to a combined bleaching and pollution treating process which substantially reduces or eliminates pollution caused by waste liquors and wash waters.

THE PRIOR ART

The prior art processes of bleaching wood pulp and other cellulosic fibers to high whiteness and brightness using chemical bleaching agents such as chlorine or hypochlorite are frequently accompanied by deleterious fiber degradation or deterioration during the bleaching. Current bleaching technology, particularly applied to the bleaching of chemical wood pulp for paper, uses chlorine, caustic soda, calcium and sodium hypochlorites, chlorine dioxide, sodium and hydrogen peroxides. With groundwood pulp, reducing agents, such as zinc or sodium hydrosulphite may be used, with or without the use of hydrogen peroxide. In the usual conventional processes, several chemicals are used in series or stages, with residues from the reaction usually being washed out between the stages. In spite of the large amount of work that has been done in this field, and the large number of multi-stage bleaching processes that have been developed, there is still no completely satisfactory answer to the problem of bleaching without some fiber degradation.

Further, the wash waters, particularly from the bleaching of wood pulps, present a disposal and pollution problem since they usually contain unexhausted bleaching chemicals as well as the materials removed from the pulp by the bleaching process.

The prior art has discovered that chlorine dioxide used in one or more stages has the property of bleaching without substantial degradation, but chlorine dioxide is quite costly and requires special handling due to its explosive tendency. Thus, chlorine dioxide does not represent a completely satisfactory solution.

The use of hydrofluoric acid to remove adventitious and adhering sand from cotton linters is known to the art as described in U.S. Patent 1,911,030. However, the use of fluorine or fluorine compounds to effect combined bleaching and removal of siliceous compounds which are internally formed within or as a part of the nodes of grasses such as bagasse is to my knowledge heretofore unknown.

Thus, it would be very desirable to provide a bleaching process which would alleviate both the fiber degradation and pollution problems of the prior art.

OBJECTIVES AND SUMMARY OF THE INVENTION

Objects

It is therefore an object of my invention to provide improved bleaching processes and also to provide bleaching processes which facilitate pollution control.

It is a further object of my invention to provide improved bleaching processes which cause substantially less fiber degradation.

It is a still further object of my invention to provide bleaching processes which yield fibers having increased brightness.

It is another object of my invention to provide bleaching processes using fluorine or a fluorine-generating compound as a bleaching agent for fibers.

It is also an object of my invention to provide a process for the combined bleaching and removal of siliceous compounds from the nodes of grasses such as bagasse, wheat straw, esparto grass and the like.

It is still another object of my invention to provide bleaching processes wherein the wash waters and waste liquors from the bleaching process can be handled in a manner to eliminate or markedly reduce the pollution of water courses to which they are usually run, or the pollution of the general environment.

Another object of my invention is to provide combined fiber bleaching and pollution removal processes.

Additional objects will be apparent, and in part obvious, from the following description and appendant claims.

Summary

In summary, I have discovered that these and other objects can be obtained by the use of fluorine and/or the reaction product of fluorine compounds, as a bleaching agent. I have also discovered that a very substantial increase in brightness can be secured in bleaching fibrous materials, such as for example, wood pulp, by treating it with fluorine compounds or gaseous fluorine and further that this bleaching is accomplished with very little fiber degradation. While my invention is particularly advantageous for the bleaching of wood pulp, it is also well suited for the bleaching of natural fibers in general. However, my bleaching process should be distinguished from processes such as are used to remove stains from fabrics. According to my bleaching process the actual whiteness and brightness of the fiber in its natural state is increased prior to its manufacture into paper or fabric. By brightness is meant the index of light reflected from a light source having a wave length of about 457 angstroms measured by the General Electric Brightness tester.

The bleaching process according to my invention can

be carried out using conventional mechanical procedures and equipment such as is for example used for bleaching with chlorine or chlorine compounds, but using at least one gaseous fluorine or fluorine compound bleaching step.

In summary, the process controlling bleaching pollution according to my invention comprises treating the waste liquors and wash waters from my bleaching process with a reactive calcium compound, conveniently lime. The fluorine constituent will be partially or completely, depending upon interfering substances, precipitated as an insoluble calcium compound. This precipitate can then be removed by conventional liquid-solid separation processes; such as for example settling, centrifuging, filtering or the like, or by a combination of such separating processes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Considering now my invention in greater detail, my invention can be conveniently described with reference to a conventional bleaching sequence.

