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2,811,518

ALKALINE REFINING OF WOOD PULP

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This invention relates to the production of refined wood pulp and has for its object the provision of improvements in alkaline refining for the production of an improved pulp in a relatively highly depolymerized state and in good yield. The invention is concerned with the refining of a pulp which has been subjected to a preliminary digestion, such as an acid sulfate digestion, under oxidizing conditions such as to effect a uniform depolymerization or degradation of the cellulose without appreciable loss of cellulose. Our invention produces a depolymerized cellulose which is especially advantageous for conversion into alkali cellulose in the viscose process. Regenerated viscose products as used today are of about 400 D. P. (degree of polymerization). Unrefined cellulose pulps are usually two to five times this D. P. In order to use such pulps in conventional viscose manufacturing operations, a great deal of degradation must be accomplished in the operation of forming the alkali cellulose.

There are two principal types of alkaline refining known as "hot" refining and "cold" refining. In hot refining, low percentages of alkali are used at high temperatures, the alpha-cellulose content being raised but at the expense of poor yield. In cold solution refining, high percentages of alkali are used at low temperatures, the alpha cellulose being raised without excessive loss in yield.

It has been recognized that oxidative degradation is a more desirable way to degrade cellulose than is hydrolysis or bleaching. (See U. S. Patent 2,542,285 for illustrative data.) However, it has been thought that oxidative degradation of the desired type could only be achieved after treatment of the cellulose with relatively strong mercerizing alkalies of 7–20% NaOH content. In pulp making and refining, the use of such strong alkalies is prohibitive in cost and has never been used successfully in producing a low-viscosity pulp for viscose manufacture in spite of the advantages in quality of such a product.

As a result of extensive investigations we have confirmed our conception that there are two principal reactions involved in the alkaline degradation and refining and that the presence or absence of oxygen, not the temperature, determines which of the two reactions takes place, and that the temperature determines only the rate, not the type of reaction.

Our invention provides an improved method of refining and depolymerizing wood pulp which comprises subjecting a pulp which has been previously subjected to a digestion treatment to an alkaline refining operation characterized by the use of an alkaline solution equivalent to from 0.2 to 6% of NaOH in solution and a pulp consistency such that the pulp is in a loose porous mass free of surface liquid film, applying an excess of gaseous oxygen to the porous pulp mass during the alkaline refining, and washing the pulp, thereby forming a pulp having relatively low aging requirement.

The reaction in the presence of excess oxygen probably cleaves the cellulose chains near the middle, and is characterized by rapid depolymerization at a high yield level of at least 90% alpha cellulose. The reaction in the absence

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of oxygen probably is an end-chopping attack near chain ends and is characterized by slow depolymerization with high loss in yield, purification occurring through the eventual eating away of the shorter chains and dissolution of the fragments. Hot refining operations now being practiced in the industry involve this latter reaction to a substantial degree, inasmuch as the conditions used promote very rapid depletion of oxygen within the reaction mass and effectively seal-off fibers from access to further oxygen except in trace quantities.

While we do not wish to predicate this invention on any theory as to the specific nature of the depolymerization of the cellulose chains, there is considerable evidence to support our belief that we effect a severance of the polymers near their centers, in any event not near the ends, because the depolymerization is not accompanied by an appreciable loss of cellulose. The end severance results in an excessive loss of cellulose manifested by the degradative solubilizing of portions of the cellulose which are lost in the refining liquors. When the cellulose is severed near the center, the two parts are lower molecular weight polymers but not soluble in the liquors. The end severance reaction which always occurs to an appreciable extent in conventional hot refining processes not only results in excessive loss of cellulose but it does not accomplish effective depolymerization because the remaining relatively large cellulose polymer does not have the aging characteristics sought.

While the method of our invention may be carried out effectively without oxidation catalysts, we prefer to incorporate in the alkaline refining chemicals one or both of the metals cobalt or manganese, preferably added to the pulp or refining liquor as water soluble compounds as oxidation catalysts.

In carrying out our improved method, we may employ pulp which has been subjected to a preliminary acid sulfite digestion followed by chlorination and washing. In the acid sulfite pulping process, a ligno-cellulose material is generally cooked in a solution of sulfurous acid, part of the sulfurous acid being combined as bisulfite. The cation combined thus with the bisulfite ion is generally known as the "pulping base." Pulping-base cations normally used include calcium, sodium, ammonium and magnesium. Pulp produced by acid sulfite digestion of wood, irrespective of the pulping base, is commonly termed "sulfite pulp."

For application of the improved alkaline purification treatment, the prior sulfite digestion of wood is not limited to any particular method or conditions, such as choice of pulping base. Likewise, the chemical properties of the pulp obtained from the sulfite digestion are not critical and any conventional sulfite digestion treatment may be used. Normally, however, the digestion will be so carried out that a screenable pulp will be obtained which may be effectively chlorinated. Such sulfite digestion conditions will normally produce yields of 40% to 50% of unrefined pulp, based on the dry initial wood.

