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P. REROLLE ET AL
DELIGNIFICATION OF CHEMICAL CELLULOSE PULPS
WITH OXYGEN AND THEN CHLORINE

3,423,282

Filed May 13, 1965

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TRIAL	CHLORINE			OXYGEN IN AN ALKALINE MEDIUM						CHLORINE			SODIUM HYDROXIDE			
	%	BRIGHT- NESS	KMNO ₄ NUMBER	% O ₂	% NaOH	% CaI	BRIGHT- NESS	KMNO ₄ NUMBER	D.P.	%	BRIGHT- NESS	KMNO ₄ NUMBER	%	BRIGHT- NESS	KMNO ₄ NUMBER	D.P.
A-1	8.5	25.5	10										2.5	27.3	6.5	
A-2	8.5	25.5	10										2.5	27.3	6.5	
A-3				1.9	6.5	1	43.4	6.1	950	2	51		0.5	50.0	3.6	
A-4				1.9	6.5	1	43.4	6.1	950	2	51		3.0	55.5	3.1	
A-5				1.9	6.5	1	43.4	6.1	950	2	51					
A-6				1.9	6.5	1	43.4	6.1	950	3	53.3		3.0	76.3	2.6	
A-7				1.4	6.5	1	41	9.2	1150	3	45.2		0.5	40.8	3.9	
A-8				1.4	6.5	1	41	9.2	1150	3	45.2		3.0	62.0	3.2	
A-9				1.4	6.5	1	41	9.2	1150	3	45.2					
A-10				1.4	6.5	1	41	9.2	1150	4	45.6		0.5	44.0	3.7	
A-11				1.4	6.5	1	41	9.2	1150	4	45.6		4.0	70.8	2.7	
A-12				1.4	6.5	1	41	9.2	1150	4	45.6					
A-13	8.5	23.4	10.1	2.1	5.0	1	53.4	1.5	1130							
B-1	9.0	21.4	13.8										2.5	21.0	6.5	1140
B-2	11.0	21.2	7.5										2.5	22.6	6.5	1070
B-3	11.0	21.2	7.5										2.5	22.6	6.5	1070
B-4				2.5	6.5	1	35.8	8.1	1070	3	40.0	4.5				
B-5				2.5	6.5	1	35.8	8.1	1070	3	40.0	4.5	1.25	42.0	2.0	
B-6				2.5	6.5	1	35.8	8.1	1070	3	40.0	4.5	3.0	50.0	1.9	
B-7				2.5	6.5	1	35.8	8.1	1070	2	36.2	6.7	1.25	44.0	3.0	
B-8				2.5	6.5	1	35.8	8.1	1070	4	41.0	5	1.25	48.6	2.3	
C-1	6.0	35.0	9.8										2.5	43.6	4.5	
C-2	6.0	35.0	9.8													
C-3				2.8	7.1		66.6	6.0	1375	3	55.0	3.7	0.5	68.7	0.7	1330
C-4				2.8	7.1		66.6	6.0	1375	3	55.0	3.7	2.5	73.8	0.7	1330
C-5				2.8	7.1		66.6	6.0	1375	3	55.0	3.7				
C-6				2.8	7.1		66.6	6.0	1375	4	58.0	3.0	0.5	65.7		
C-7				2.8	7.1		66.6	6.0	1375	4	58.0	3.0	3	88.1		
C-8	6	36	8.6	2.8	5		73.0	3.3	1540							

FIG. 1

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TRIAL	SODIUM HYPOCHLORITE			HYDROGEN PEROXIDE			CHLORINE DIOXIDE			SODIUM HYDROXIDE		HYDROGEN PEROXIDE		CHLORINE DIOXIDE		
	17° O/° Cl ₂	BRIGHT- NESS	KMnO ₄ NUMBER	%	BRIGHT- NESS	D. P.	%	BRIGHT- NESS	D. P.	%	BRIGHT- NESS	%	BRIGHT- NESS	%	BRIGHT- NESS	D. P.
A-1							1	50.5		0.5	53			0.3	81	1045
A-2							1	50.5				0.2	73.6	0.3	87	1085
A-3							0.9	88.0	1000							
A-4							0.6	85.5	980							
A-5				0.5	74.7		0.6	89.2	990							
A-6							0.6	86.0	1000							
A-7							1	84.9	1000							
A-8							0.6	82.4	985							
A-9				0.5	71.5		0.3	87.0	1038							
A-10							1	86.0	1005							
A-11							0.6	84.5	950							
A-12				0.5	74.2		0.3	88.4	940							
A-13							1	86.2	1080							
B-1							0.76	45.6		0.5	48.3			0.38	72.6	1005
B-2							0.76	43.0		0.5	47.4			0.38	74.8	1080
B-3							0.76	43.0				0.7	72.5	0.38	85.7	1065
B-4				0.4	55.0		0.7	88.0	1000							
B-5							1	86.7	1030							
B-6							0.9	84	1040							
B-7							1	84	1100							
B-8							1	87.2	990							
C-1	2.0	80.4	3.4				0.3	84.7	1260							
C-2	2.5	62.8	3.5	1.0	83.6	1530										
C-3							0.6	91.0	1270							
C-4							0.6	91.4	1360							
C-5				0.5	87.5		0.3	91.8	1440							
C-6							0.6	92.3	1430							
C-7							0.4	91.2	1200							
C-8							0.9	91.0	1520							