A conventional bleaching sequence, for example, uses a series of stages which for covenience are designated by certain letters. For example, C is used to designate chlorination, E for extracting using caustic soda, H for sodium or calcium hypochlorite, D for chlorine dioxide and P for hydrogen peroxide. Thus, for example, a bleaching sequence for a sulphite pulp might be designated as CEH; C for chlorination, E for caustic soda extraction, and H for hypochlorite. A bleaching cycle for sulphate pulp might be designated as CEHED; i.e. chlorination, extraction, hypochlorite, extraction and chlorine dioxide. Another cycle might be six stage as CEHEHD; i.e. chlorination, extraction, hypochlorite, extraction, hypochlorite and chlorine dioxide. Another cycle might be CEDED. It is apparent that many other combinations may be used according to the properties desired in the bleached pulp and the starting material used in the process.

The C stage is used mostly for purification of the pulp by chlorinating the non-cellulosic materials present such as lignin. The E stage is used to solubilize and wash out chlorinated substances. The H stage is used to bleach and whiten the pulp and the D stage is added to further whiten the pulp without substantially decreasing its strength. The P stage is sometimes used at the end to reduce loss of brightness of the pulp upon aging.

In each stage it is important to control the concentration or "consistency" of the pulp in suspension in water (called consistency by the industry), the percentage of the chemical used based upon the amount of fiber present, the temperature, the contact time, sometimes known as "dwell" time, and the pH.

In the first stage of my process, I can use a fluorine gas previously dissolved in water or passed directly into the pulp suspension. Alternatively gaseous fluorine can be generated in the presence of the pulp. Another suitable source of fluorine is commercial anhydrous hydrogen fluoride; this can be added directly to the pulp suspension alone or in combination with gaseous fluorine or sodium fluoride. Further, any fluorine compound which will act, or can be suitably activated to act, as a fluorinating or oxidizing agent can be used in the practice of my invention. The effects of the fluorine or its compounds upon the pulp are completed before the pulp is exposed to human contact. The fluorine bleaching treatment of my invention can be carried out by contacting the pulp with fluorine or a suitable fluorine compound in an amount equal to 0.5 to 9 percent by weight based on the weight of the pulp at a temperature of about 90 to 160° F. for a period of 1 to 4 hours. Suitable bleaching agents which can be used in any process include fluorine, hydrofluorine acid and oxygen difluoride.

I prefer to designate my fluorine stage as F so that it can be written for example in a bleaching sequence as FEH meaning: fluorine, extraction and hypochlorite. Other examples where a fluorine stage can be used in

place of a chlorine stage, according to my invention, include systems designated FEHED, FEHEHD, FEDED, FED and the like.

Particulraly useful forms of fluorine compounds are the oxy compounds, such as for example, oxygen difluoride (OF_2). Oxygen difluoride can conveniently be prepared in a continuous process by bubbling fluorine into a 2% by weight solution of sodium hydroxide. The effluent from this process is an oxygen difluoride gas that can be passed directly into the pulp at any stage of my bleaching process. This is particularly useful in a final superbleaching stage such as is usually carried out by the use of chlorine dioxide. Even where chlorine dioxide is used in a stage other than the final stage, oxygen difluoride can be used to replace it in that stage. Oxygen difluoride is a particularly suitable source of fluorine for the purpose of my invention since it decomposes into the components oxygen and fluorine at the temperatures of operation used in the normal bleaching system. Hereafter, I shall for convenience, designate the use of oxygen difluoride as the O stage.

