United States Patent Office 2,872,313 Patented Feb. 3, 1959

2,872,313

PULPING OF PAPER BROKE CONTAINING WET-STRENGTH RESINS

Ronald R. House, Darien, and Yun Jen, Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application September 8, 1955 Serial No. 533,259

3 Claims. (Cl. 92—1.4)

This invention relates to the pulping of wet-strength paper broke. More particularly, the invention relates to the pulping of broke carrying high molecular weight material or resin as agent imparting wet strength, so as to form a pulp which can be sheeted either alone or in admixture with fresh pulp to yield good quality paper.

In all paper mills a certain amount of the product is lost as "trim" or "broke," and every effort is made to repulp this paper thereby eliminating waste. Paper carrying rosin size, wax size, starch, clay, gums and similar additives can be charged directly into the beater and reduced to a pulp without difficulty by the normal action thereof, although a short alkali soak is sometimes found helpful. Wet-strength webs (i. e., webs composed of cellulose fibers bonded together by an absorbed content of wet strength resin) are not affected by this treatment to more than a negligible extent, and up to the present pulping of these webs has been deemed to require in combination an elevated temperature, an acid pH, and intensive mechanical disintegration assisted by steam jets. The method and apparatus therefor are respectively disclosed in U. S. Patents Nos. 2,394,273 to Thomas and 2,423,097 to Goehler et al.; see also the article by J. C. Barthel in the March 21, 1955, issue of the Paper Trade Journal and the article by Trout in TAPPI 34, 539 (1951).

The discovery has now been made that the pulping of wet-strength broke is greatly facilitated by contacting the broke with a dilute aqueous solution of an oxidizing salt and maintaining the broke in contact therewith until the fiber-resin-fiber bonds therein have substantially loosened, that is, loosened to the point where the broke can be pulped in conventional pulping equipment such as a beater, hydropulper, refiner or dynapulper. We have found that in the great majority of instances soaking the broke for less than an hour in a preferred salt solution loosens the fiber-resin-fiber bonds so extensively that the broke need not be subjected to the steam-jet disintegration referred to above and can be added directly to the mechanical pulper, and that in other instances the bonds are loosened to such an extent that much milder mechanical disintegration is sufficient as compared to the disintegration that would otherwise be necessary.

The process is useful in connection with broke containing any adsorbed wet strength resin.

The invention does not depend upon any particular times, temperatures concentrations, or pH values. Good results have been obtained with oxidizing salt concentrations of ¼% to 5%, contact times of from a minute or less to an hour or two, and temperatures varying from room temperature to the boil.

According to one method for employing the present invention broke, trim, or other scrap is charged directly to a dilute aqueous solution of an oxidizing salt in a tank and allowed to soak in the solution until the fiber-resin-fiber bonds have substantially loosened. Stirring is helpful but not necessary, and no pH adjustment is generally required. When the desired loosening has occurred the solution is drained off, after which the paper is ready for pulping.

Preferably at the beginning of the soak a substantial excess of oxidizing salt is present so as to avoid undue prolongation of the treatment. The pH of the oxidizing salt solution ordinarily need not be adjusted and satisfactory bond loosening takes place with minimal harm to the fibers with solution having pH values between about 7 and 10. A wetting agent may be added and is sometimes helpful particularly in connection with oily or waxy broke and a hot oxidizing salt solution is used. Temperatures between 115° F. and 180° F. are suitable. The precise amount of oxidizing salt which should be added in each instance varies because of the difference in effectiveness of particular salts in loosening the fiber-resin-fiber bonds and the strength of the bonds resulting principally from the amount and kind of wet strength-resin present. Hence the optimum kind, amount and concentration of oxidizing agent in the solution are best predetermined by laboratory trial, using the procedures shown in the examples below as guides. Termination of the treatment occurs when the fiber-resin-fiber-bonds have loosened to such an extent that the broke can be disintegrated in ordinary papermaking equipment at hand.

