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PROCESS FOR THE DISINCRUSTATION OF FIBROUS VEGETABLE MATERIALS

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This invention relates to a process for the disincrustation or deligninification of fibrous vegetable materials containing cellulose including wood, grass, straw, bagasse and bamboo. All percentages herein are on a weight basis.

This application is a continuation-in-part of my application Serial No. 315,431, filed October 17, 1952, and now abandoned.

It is well known that chlorine dioxide reacts with incrustants of fibrous plant materials to condition them so that the incrustants can subsequently be extracted from the fibrous plant by alkaline solutions, thus producing a loose fiber mass or pulp. Such procedures, heretofore employed, require high and uneconomical amounts of chemicals especially since the treatments must usually be applied repeatedly with intermediate extraction to obtain appreciable disincrustation of the fibrous material.

It has also been proposed to pulp wood and other fibrous plant materials by the sulfite or sulfate process and then bleach the resultant pulp to the desired degree of whiteness employing hypochlorite or chlorine dioxide bleaches. Sulfite and sulfate pulping procedures result in residues and effluents which present serious pollution problems. The sulfite process as currently practiced presents a serious effluent pollution problem and sulfate pulping processes present serious air pollution problems largely due to sulfur compounds escaping into the atmosphere.

It has been proposed to produce pulp from wood and other vegetable plant material by treating the same with a solution containing potassium chlorate and a large excess of hydrochloric acid over and above the amount required for complete reaction with the potassium chlorate. Still another process has been proposed, which involves the use of a mixture of sodium chlorate and hydrochloric acid in which a large excess of chlorate is used. In both of these latter procedures the proportions of chlorate and acid and their respective concentrations are such that a reaction takes place immediately between the chlorate and acid when mixed to produce chlorine dioxide and chlorine, which attack the lignins and other incrustants in the outer walls or surfaces of the fibrous materials.

In all of the above noted procedures including those involving the useof chlorates and acid, the lignins or incrustants in the outer layers of the wood or other vegetable fibrous material react while little or no reaction takes place within the core or inner layers of the wood or other vegetable fibrous material. Accordingly, a mass of fibers or pulp results which is of uneven quality and frequently has poor strength characteristics. Furthermore, these procedures involve the use of relatively large excesses of reacting solutions with consequent uneconomical consumption of chemicals. Even with such large excesses of treating solutions and relatively long periods of reaction, of the order of a day and even longer, these procedures result largely in attack on the incrustants and/or lignin on or in the surface of the vegetable fibrous material with consequent production of pulp of uneven quality or relatively poor strength.

It is an object of the present invention to provide a novel process of pulping wood and other fibrous plant materials which results in a pulp of improved quality and improved strength characteristics.

It is another object of this invention to provide a pulping process which results in a pulp of improved brightness and this with little or no deleterious effect on the strength of the fibers.

It is still another object of this invention to provide such process which is economical to carry out in that the consumption of chemicals required for its practice compare favorably with other chemical pulping procedures.

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

In accordance with this invention the wood or other vegetable fibrous material, after conditioning, if necessary to produce chips or relatively small particles, is first impregnated thoroughly and substantially completely with an alkali metal or alkaline earth metal chlorate under conditions such that substantially no reaction takes place between the vegetable fibrous material and the chlorate. After this impregnation treatment, as a result of which the chlorate impregnates the core or inner layers of the vegetable fibrous material, as well as the outer surface thereof, the resultant impregnated vegetable fibrous material is treated to cause the chlorate to react to form chlorine dioxide and chlorine in situ which react with the lignin and other incrustants to permit their ready removal. This removal may readily be effected by alkaline extraction, employing, for example, a caustic soda extraction employing a solution having a concentration not exceeding about 25%, preferably below about 10%, and at temperatures below the boiling point of the caustic solution, preferably within the range of 30° to 85° C.