The amounts of fluorine compounds to be added in my novel process will closely parallel the amounts of chlorine compounds which would be used in a chlorine system. Thus, if fluorine is added, it is used in the amount of 4 to 9%, usually about 7% by weight based on the pulp in the first stage, and the gaseous fluorine, added as such or generated in the pulp. Typically, a 3% pulp consistency is used. The bleaching reaction can, for example, be carried out at the temperature of about 80 to 90° F. with a retention time of about 1 to 4 hours, usually about 1½ hours. The extraction stage with caustic soda can be carried out with a solution of ½ to 3% by weight caustic soda, preferably about 2½% caustic soda at a pulp consistency of preferably about 12% and a temperature of about 120° F. to 180° F. for a period of preferably about 1 hour and an alkaline pH. In the dioxide stage of the process, the reaction would be carried out preferably with about 0.5% of the fluorine compound at preferably about 12% by weight consistency, at a temperature about 160° F. for a period of about 1 hour. In normal operation, the pulp would be washed between stages. If the pulp were to be treated with a peroxide, it would be a final treatment of the bleached pulp using about 1% usually without subsequent washing. More broadly this embodiment of my invention comprises the steps of: fluorination of the pulp with fluorine or a suitable fluorine compound; washing and extracting the pulp with a sodium hydroxide solution; treating the pulp with oxygen difluoride; and then washing and recovering the bleached product. A more specific form of this general embodiment the fluorination is carried out using a gaseous hydrogen fluoride at a fluorine concentration of 2 to 9% and the oxygen difluoride treatment is carried out with .5 to 15% of the compound (i.e. oxygen difluoride) and a pulp consistency of 3 to 12%.

Considerable variation can be practiced in the amount of chemicals, consistency of the pulp, temperature, dwell time and the number and sequence of steps; and can be arranged to obtain the desired results as to pulp quality, brightness, opacity, strength, viscosity, permanganate number and the like, within, of course, the limits of the original pulp and the effectiveness of the chemical employed. Optimum operating conditions can be obtained by routine experimentation.

Groundwood pulps are bleached according, to the prior art process, in a single stage using about 1% sodium or zinc hydrosulphite at 2 to 5% consistency for about 1 to 2 hours, a temperature of about 110 to 150° F. and a pH of about 4.5 to 6 for the zinc and a pH of about 6–7 for the sodium salt. The single stage can be supplemented by a subsequent stage of 1% sodium or hydrogen peroxide (stabilized with sodium silicate and magnesium sulphate) at 10 to 15% consistency and an alkaline pH for about 3 to 4 hours at 100° F. In accordance with my

invention such pulps can be bleached by employing an F or an O stage in substitution of or in conjunction with the prior art stages.

My process can also be used effectively to simultaneously bleach and remove (dissolve) siliceous compounds from the nodes of grasses such as bagasse, wheat straw and esparto grasses and the like. These grasses contain internal siliceous compounds within their nodes and thus can be rendered suitable for paper pulp only with extreme difficulty. However, according to my process, the grass fiber can be bleached and the siliceous compounds removed by the addition of a fluorine step and/or the substitution of a fluorine step for one chlorine or alkaline steps used in the processes of the prior art. Thus, the same sequence of steps and conditions can be applied to effect the simultaneous bleaching and removal of nodular siliceous compounds as described above with respect to normal fiber bleaching, according to my process.

Considering now the pollution control embodiment of my invention. As noted previously, the waste liquors and wash waters, particularly from the bleaching of wood pulps, present a disposal problem since they usually contain unexhausted bleaching chemicals and also the materials removed from the pulp by the bleaching process. When such waters contain a fluorine compound, as from one of the bleaching processes according to my invention, their pollution potential can be substantially reduced or eliminated. Thus, according to my invention, these waste liquors and wash waters are treated with a calcium compound in reactive form, conveniently lime. The fluorine constituent will be partially, or completely, depending upon the presence of interfering substances, precipitated as a substantially insoluble calcium compound, which can drag down pollutants which may be in suspension within the waste liquor and wash water. The precipitation conditions such as for temperature and pH can be adjusted to further enhance this effect. The precipitate and any entrapped pollutants can be removed by conventional liquid-solid separation means such as for example, settling, centrifuging, filtering and the like; or by a combination of such means.

In a further embodiment, an aluminum compound, such as papermakers alum and the like, can be added to assist in the separation of the precipitate.

Since calcium fluorides are considered non-toxic the resulting insoluble calcium precipitate can be used as a land fill material. Further where the calcium fluoride precipitate is substantially free, or can be conveniently freed, from bleach residues and other contaminants, the precipitate can be used as a source of fluorine for my bleaching processes.