The principal commercially available oxidizing agents have been tested, including sodium hypochloride ($NaClO$), sodium chlorite ($NaClO_2$), sodium chlorate ($NaClO_3$), potassium chlorate ($KClO$), calcium hypochlorite [$Ca(ClO)_2$], ammonium persulfate

$$[(NH_4)_4S_2O_8]$$

and sodium peroxide (Na_2O_2). The alkali metal cations generally give substantially the same results as the alkali earth metal cations. From this it appears that the particular cation associated with the oxidizing anion has no pronounced effect and thus that any water-soluble oxidizing salt may be employed. Colorless agents such as the foregoing are preferred but colored agents such as potassium permanganate may also be used and yield colored pulps. The anion so far causing the most rapid pulping action appears to be the hypochlorite anion and hence the water-soluble metal hypochlorites are preferred.

Example 1

The effectiveness of a number of colorless oxidizing salts as pulping agents for several representative wet-strength papers is illustrated by the following. All tests were run at room temperature without pH adjustment and the solutions were not agitated. In each instance 100 cc. of solution was employed containing the percentage of oxidizing salt shown in the table and paper strips weighing about 0.5 gm. were employed as the test samples.

The strips were tested by cautiously pulling the sheets with the fingers in the same manner that cloth is tested for tendering, and the decrease in fiber-resin bonding was rated on a uniform scale according to which 0 designates practically no loss of strength (equivalent to no loss in bonding), 3 designates practically complete loss of wet strength, and 1 and 2 designate proportionate intermediate values.

On this scale, wet strength paper having a terminal bond strength rating between 2 and 3 can be pulped in a commercial beater without need for steam-jet treatment, and a rating of 1–2 represents a very material loosening of the bonds.

The paper employed had been prepared in the labora-

tory in uniform manner by forming a beaten suspension of commercial unbleached northern kraft fibers at about 0.6% consistency, adding 3% of the wet strength resin shown in the table followed by 2% of alum (weights based on the dry weight of the fibers) adjusting the pH to the value shown in the table with dilute NaOH or HCl as required, sheeting the suspension on a laboratory handsheet machine at a basis weight between 45 and 50 lbs. per 25" x 40"/500 ream, pressing the sheets between blotters, and drying the sheets at a temperature between 240° and 260° F. for a time between 2 and 10 minutes to give the initial wet strength shown in the table.

The "ethylenimine resin" was prepared by homopolymerizing ethylenimine to the high viscosity necessary for wet strength purposes. The resin was essentially a high molecular weight polyalkylenepolyamine.

The "Hofmann" resin was a linear carbon chain polymer every other chain carbon atom of which carried an amino group. The resin was prepared in accordance with Example 4 of copending application Serial No. 363,394, filed June 22, 1953, by myself et al.

The "Epi-TETA" resin was prepared by the condensation of 0.6 mol of epichlorhydrin with 0.2 mol of triethylenetetramine, as shown in Example 1 of U. S. Patent No. 2,595,936.

The "IBPA–DCE" resin was made by refluxing 131.2 gm. of 3,3'-iminobispropylamine, 87.5 gm. of 1,2-dichlorethane, and 50 cc. of water for two hours. The resin was essentially a straight chain polyazoalkane probably containing a few six-membered rings resulting from condensation of dichlorethane with the polymeric —NH—CH_2CH_2—NH— linkages formed by reaction of 3,3'-iminobispropylamine with 1,2-dichlorethane.

Results are as follows:

No.	Test Paper			NaClO 0.65% 0.5 Min.	NaClO 0.65% 1 Min.	NaClO 0.65% 2 Min.	NaClO 0.65% 15 Min.	NaClO 2% 5 Min.	NaClO 2% 15 Min.	5% $NaClO_2$ 2 Min.	5% $NaClO_2$ 5 Min.	5% $NaClO_2$ 15 Min.	5% $Ca(ClO)_2$ 2 Min.	5% $Ca(ClO)_2$ 4 Min.	5% $Ca(ClO)_2$ 15 Min.	5% $(NH_4)_2S_2O_8$ 2 Min.	5% $(NH_4)_2S_2O_8$ 4 Min.	5% $(NH_4)_2S_2O_8$ 15 Min.	5% $ZnHSO_2$ 5 Min.	5% $ZnHSO_2$ 15 Min.
	Wet Strength Resin [1]	pH[2]	WS[3]																	
1a	Ethylenimine	4.5	5.3	1	2	3				2	3		2	3		3	3		1	2+
1b	do	9.0	6.9	1	2	3					2	3	1+	2+	3	1+	2+	3	1	2+
2a	Hofmann	4.5	5.6				2+													
2b	do	9.0	6.8		1	1+	2+	2	2+		1	2+	1	1+	2+	1	1+	2+	1	2+
3a	Epi-TETRA	4.5	4.0							1	2	2+	1+	2+	3	2	2+	3	2+	3
3b	do	9.0	4.9	1	2	3				1	2	2+	1+	2+	3	1+	2+	3	1	2+
4a	IBPA-DCE	4.5	5.2	1	2	3						3			3			3		2+
4b	do	9.0	6.8	1	2	3						3			3			3		2+

