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[54] **METHOD OF TREATMENT OF WOOD PULP FOR GREATER EFFICIENCY IN WOOD UTILIZATION**

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[58] **Field of Search** ..... 162/72, 82, 168, 164; 260/615 B, 484 R

[56] **References Cited**

UNITED STATES PATENTS

2,999,045	9/1961	Mitchell et al.	162/72
3,036,118	5/1962	Jackson et al.	260/615 B
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OTHER PUBLICATIONS

Casey "Pulp and Paper" Second Ed., Vol. II, pp. 223–227.

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[57] **ABSTRACT**

The addition of certain surfactant polyoxyethylene polyoxypropylene block copolymers in the sulfate pulping process results in increased yields of pulp.

5 Claims, No Drawings

METHOD OF TREATMENT OF WOOD PULP FOR GREATER EFFICIENCY IN WOOD UTILIZATION

BACKGROUND OF THE INVENTION

1. Field Of The Invention

The present invention relates to preparation of pulpwood using the sulfate pulping process. More specifically, the present invention relates to improvements in yield of pulp per ton of wood digested by the use of certain polyoxyethylene polyoxypropylene digester additives.

2. Prior Art

The cellulosic and non-cellulosic carbohydrate fibers present in wood are held together to form a semiplastic solid by lignin, a complex polymer composed of hydroxyphenylpropane units. This complex polymer binds the wood fiber partially by an amalgamation between the fiber walls, by an absorption within the fiber walls and partially, it is believed, by chemical bonding between the cellulose and the lignin. Delignified, or partially delignified, cellulose fibers are required for the production of certain papers and pulp products. In the sulfate process for the preparation of pulpwood, a solution of sodium hydroxide and sodium sulfide is used to degrade the lignins to obtain these cellulose fibers. To degrade these materials, moderately high temperatures and pressures are employed to expedite the penetration and diffusion of the sodium, sulfide and hydroxyl ions into the wood structure. As far as we know, the use of additives to increase this penetration resulting in increased yields has not been successful. At the present rate of production, wood supplies are being rapidly depleted in spite of industry efforts to encourage reforestation on private lands, and to practice tree planting and controlled cutting on its own lands. Other forms of wood salvage such as the use of barked and chipped sawmill waste, slabs, edgings and plywood cores have been followed up to obtain raw materials. Even the utilization of sawmill sawdust has been employed. It is quite evident that any improvements in yield would be welcomed by the pulp and paper industry.

One of the major advantages of the sulfate pulping process is its ability to pulp both coniferous and deciduous wood in greater variety than other processes. Among the coniferous species which can be pulped are the Western-red cedar, Cypress, Balsam fir, Noble fir, White fir, Douglas fir, Canadian and Western Hemlock, Larch, Loblolly pine, Ponderosa pine, White pine and Redwood, and of the spruce species, Engelman, Sitka, and White. The deciduous species which can be used are: Ash, Basswood, Beech, Birch, Chestnut, Elm, Gum, Red and Sugar Maple, Northern, Post and White Oak, Sweetgum, the Big Leaf and Quaking Poplars, and the Tulip trees.

SUMMARY OF THE INVENTION

It has now been discovered that the addition of minimal amounts of certain surfactant polyoxyethylene polyoxypropylene digester additives to the sulfate liquor results in an increased yield of pulp per ton of wood used, with no corresponding loss of pulp brightness, tensile and bursting strength.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The wood chips which are to be pulped are charged