Similarly, the invention is not limited to the use of any particular wood in the sulfite digestion. Any soft or hardwood which can be satisfactorily pulped by the acid sulfite process may be used. Suitable woods include Western hemlock, spruce, Southern pine, black gum, birch, maple, alder and ash.

The alkaline oxidative refining process of the invention is not limited to pulps prepared by acid sulfite digestion; but may also be applied to digested pulps of the pre-hydrolyzed kraft type and even to refined and bleached pulps from wood, cotton and other celluloses.

Following digestion, the pulp is washed in any conventional or convenient manner such as in a blowpit or by drum washers. The washed pulp in aqueous suspen-

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sion is then chlorinated with elemental chlorine according to conventional practice for the digested pulp. The amount of chlorine used is generally such that there will be a small excess after the time allotted for the reaction. This treatment may be carried out at any convenient pulp consistency. Following chlorination, the pulp is again washed thoroughly with water, using, for example, a rotary drum washer.

The washed pulp is then subjected to an alkaline refining treatment of the invention with any suitable alkaline liquor of relatively low caustic content. As the alkaline refining agent we may use any of the following chemicals or mixtures thereof, NaOH, Na₂CO₃, Na₂SO₃, Na₂S. In refining operations requiring the use of Na₂SO₃, such liquor would advantageously include also Na₂CO₃ with or without NaOH, Na₂S or Na₂CO₃ plus Na₂S. In accordance with our invention, moreover, we aim to effect not only an alkaline refining but an accompanying depolymerization to accomplish aging reduction to the end that the pulp is advantageous for use in conversion into viscose.

Our invention involves several essential differences from conventional alkaline refining. We carry out the alkaline digestion in the presence of excess oxygen with the pulp in a loose fluffy and porous state so that the fibers will always be effectively contacted with an excess of gaseous oxygen such as air or pure oxygen. The pulp is not immersed in liquor and does not have liquid film on the fibers. In contrast to other hot alkaline refining processes in which consistencies of less than 10% are advised, we use a consistency in excess of 28% to ensure against localized depletion of oxygen in regions protected by a liquid film. While we may use a consistency as high as 60%, it is advantageous to use a more easily attainable consistency in the range of from 35 to 50% for most refining operations, and at a temperature of from 50° C. to 130° C.

While it has been the prevailing belief that in order to obtain uniform alkaline oxidative depolymerization of this type it is necessary to use around 18% NaOH (mercerizing concentration), we use an alkaline liquor containing chemicals equivalent to 1% to 6% expressed as NaOH on the basis of the solution. The amount of alkaline chemicals, when expressed as NaOH, vary from 0.5% to 24% based on the pulp.

After completion of the refining treatment and washing, the pulp may be bleached to a high degree of brightness by any method which will not impair the high quality of the pulp, such as by sodium or calcium hypochlorite. The fullest advantages, however, are obtained by bleaching with aqueous solutions of chlorine dioxide or acidified sodium chlorite. The bleaching may be carried out at either high or low pulp consistencies and either batchwise or in continuous bleaching equipment.

Our invention produces a high alpha-cellulose pulp characterized by high chain length uniformity and a low content of such impurities as pentosan, mannan and lignin, and is particularly suitable for conversion into viscose since the aging of the alkali cellulose is very materially reduced.

The following examples illustrate alkaline refining operations of the invention carried out on batches of digested, chlorinated and washed pulp stock from Western hemlock, or Southern pine wood.

EXAMPLE I

(Purification and depolymerization)

(a) A Western hemlock chlorinated sulfite pulp stock of 2000 D. P., 90.0% alpha cellulose content and 16% consistency was fed to a screw press in which the consistency was raised to 35%. NaOH was added to extent of 10% based on the cellulose (approx. 3% NaOH concentration on total weight), and MnSO₄ was added to extent of 10 p. p. m. manganese based on the cellulose. This pressed chemically-treated stock was fed into a heated reaction vessel as a porous mass, the fibers of

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which were substantially free from a surface film of liquid, and while being agitated were supplied with an excess of oxygen (either as air or pure oxygen) and heated at a temperature of 100° C. for one hour. This treated stock was then washed to give a 1000 D. P., 95% alpha pulp in yield of 93%.

(b) Conventional hot refining under the same conditions without excess oxygen gave a 2000 D. P., 95% alpha pulp but at a yield of only 85%.

(c) Use of 1 p. p. m. cobalt, added as cobalt sulfate, gave the same result as 10 p. p. m. manganese.