[1] For description of resins see text above.
[2] pH after addition of wet strength resin to pulp. Pulps were sheeted at this pH.
[3] Wet strength, lb./in. (adjusted to 50 lb. basis weight).

The results show that in every case rapid and extensive loosening of its fiber-resin-fiber bonds was effected, the speed of loosening depending principally on the variables shown in the table.

Example 2

The pulping of paper containing a phenol-resorcinol-formaldehyde-bisulfite wet-strength resin is illustrated by the following. This resin was selected as it is generally considered to give outstandingly permanent wet strength at alkaline pH.

The resin corresponded to the resin of Example 3 of Canadian Patent No. 473,753 and was prepared by refluxing a reaction mixture comprising 131.6 parts of phenol, 9.5 parts of sodium metabisulfite, 66 parts of resorcinol and a total of 243.4 parts of 37% formaldehyde to a Gardner-Holdt viscosity of H under conditions set forth in the patent.

Wet strength paper containing the resin was made according to Example 1. The paper was heated for 2 minutes at 240° F. and had a wet strength of 7.5 lbs./in. The paper was tested in the same manner as the paper of Example 1 in dilute sodium hypochlorite solution at room temperature and pH 10 with following results:

NaClO Strength	Paper Strength After [1] — 1 Min.	2 Min.	10 Min.	15 Min.	30 Min.
0.5%			1	2	2-3
2.0%	1	2		2-3	

[1] For explanation of ratings see Ex. 1.

These results show that a paper which is very resistant to alkali is quickly made ready for pulping when treated according to the present invention.

Example 3

The effect of heat is illustrated by the following.

The procedure of Example 2 was repeated except that the concentration of the sodium hypochlorite was decreased to 0.25% and the temperature increased to 65° C. A pulping value of 1–2 was obtained in 10 minutes and a value between 2–3 and 3 in 30 minutes, showing that moderate temperature greatly accelerates the loosening of the bonds by the oxidizing salt.

Example 4

The procedure of Example 1 was repeated using paper prepared by addition of 3% (dry fiber basis) of the melamine-formaldehyde acid colloid of U. S. Patent No. 2,345,543 to slush stock followed by 1% alum. The paper was dried at 240° F. for 2 minutes and had wet strength of 10 lb./in.

The paper was soaked in 0.25% sodium hypochlorite solution at 65° C. for 30 minutes. The paper had a pulping rating of 1 at 30 minutes and a rating of 2–3 at 60 minutes.

We claim:

1. A process for the pulping of paper broke composed of cellulose fibers bonded together by an adsorbed content of at least one wet-strength resin which comprises: slurrying said broke with a dilute aqueous solution of an inorganic oxidizing salt thereby loosening the fiber-resin-fiber bonds in said broke, and then subjecting the broke to mechanical pulping.

2. A process according to claim 1 wherein the oxidizing salt is a water-soluble colorless metal hypochlorite.

3. A process according to claim 1 wherein the oxidizing salt solution is hot.

References Cited in the file of this patent

UNITED STATES PATENTS

1,576,994 Plumstead ---------- Mar. 16, 1926

(Other references on following page)

5

UNITED STATES PATENTS

1,992,977	Wells	Mar. 5, 1935
2,525,594	Fennel	Oct. 10, 1950
2,580,161	Driessen	Dec. 25, 1951
2,641,164	Hill	June 9, 1953

FOREIGN PATENTS

288,640	Germany	Nov. 10, 1915

6

265,055	Great Britain	Feb. 3, 1927

OTHER REFERENCES

Casey: "Pulp and Paper," vol. 1, page 602 (1952), Interscience Publishers, Inc., New York.