to the pulping basket on an oven-dry wood basis. The moisture content of the wood must be determined as it is desirable to maintain the liquor-to-wood ratio within certain ranges. The liquor-to-wood ratio can vary from about 2/1 to about 6/1, preferably from about 3/1 to about 5/1. The moisture content of the wood can contribute as much as 50 percent of the water present in the cooking liquor. Knowing the moisture content of the wood chips, the cooking liquor is prepared by dissolving the required amounts of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) in water. The percentage of total active alkali to be used depends on the species of wood to be pulped and on the degree of delignification of the wood desired, i.e., whether a "board" grade of pulp with moderate delignification or a "bleaching" grade of pulp with as much delignification as possible is being made. This concentration generally varies from about 12 percent to about 25 percent total active alkali, preferably from about 15 percent to about 22 percent. Total active alkali is expressed as percent sodium oxide (Na_2O) based on the oven dry weight of the wood charged to the digester. This Na_2O represents both the amount of NaOH and Na_2S to be used. The Na_2S used will furnish about 15 percent to about 25 percent of the total Na_2O, while the remainder will be furnished by the NaOH. In actual plant practice, some of the pulping liquor may be recirculated so that the total Na_2O content may include salts such as sodium carbonate, sodium hydrosulfide, sodium sulfate and sodium thiosulfate. This is due to the addition of some black liquor to freshly prepared cooking liquor. The black liquor is that liquor which is obtained from a previous pulping run and may constitute from about 10 percent to about 50 percent of the cooking liquor added to a fresh charge of wood chips.

Also of interest is the sulfide content of the cooking liquor. This is usually expressed as Sulphidity which is the percentage ratio of Na_2S, expressed as Na_2O, to the total active alkali.

The digester additive is best added to the cooking liquor before it is circulated through the wood chips. After the sulfate cooking liquor has circulated through the wood chips for about five minutes, the air in the digester is purged and steam is allowed to enter the digester to its maximum pressure which may range from 125 to 150 psig. The temperature may range from about 250° F. to about 400° F., preferably from about 300° F. to about 375° F. This temperature and pressure are maintained from about 0.5 hour to about 6 hours, preferably, from about 0.5 hour to about 3 hours.

At the end of the required time at the specific temperature and pressure, the digester is blown to the blow tank, the weak black liquor drained, and the pulp is then coarse screened and washed by such processes as are well known to those skilled in the art.

The surfactant additives contemplated for use in the subject invention are essentially those disclosed by D. R. Jackson et al. in U.S. Pat. No. 3,036,118 issued on May 22, 1962. These are surface active agents obtained by condensing ethylene oxide with a low molecular weight reactive hydrogen compound forming a polyoxyethylene polyol and then further condensing this polyol with propylene oxide. The structural formula of these surfactants corresponds to

$$R[(C_2H_4O)_n(C_3H_6O)_m]_xH$$

wherein R is the nucleus of a reactive hydrogen com-

pound, x has a value of 2 to 6, m has a value such that the oxypropylene chain has a molecular weight from about 900 to 25,000, preferably from 900 to 5,000, and n has a value such that the weight of oxyethylene groups constitutes from about 10 to 90 weight percent, preferably 10 to 60 weight percent, of the mixture. The concentration of surfactant may vary from about 0.05 percent to 1.0 percent, preferably from about 0.1 percent to 0.5 percent, based on the weight of oven dry wood.

The above surfactants are prepared by the reaction of propylene oxide with an ethylene oxide condensate of a reactive hydrogen compound. The reactive hydrogen compound must be a relatively low molecular weight, water-soluble compound having at least two and preferably not more than six reactive hydrogen atoms. One class of such compounds is the low molecular weight, aliphatic, polyhydric alcohols such as ethylene glycol, propylene glycol, 2,3-butylene glycol, 1,3-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, glycerol, trimethylolpropane, sorbitol, sucrose and the like. Other classes that can be used are alkylamines, alkylene polyamines, cyclic amines, amides and polycarboxylic acids. These surfactants and their method of preparation are adequately described in the aforementioned patent, U.S. Pat. No. 3,036,118.

The surfactants employed in the following examples are defined as follows:

Nonionic No. 1 is a polyoxypropylene adduct of a polyoxyethylene glycol wherein the polyoxypropylene chain has a molecular weight of about 1700 and the oxyethylene content is about 15 percent by weight of the mixture.