FIG. 2

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DELIGNIFICATION OF CHEMICAL CELLULOSE PULPS WITH OXYGEN AND THEN CHLORINE

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7 Claims

ABSTRACT OF THE DISCLOSURE

Delignification and bleaching of chemical pulp in two stages is provided by treating the pulp with oxygen at an elevated temperature above room temperature for no more than a few hours and under less than 15 bars pressure, and then subsequently treating the pulp with chlorine at room temperature for not more than one hour.

This invention relates to a method for the two-stage delignification of chemical cellulose pulps.

The bleaching of chemical cellulose pulps for the production of paper or for dissolving for chemical uses normally demands several successive treatments to reach the required residual lignin content and brightness.

The action of chlorine, either in the gas state or dissolved in water, upon the lignin chemical wood pulps is well known and has been the subject of many investigations. Chlorine is almost universally used as the primary reagent in multi-stage bleaching methods.

The brightening and delignifying action of oxygen is also well known the recent work of Nitikin and Akim (Transactions of the Leningrad Academy of Forestry 75 (1956), 77 (1958), 85 (1960); Bumazhnaya Promyshlennost 12 (1960), as well as U.S. Patent No. 3,024,158, granted on July 2, 1958 to the Kimberley-Clark Corporation, French Patent No. 1,310,248, granted on March 6, 1961 to the Champion Papers Corp., and French Patent No. 1,387,853, granted on September 19, 1963 to the applicant for "Delignification and bleaching of chemical and semichemical cellulose pulps," all pertain to the matter. It should be observed that the action of oxygen, unlike that of chlorine, occurs in alkaline medium. On the other hand, there is an undeniable commercial advantage in the use of oxygen rather than of air, since the pressures may be considerably reduced, which is desirable owing to the large volumes involved.

It is a well-known fact that in the practice of the multiple-stage bleaching of cellulose pulps, it is desirable to alternate the stages, with a change of medium and of oxidizer at each step.

For instance, an alkaline-medium hydrogen peroxide stage may precede or follow an acidic-medium chlorine dioxide stage. This is usually explained by the possibility of reaching at each successive change deeper layer of fiber or chromophorous groups made accessible by the previous reaction. This principle is in fact partly applied when chlorination is followed by neutralization or alkaline extraction, which facilitates the dissolution of the chlorolignins, in this case, no second stage of delignification is therefore involved.

The bleaching of cellulose fibers by subjecting the pulp to the action of chlorine, then of air or oxygen, is known through U.S. Patent No. 2,147,618, granted on April 1, 1936 to the West Virginia Pulp Corp. This procedure makes it possible to reduce the number of stages, at the price, however, of a high consumption of chemicals and

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of a comparatively protracted chlorine treatment, sometimes renewed under the same conditions before contacting the pulp with oxygen.

According to the present invention, a method has now been found which makes it possible to obtain, in only two or three stages, starting from very hard pulps, almost entirely delignified pulps, which, by the conventional method using chlorine, then soda, and finally hypochlorite or chlorine dioxide, can only be obtained in three or four stages.

The method of the invention has the great additional advantage of increasing the brightness at each stage of the delignification with low consumption of chemicals, whereas, in common practice, the chlorination and alkaline extraction are attended by a decrease of the brightness, or in the most favorable cases by the preservation of the brightness at its former level. This method for the two-stage delignification of cellulose pulps is featured by the treatment of the cellulose pulps by oxygen in an alkaline medium, then by chlorine.

The oxygen treatment may be effected in the presence of a delignification catalyst which preserves the physical and strength properties of the pulps, such as magnesium carbonate.

The oxygen treatment is effected at higher temperature than room temperature preferably between 80° C. and 130° C. (176° F. and 266° F.), more particularly between 80° C. and 100° C. (176° F. and 212° F.). The time at maximum temperature does not exceed a few hours, preferably 1 to 3 hours, and the pressure is moderated and does not exceed 15 bars.

The chlorine treatment is effected at room temperature for one hour at most.

The method of the invention may be applied according to the following embodiment, which gives outstanding results.