For a paper making pulp, sufficient caustic soda should be used in the caustic extraction treatment to remove the chlorinated incrustants without substantial attack on the hemi-cellulose. Normally about 5% caustic soda based on the weight of the pulp (dry basis) will be sufficient for this purpose. If a high alpha cellulose pulp is desired, the amount of caustic soda used in the caustic extraction step may be increased to 10% to 20% and the extraction may be carried out at a higher temperature, of the order of 100°–120° C.

In accordance with a preferred embodiment of this invention, the wood chips or other vegetable fibrous material is first treated with an aqueous solution of alkali metal or alkaline earth metal chlorate. Aqueous solutions of sodium chlorate, potassium chlorate, calcium chlorate or barium chlorate may be employed. Particularly preferred is the thorough and compelte impregnation of the fibrous material with an aqueous solution of sodium chlorate. The amount and concentration of chlorate solution used is such that the vegeable fibrous material absorbs from about 2% to 30% of its dry weight of the chlorate salt. The impregnation may be carried out under any desired pressure conditions including sub- and superatmospheric pressure conditions.

As the chlorate salt will not react with the vegetable fibrous material until the salt is activated, as explained more fully hereinafter, neither its concentration in the aqueous solution employed, nor the temperature at which the impregnation is carried out is critical. The chlorate concentration of the impregnating solution used will depend upon the nature of the vegetable fibrous material treated and the amount of chlorate salt it is desired to deposit within the fibrous material. For any given vegetable fibrous material the amount of impregnating solution to be used to deposit the desired amount of chlorate

salt within the vegetable fibrous material can readily be determined by subjecting a sample of the fibrous material to test. Thus, for purposes of illustration, samples of the vegetable fibrous material may be immersed in a solution of given concentration of chlorate salt for variable periods of time and at desired temperatures of operation and analyzed to determine the maximum amount of impregnating solution which the sample will absorb. This data will indicate the conditions under which substantially complete impregnation takes place; the impregnation step should be carried out under conditions of solution concentration, time and temperature which will give such maximum impregnation and will result in deposit within the fibrous material of from 2% to 30% of chlorate salt or based on the dry weight of the fibrous material.

Following the impregnation, as hereinabove described, the chlorate is activated or caused to react, desirably by passing a stream of hydrogen chloride, in the gaseous phase in contact with the impregnated vegetable fibrous material from which the excess of impregnating solution has been drained off. The hydrogen chloride gas reacts with the chlorate to liberate chlorine dioxide and chlorine in situ, i. e., within the fibers. The chlorine dioxide and chlorine thus produced react with the incrustants both inside and on the outside of the fibrous materials to condition them for ready removal.

The activation should preferably be carried out at a temperature below about 75° C., preferably between 20° to 50° C. Higher temperatures may result in deleteriously affecting the quality of the fibers.

Preferably before this activation treatment and following the draining to remove excess impregnating solution, the chips are dried. This can be accomplished by passing a current of air or other inert gas through the chips. In this way a saving in the amount of hydrogen chloride required to effect the activation is effected.

The excess impregnating solution which is removed from the fibrous material may be reused in the process. The amount of excess solution is immaterial, although obviously a large excess, such as to provide an unnecessary pumping or other handling problem should not be used.

As above noted, the impregnated vegetable fibrous materials after impregnation should contain from 2% to 30% of its dry weight of chlorate salt. The exact amount of chlorate salt within this range will depend on the nature of the pulp desired. Thus, a partially delignified pulp, i. e., semi-chemical pulp, will require less chlorate than a chemical pulp. Accordingly, for a semi-chemical pulp, an amount of chlorate within the lower portion of this range is employed. For a chemical pulp, an amount of chlorate near the upper portion of this range is used. The quantity of chlorate employed will also vary depending upon the type and nature of the vegetable fibrous material impregnated therewith.