Nonionic No. 2 is a polyoxypropylene adduct of a polyoxyethylene glycol wherein the polyoxypropylene chain has a molecular weight of about 2200 and the oxyethylene content is about 25 percent by weight of the mixture.

Nonionic No. 3 is a polyoxypropylene adduct of a polyoxyethylene glycol wherein the polyoxypropylene chain has a molecular weight of about 2500 and the oxyethylene content is about 25 percent by weight of the mixture.

Nonionic No. 4 is a polyoxypropylene adduct of a polyoxyethylene glycol wherein the polyoxypropylene chain has a molecular weight of about 1000 and the oxyethylene content is about 55 percent by weight of the mixture.

The following examples are presented to illustrate the invention. The results were obtained with a laboratory digester. The laboratory digester is known to correlate well with actual plant operations. The procedure employed was as follows:

This laboratory digester consists of a jacketed shell constructed of 316 stainless steel with a tight fitting gasketed lid, secured by a lug bolt and nut system. The system is pressure proof to 300 lbs./in.^{2} gage (Static Test) and the jacket is also proof to the same pressures. The wood chip charge is contained in a stainless steel wire mesh basket (18–20 mesh). The digester is piped to allow circulation of cooking liquor at the start of and at intervals during a cook. Circulation of the liquor at cooking pressures is accomplished by a positive displacement pump of the rotary eccentric type. The circulation of the cooking liquor is from top to bottom of the digester.

The heating of the digester and charge is accomplished by the use of live steam (maximum pressure available 140 lbs./in.^{2} gage). The steam supply passes to a pressure regulator and then to the digester jacket (indirect heating) or directly to the digester charge in the shell (direct heating).

The digester is equipped with a condenser to condense the volatile malodorous byproducts of cooking and a drainage system for removal of the black liquor at the end of the cook.

The digester was steamed to the maximum pressure required by incrementally increasing the pressure. At the end of 60 minutes the pressure reached 100–150 psig. The cooking cycle times ranged from 0.5 to 3.0 hours. At the end of the cycle, the pressure was relieved rapidly by opening the gas-off valve and discharging the volatile malodorous by-products through a condenser. The black liquor was discharged to the sewer under slight pressure. The digester lid was removed when atmospheric pressure was reached and the charge was washed with an amount of water five to six times the volume of the charge. The pulp was defibered at low consistency with a high-speed propeller agitator, screened through a 0.010 inch cut plate, collected and dewatered by centrifuging using a 100 mesh wire screen belt. The yield was calculated on an oven dry basis.

EXAMPLE I

Wood: Loblolly Pine Chips	
Total Active Alkali, percent	16.5
Sulphidity	26.0
Liquor-to-Wood Ratio	3/1
Maximum Pressure, psig.	130
Temperature, °F.	350
Additive, percent, based on oven-dried chips	0.2

Run	Additive	% Yield	% Increase in Yield
1	—	51.9	
2	—	48.6	
3	—	49.6	
4	—	50.5	
5	—	49.1	
6	—	48.5	
7	—	49.7	
Ave.	—	49.7	—
8	Nonionic No. 3	58.6	
9	Nonionic No. 3	55.7	
10	Nonionic No. 3	56.2	
Ave.	Nonionic No. 3	56.8	14.3
11	Nonionic No. 2	53.7	
12	Nonionic No. 2	54.1	
13	Nonionic No. 2	52.0	
14	Nonionic No. 2	52.0	
Ave.	Nonionic No. 2	52.9	6.4

EXAMPLE II

Wood: Loblolly Pine Chips	
Total Active Alkali, percent	21.25
Sulphidity, percent	26
Liquor-to-Wood Ratio	3/1
Maximum Pressure, psig.	130
Temperature, °F.	350
Additive, percent, based on oven-dried chips	0.2