(d) Use of 18% NaOH reacted for one hour at 100° C. gave a pulp of 500 D. P. and 95.0% alpha in yield of 92%.

(e) In a two-stage sequence, repeat of treatment (a) on the effluent stock from (a) gave a 500 D. P., 94.5% alpha pulp in overall yield of 92%.

(f) For comparison, in a conventional two-stage sequence, repeat of treatment (b) on the effluent stock from (b) gave a 2000 D. P., 96.0% alpha pulp, but an overall yield of only 76%.

EXAMPLE II

(Depolymerization)

(a) A Southern pine steam prehydrolyzed alkaline cooked kraft pulp stock of 1800 D. P., 97.0% alpha treated with 8% NaOH (on the pulp) and 5 p. p. m. manganese at consistency of 30% for one hour at 110° C. in an excess of oxygen gave a 700 D. P. pulp of 96.5% alpha in yield of 98.5%.

(b) A conventional hot refining treatment under the same conditions but without excess oxygen gave a 1750 D. P. pulp of 96.7% alpha but in yield of only 91%.

EXAMPLE III

(Depolymerization in hot part of a cold-hot sequence)

(a) A Western hemlock chlorinated sulfite pulp stock of 1500 D. P. was refined in a cold 6% solution of NaOH at 20° C. giving an 1800 D. P. pulp of 96% alpha which was pressed to a consistency of 30%, treated with 1 p. p. m. cobalt and heated in an excess of oxygen for 30 minutes at 120° C., giving a 400 D. P. pulp of 95.8% alpha at 98% hot stage yield.

(b) A Southern pine chlorinated and mildly bleached (to whiten) pulp stock of 1000 D. P. was cold-caustic refined in 10% NaOH solution at 10° C., giving a 1600 D. P. of 99.3% alpha which was treated with 1 p. p. m. cobalt, pressed (without washing to remove any of retained NaOH) to a consistency of 33%, and heated for one hour at 50° C. in an excess of oxygen giving a 500 D. P. pulp of 99.0% alpha in yield of 99.5% for the hot stage.

EXAMPLE IV

(a) A Western hemlock chlorinated sulfite pulp stock of 1800 D. P. and 91.0% alpha cellulose content was contacted with an excess of 6% NaOH solution containing 0.2 p. p. m. of cobalt sulfate, then pressed out to a consistency of 50%. This pressed, chemically-impregnated cellulose stock (free of surface liquor) was fluffed to a porous mass and introduced into a pressurized chamber at 130° C. while being exposed to an excess of oxygen for ten minutes. The treated stock was washed to yield a 96.8% alpha pulp of 500 D. P. in yield of 90.5%.

(b) The above NaOH-treated stock could be brought with difficulty to a consistency of 60% prior to exposure to heat and oxygen, but the pressure required was of the order of 600 pounds per square inch as compared with 100 pounds for 50% consistency and 10 pounds for 28% consistency.

This application is a continuation-in-part of our co-pending application Serial No. 289,672, filed May 23, 1952, now abandoned.

In the aforementioned alkaline digestion, and in other alkaline pulp refining treatments, we may incorporate in

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the alkaline treatment liquor one or more water soluble nonionic, or effectively nonionic, polymeric compounds having a hydrophobic nucleus and a plurality of hydrophilic terminal polyethylene oxide chains, typical of which are the Pluronics, for example L-64, and the Tetronics, for example, 702.

We claim:

1. The method of refining and depolymerizing wood pulp which comprises subjecting a pulp which has been previously subjected to a digestion treatment to an alkaline refining operation characterized by the use of an alkaline solution equivalent to 0.2 to 6% of NaOH in solution and a pulp consistency of from 28% to 60% whereby the pulp is in a loose porous mass free of surface liquid film, carrying out the alkaline refining at a temperature of from 50° C. to 130° C., applying an excess of gaseous oxygen to the porous pulp mass during the alkaline refining, and washing the pulp, thereby forming a pulp having relatively low aging requirement.

2. In the method of claim 1, using an alkaline liquor

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containing at least one of the compounds Na_2SO_3 , Na_2CO_3 , Na_2S and NaOH.

3. In the method of claim 1, using a metal of the group consisting of manganese and cobalt as an oxidation catalyst.

4. In the method of claim 1, carrying out the alkaline refining on pulp having been given an acid sulfite digestion followed by chlorination and washing.

5. In the method of claim 1, carrying out the alkaline refining on pulp having been given an acid prehydrolysis followed by alkaline digestion, chlorination and washing.

6. In the method of claim 1, effecting alkaline depolymerization of a refined and bleached cellulose.

References Cited in the file of this patent

UNITED STATES PATENTS

1,860,432	Richter	May 31, 1932
2,159,676	Richter et al.	May 23, 1939
2,542,285	Mitchell	Feb. 20, 1951