Also, where the so treated waters contain useful material in solution, these materials can be recovered after the calcium precipitate is removed by evaporation.

A further understanding of my invention can be had from the following illustrative, but non-limiting examples of specific, but non-limiting, modes of the invention.

EXAMPLE I

100 grams of a southern pine sulphate pulp having a viscosity of 58.0 centipoises at 3% consistency is treated with 5% by weight fluorine gas, added as such, at a temperature of 75° F. for a retention time of one hour. The pulp is then washed. The second stage is a treatment with 2.0% caustic soda for one hour at 12% consistency and 160° F. The pulp is then washed. The third stage is a treatment with 1.5% sodium hypochlorite for 2½ hours at 12% consistency, pH 10.0 and 95° F. The pulp is then washed. The fourth stage is extraction using 1.0% by weight caustic soda for 1 hour at 12% consistency and 160° F. The pulp is then washed. The fifth stage is a treatment with 1% by weight chlorine dioxide based on the pulp for several hours at 12% consistency and 160° F. The pulp is then given its final washing and the brightness will be about 90.

In this example, oxydifluoride can be used to replace chlorine dioxide in the fifth stage.

EXAMPLE II

100 grams of a soft wood sulphite pulp is bleached by the FEH sequence with washings between the stages and at the end. In the F stage 3% by weight fluorine is used at 3% consistency for ½ to 1 hour at 60° F. with a pH of 2–3, and the E stage 0.5% caustic soda is used at 8% consistency for one hour at 110° F., and in the H stage 3% by weight available chlorine is used at 12% consistency for 2½ hours at 80° F. The pulp brightness will be about 87.

In making dissolving pulp, where a "caustic soak" stage is used, a final treatment with peroxide is precluded by the presence of silicates in the peroxide solution. In place of the P stage an O stage can be employed.

EXAMPLE III

100 grams of an aspen semi-chemical pulp cooked by the cold soda process with a brightness of 39 is treated with 2% zinc hydrosulphite followed by 1% by weight oxydifluoride based on the total amount to obtain a brightness of about 63.

EXAMPLE IV

100 grams of a groundwood pulp with a brightness of 58 is treated with 1% oxydifluoride to obtain a brightness of about 65.

EXAMPLE V

In this example, the liquors and wash waters from Example I are treated with lime to precipitate the fluorine constituents. Sufficient lime is added to neutralize and precipitate the fluorine constituents. The precipitate is removed by filtration.

What is claimed is:

1. A process for bleaching wood pulp which comprises the steps of:
   (a) contacting the pulp with a quantity of oxygen difluoride equal to about 0.5 to 9% by weight, based on the weight of the pulp, for a sufficient time to bleach said pulp and to yield waste waters containing fluorine constituents, and
   (b) treating said waste waters with a reactive calcium compound whereby insoluble precipitates of calcium and fluorine are formed.

2. The process of claim 1 wherein said pulp is contacted with said oxygen difluoride for about 1 to 4 hours at a temperature of about 90 to 160° F. and wherein said reactant calcium compound is lime.

3. A process for bleaching wood pulp which comprises the steps of:
   (a) contacting the pulp with a quantity, equals to about .5 to 9% by weight based on the weight of the pulp, of a bleaching agent selected from the group consisting of fluorine, hydrofluoric acid, and oxygen difluoride, for about 1 to 4 hours at a temperature of about from 60 to 160° F., whereby said pulp is bleached and whereby waste waters containing fluorine constituents are formed;
   (b) washing, and extracting the pulp with a ½ to 3% caustic soda solution at a temperature of about 120 to 180° F.,
   (c) washing, and then treating the extracted pulp with oxygen-difluoride in an amount equal to about .5 to about 15% by weight, based on the weight of pulp, wherein the pulp is further bleached and wherein waste waters containing fluorine constituents are formed; and,
   (d) treating the fluorine constituents containing waste waters from at least one of said fluorine type treating steps with a reactive calcium compound whereby

insoluble precipitates of calcium and fluorine are formed.

4. The process of claim 3 wherein said reactive calcium compound is lime.

5. The process of claim 3 wherein at least a portion of said insoluble precipitates of calcium and fluoride are recovered and recycled back to the bleaching process as a source of fluorine containing bleaching agents.

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