Theoretically 2 mols of hydrogen chloride are required for each mol of chlorate to produce chlorine dioxide and chlorine from the chlorate in the activation step. However, as a practical matter, smaller amounts of hydrogen chloride may be employed probably because additional hydrogen chloride is formed due to organic chlorination in accordance with the following reaction:

$$RH+Cl_2=RCl+HCl$$

in which equation R is an organic radical corresponding to the lignins, pentosans, etc. present.

Among the vegetable fibrous materials which can be treated in accordance with this invention are the coniferous woods, such as pine, fir and spruce, or hardwoods, such as oak, poplar, beech, birch, aspen, eucalyptus and other gum woods, and grasses and similar plants such as bagasse, straw and bamboo.

The time of impregnation is dependent upon the species of plant material, its possible water content, pretreatments, if any, such as steaming, defibration, to which the fibrous material has been subjected, the manner of effecting the impregnation, e. g., simple soaking, soaking under hydraulic pressure, temperature, degree of comminution of the fibrous material, etc. The impregnation time may therefore vary from a few minutes to a day or even longer.

The time of activation is usually short, of the order of about 15 minutes to 1 or 2 hours will usually be found sufficient. Prior to caustic extraction to remove the lignins and other incrustants, it is beneficial to wash the material with water thus removing hydrochloric acid, water-soluble organic acids and water-soluble organic chlorides with consequent saving in alkali which would otherwise be used up.

The following examples are given for purposes of illustrating the invention. It will be understood this invention is not limited to these examples. In these examples the pulp produced was tested in the standard manner by subjecting sheets made therefrom to testing procedures which were carried out in accordance with recognized accepted standards (TAPPI).

Example I.—Sodium chlorate employed in the impregnating step

150 grams of Brazilian hardwood chips (Açoito Cavallo) were steamed for about 20 minutes at atmospheric pressure. The resultant chips were impregnated with 400 cc. of an aqueous solution containing 212.73 grams per liter of sodium chlorate at room temperature. At the end of about 20 hours the chips were thoroughly impregnated and contained 13.5% sodium chlorate based on the dry weight of the wood. This value will be referred to in the other examples as "chlorate consumption." At the end of the impregnation treatment, the mixture was centrifuged to remove the excess solution.

About 250 grams of dry hydrogen chloride gas was passed through the centrifuged material for a period of 3 hours, the temperature being maintained below 45° C. The thus treated wood was then extracted with 500 grams of a 2% caustic soda solution at about 80° C. Sheets made from this pulp when tested showed a tear strength of 9640 meters and a "double folds" of 1029.

Example II.—Calcium chlorate employed in impregnating step

250 grams of eucalyptus chips were soaked in 800 cc. of a 5% caustic soda solution at room temperature and thereafter partially defibered on a disc refiner. The resultant material was then washed with water to remove the alkali and impregnated with 600 cc. of a solution containing 217.29 grams per liter of calcium chlorate. This impregnation treatment required about one hour. The chlorate consumption was 10.2%.

Through the impregnated material were passed 40 grams of hydrogen chloride gas for a period of 2½ hours, maintaining the temperature below 45° C. The thus treated material was then extracted with caustic soda solution and washed with water as in Example I.

Sheets made from the pulp thus produced had a tear strength of 8910 meters and a "double folds" of 1683.

The yield in this example was 71.3% based on the weight of chips treated.

The invention may be employed not only for the complete or partial disincrustation of fibrous materials, but also for further delignification of vegetable fibrous material, e. g., semi-chemical pulp, produced by other methods.

It will be noted that in the process of this invention the chlorate is supplied in about the amount required to produce sufficient chlorine dioxide and chlorine upon subsequent activation to effect the desired disincrustation and delignification. Large excesses of chemicals are not needed or even desirable, as is the case in prior procedures. Surprisingly, pulp of more uniform quality and better strength characteristics is obtained, even though

this invention involves the use of appreciably smaller amounts of chemicals for treating the fibrous material. This is believed to be due to the feature of this invention involving generation of chlorine dioxide and chlorine within the fibrous material. Moreover, in this invention the activation resulting in reaction of chlorine dioxide and chlorine with the incrustants takes place at relatively low temperatures, preferably below about 50° C. Accordingly, the plant cellulose is subject to little or no chemical damage and a higher yield of pulp of improved strength characteristics results.