Run	Additive	% Yield	% Increase in Yield
15	—	45.6	
16	—	47.1	
17	—	47.1	
18	—	47.0	
Ave.	—	46.5	—
19	Nonionic No. 3	51.3	
20	Nonionic No. 3	51.4	

-Continued

EXAMPLE II

Wood: Loblolly Pine Chips			
Total Active Alkali, percent		21.25	
Sulphidity, percent		26	
Liquor-to-Wood Ratio		3/1	
Maximum Pressure, psig.		130	
Temperature, °F.		350	
Additive, percent, based on oven-dried chips		0.2	
Run	Additive	% Yield	% Increase in Yield
21	Nonionic No. 3	50.7	
22	Nonionic No. 3	50.8	
Ave.	Nonionic No. 3	51.1	12.0

EXAMPLE III

Wood: Mixed Softwood from South Dakota			
Total Active Alkali, percent		21.5	
Sulphidity, percent		26.0	
Liquor-to-Wood Ratio		3/1	
Maximum Pressure, psig.		130	
Temperature, °F.		350	
Additive, percent based on oven-dried chips		0.2	
Run	Additive	% Yield	% Increase in Yield
23	—	39.9	
24	—	39.4	
25	—	38.3	
26	—	39.2	
27	—	38.6	
28	—	40.6	
29	—	39.4	
Ave.	—	39.2	—
30	Nonionic No. 3	41.8	
31	Nonionic No. 3	41.0	
32	Nonionic No. 3	40.7	
33	Nonionic No. 3	42.4	
Ave.	Nonionic No. 3	41.5	5.9
34	Nonionic No. 1	42.9	
35	Nonionic No. 1	43.6	
36	Nonionic No. 1	41.7	
37	Nonionic No. 1	42.2	
Ave.	Nonionic No. 1	42.5	8.4

EXAMPLE IV

Wood: Mixed Northern Hardwood Chips		
Total Active Alkali, percent		15
Sulphidity, percent		11
Liquor-to-Wood Ratio		5/1
Maximum Pressure, psig.		96
Additive, percent, based on oven-dried chips		0.2
Run	Additive	% Yield
1	—	47.0
2	Nonionic No. 4	49.0
3	Nonionic No. 1	54.2
4	Nonionic No. 2	51.2

EXAMPLE V

Wood: Mixed Southern Hardwood Chips		
Total Active Alkali, percent		21.5
Sulphidity, percent		26.0
Liquor-to-Wood Ratio		5/1
Maximum Pressure, psig.		110
Additive, percent, based on oven-dried chips		0.2
Run	Additive	% Yield
1	—	43.4
2	Nonionic No. 1	46.7
3	Nonionic No. 3	46.1

The effect of concentration of the nonionic surfactants is tabulated in Example VI, below. The cooking conditions employed were as follows:

EXAMPLE VI

Wood: Loblolly Pine Rescreened Chips				
Total Active Alkali, percent			21.5	
Sulphidity, percent			26.0	
Liquor-to-Wood Ratio			3/1	
Maximum Pressure, psig.			130	
Maximum Temperature, °F.			350	
Run	Additive	%	% Yield	% Increase in Yield
1	—		46.2	—
2	—		44.4	—
3	—		46.1	—
4	—		43.2	—
5	—		44.8	—
6	—		45.0	—
Ave.			45.0	
7	Nonionic No. 1	0.2	49.2	
8	Nonionic No. 1	0.2	48.3	
9	Nonionic No. 1	0.2	47.8	
10	Nonionic No. 1	0.2	47.8	
Ave.	Nonionic No. 1	0.2	48.2	7.1
11	Nonionic No. 1	0.3	51.4	
12	Nonionic No. 1	0.3	51.2	
13	Nonionic No. 1	0.3	48.0	
14	Nonionic No. 1	0.3	49.6	
Ave.	Nonionic No. 1	0.3	50.0	11.1
15	Nonionic No. 1	0.4	46.4	
16	Nonionic No. 1	0.4	46.7	
17	Nonionic No. 1	0.4	48.4	
18	Nonionic No. 1	0.4	47.8	
Ave.	Nonionic No. 1	0.4	47.3	5.1
19	Nonionic No. 2	0.2	49.7	
20	Nonionic No. 2	0.2	48.8	
Ave.	Nonionic No. 2	0.2	49.2	9.3
21	Nonionic No. 2	0.3	53.0	
22	Nonionic No. 2	0.3	50.7	
Ave.	Nonionic No. 2	0.3	51.8	15.1
23	Nonionic No. 2	0.4	52.5	
24	Nonionic No. 2	0.4	52.9	
Ave.	Nonionic No. 2	0.4	52.7	17.1
25	Nonionic No. 3	0.2	47.7	
26	Nonionic No. 3	0.2	48.3	
Ave.	Nonionic No. 3	0.2	48.0	6.7
27	Nonionic No. 3	0.3	50.9	
28	Nonionic No. 3	0.3	49.6	
Ave.	Nonionic No. 3	0.3	50.2	11.5
29	Nonionic No. 3	0.4	50.0	
30	Nonionic No. 3	0.4	48.0	
Ave.	Nonionic No. 3	0.4	49.3	9.5

The burst and tear factors and the breaking length were determined at a 500 Canadian Standard Freeness. These physical properties were determined according to the standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI). The TAPPI standards employed were T404m, T403m and T414m. Table I below indicates that the changes in these pulp properties as reflected by the percentage change in burst factor, tear factor and breaking length were essentially insignificant. The sheets were prepared according to TAPPI standards T205 and T220.

Table I

Additive	Percent Additive	Percent Increase in Yield	Percentage Change Burst Factor	Tear Factor	Breaking Length
Nonionic No. 1	0.2	7.3	+6	−8	+11
Nonionic No. 1	0.3	11.2	+7	−7	+7
Nonionic No. 2	0.2	9.6	+10	−10	+19
Nonionic No. 2	0.3	15.4	+14	−10	+12
Nonionic No. 3	0.2	6.7	−15	+8	−9
Nonionic No. 3	0.3	11.2	−8	+4	−2

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the preparation of pulpwood by the digestion of wood chips in an aqueous alkaline liquor in which the total active alkali consists substantially of sodium sulfide and sodium hydroxide at a maximum temperature of 400° F., the improvement which comprises carrying out the digestion in the presence of a digester additive whose structure corresponds to the formula

$$R[(C_2H_4O)_n(C_3H_6O)_m]_xH$$

wherein R is the nucleus of a reactive hydrogen compound, selected from the group consisting of ethylene glycol, propylene glycol, 2,3-butylene glycol, 1,3-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, glycerol, trimethylolpropane, sorbitol, methylamine, ethylamine, propylamine, butylamine, hexylamine, ethylenediamine, 1,6-hexanediamine, diethylenetriamine, piperazine, 2-methylpiperazine, 2,5-dimethylpiperazine, acetamide, succinamide, benzenesulfonamide, adipic acid, succinic acid, glutaric acid, aconitic acid, diglycollic acid, citric acid, glycollic acid and ethanolamine, *m* has a value such that the oxypropylene chain has a molecular weight from about 900 to 25,000, and *n* has a value such that the weight of oxyethylene groups constitutes from about 10 to 90 weight percent of the mixture said digester additive is present in an amount of about 0.05 to 1.0% based on the weight of oven dry wood to sufficiently increase the pulp yield.

2. The process according to claim **1** wherein the total active alkali ranges from about 15 to 22 percent of the oven-dried weight of wood chips.

3. The process according to claim **1** wherein the liquor-to-wood ratio is from about 3/**1** to 5/**1.**

4. The process according to claim **1** wherein the concentration of additive ranges from about 0.1 to 0.5 percent of the oven dry weight of wood chips.

5. The process according to claim **1** wherein the nucleus of the digester additive is ethylene glycol.

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