Furthermore, this invention does not result in the production of gaseous by-products which cause air pollution problems, nor does it produce by-product solutions which cannot readily be treated so as to condition them to avoid any effluent disposal problems. Moreover, the pulp produced by this process approaches in strength the standard unbleached sulfate or kraft pulp, but is far superior to these pulps in brightness. The pulp produced by this process is superior in strength to sulfite pulp, which it approaches in brightness. Furthermore, the yield from this process is surprisingly high, up to 70%, whereas, neither the sulfate nor the sulfite process normally gives yields above 50%. When producing semi-chemical pulps with this process the yields may exceed 75%.

It will be further noted that a preferred embodiment of the process of this invention requires as raw material for the treatment of the fibrous vegetable material containing cellulose, sodium chlorate, hydrogen chloride and caustic soda. All of these materials are produced from sodium chloride by well known techniques. Accordingly, this process requires as the raw material for its practice only sodium chloride. Some of the sodium chloride used in the process can be recovered from the liquors resulting from the caustic extraction, either by burning the organic matter in the liquors or by acidifying and then evaporating the resultant supernatant solution. Hence, this process is exceptionally economical to practice in that it involves the use of a raw material (sodium chloride) which is plentiful, cheap and readily available, and this raw material can be recovered in a form so that it can be reused.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for the disincrustation of wood chips, which comprises soaking the wood chips in a chemically stable aqueous solution of an alkali metal chlorate until the chips are substantially completely impregnated with said chlorate, removing the portion of said aqueous solution of alkali metal chlorate which has not penetrated the wood chips and thereafter treating the impregnated chips with hydrogen chloride gas to react with the said chlorate within the chips and effect the desired disincrustation of the wood chips.

2. The process as defined in claim 1, in which the amount of chlorate introduced into the chips is from 2% to 30% by weight based on the dry weight of the chips.

3. The process as defined in claim 1, in which after the impregnation the impregnated wood chips are dried to remove excess moisture and thereafter treated with the hydrogen chloride gas.

4. A process for the disincrustation of wood chips, which comprises soaking the wood chips in a chemically stable aqueous solution of sodium chlorate until the chips are completely impregnated and contain from 2% to 30% of their dry weight of sodium chlorate, separating the impregnated wood chips from the aqueous solution of sodium chlorate which has not penetrated the wood chips, and thereafter passing gaseous hydrogen chloride through the impregnated chips to react with the sodium chlorate within the chips and effect the desired disincrustation of the wood chips.

5. A process for the disincrustation of vegetable fibrous materials, which comprises the steps of soaking the vegetable fibrous material in an aqueous solution substantially free of acid and containing a chlorate from the group consisting of alkali metal chlorates and alkaline earth metal chlorates to substantially completely impregnate the vegetable fibrous material with said aqueous solution of said chlorate, removing the portion of the aqueous solution of said chlorate in which said vegetable fibrous material has been soaked which portion has not penetrated the vegetable fibrous material from the impregnated vegetable fibrous material and after said removal of the aqueous solution passing hydrogen chloride gas through the impregnated vegetable fibrous material to react with said chlorate within and on the vegetable fibrous material to generate chlorine dioxide and chlorine which reacts with the incrustants within and on the vegetable fibrous material to condition them for ready removal.

6. The process defined in claim 4, in which the wood chips are steamed prior to soaking them in the aqueous solution of sodium chlorate.

7. The process defined in claim 5, in which the amount of said chlorate with which the fibrous material is impregnated is from 2% to 30% of the dry weight of the fibrous material and said reaction between said chlorate and the hydrogen chloride is carried out at a temperature below 75° C.

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