According to one embodiment, cellulose pulps are treated by oxygen in an alkaline medium, then by chlorine. The chlorination has the rather remarkable feature of being effected at a higher pH than is usual, since the pulp emerges from the alkaline medium oxygen treatment at high pH; once the pulp has been washed, owing to the alkalinity and the low amount of chlorine, the chlorine treatment does not lead to such low pH's as in the usual chlorination procedures. The result is that in some cases, the chlorination is attended by an increase in brightness due to the presence of hypochlorous acid, while the degradation which might have been feared does not occur. This highly interesting result is due to the low concentration of chlorine, to the short duration of the reaction, and to the fact that the lignin is in a state of particular reactivity towards chlorine.

As in the case of conventional bleaching, the chlorination should be followed by an alkaline treatment, which may be either a true alkaline extraction with intermediate washing, or, if definite increase of brightness is required at that stage, a hydrogen peroxide stage or a neutralization with caustic without intermediate washing, the residual chlorine being converted to hypochlorite in situ. In the latter case, the exhaustion of the chlorine is very fast and can occur at comparatively low temperatures; such conditions are high desirable, as they hinder the degradation of cellulose.

The advantages of the method are considerable; they result in a significant reduction of the amounts of chlorine consumed, i.e., a decrease of 50–70% of the total chlorine, both as hypochlorite or chlorine dioxide and as free chlorine. On the other hand, the method of the invention makes it possible to obtain semibleached pulps in two stages, under better conditions than with hypochlorite, and, with highly delignified pulps, to make maximum

use of the true bleaching agents, hydrogen peroxide and chlorine dioxide, with which increases in brightness up to 35 and 45 points respectively may be obtained in the final stage.

According to a preferred embodiment of the invention the chlorine treatment is effected at room temperature. In the case of initial chlorination, the duration should preferably be around one hour, whereas in chlorination after oxygen treatment, the duration is much shorter, preferably around 15 minutes. This reduction of the duration and the decrease in the chlorine consumption evidence one of the advantages of the method of the invention.

The oxygen treatment is effected on the unbleached pulp, which is treated in an electrically-heated autoclave by a solution of sodium hydroxide, optionally in the presence of a delignification catalyst which preserves the physical and strength properties of cellulose pulps, such as magnesium carbonate, at elevated temperatures between 80° C. and 130° C., more particularly between 80° C. and 100° C. Oxygen is introduced into the autoclave until the desired pressure (up to 15 bars at maximum temperature) is obtained. The time at maximum temperature is a few hours at most.

The following examples, given as illustration, do not limit the scope of the invention.

The delignification stages were effected under the following conditions:

Chlorination was effected on cellulose pulps at 4% concentration by weight, at 20° C. (68° F.). The time was one hour for initial chlorination, 15 minutes for chlorination after oxygen treatment.

Cellulose pulps subjected to oxygen treatment in alkaline medium usually were at 7% concentration; the choice of this concentration resulted from the treatment in a rotating autoclave. The amount of caustic was preferably 5% to 10% on the pulp, according to the nature and degree of delignification of the latter. Magnesium carbonate was optionally used as delignification catalyst, preferably at 1% concentration.

The various conventional bleaching treatments following upon delignification according to the invention were effected under the conditions described hereafter.

The sodium hydroxide treatment, in the case of conventional alkaline extraction, was effected on cellulose pulps at 10% concentration, at elevated temperature up to 65° C. (150° F.), and lasted two hours.

For neutralizations with chlorine residues, the pulp concentration was 4% and the temperature 30° C. (86° F.); the treatment was continued until the chlorine was entirely exhausted.

Treatment with sodium hypochlorite was applied to cellulose pulps at 4% concentration, at 40° C. (104° F.), until 90% of the available chlorine was consumed, with a maximum time of 4 hours. The medium was buffered with sodium hydroxide and a silicate, so as to get a pH between 9 and 11.

Treatment with hydrogen peroxide was effected on pulps at 15% concentration, at 65° C. (150° F.), in 5 hours' time. The bleaching liquor was buffered with 3% 40-42 Bé sodium silicate on the pulp, and the required amount of sodium hydroxide was added to bring the pH in the neighborhood of 11 at the outset of the bleaching operation.

Treatment with chlorine dioxide was effected at 65° C. for 5 hours on pulps at 6% concentration (the limit being enforced for laboratory trials only).

The concentrations given in the examples are concentrations by weight. Except for sodium silicate, the amount of which is based on the commercial product, and for sodium hypochlorite, given as active chlorine, all bleaching or delignifying agents are given as chemically pure products on bone-dry pulp, either unbleached for oxygen treatment and former treatments, or oxygen-treated for

later treatments, i.e., as chlorine oxygen, sodium hydroxide, magnesium carbonate, chlorine dioxide and hydrogen peroxide.

The brightness was measured with a Zeiss Elrepho with R 46 Tappi filter.

Permanganate numbers were determined with 40 ml. for unbleached pulps and 25 ml. for other pulps.

Degrees of polymerization were determined with cupriethylenediamine, and computed according to AFNOR Standard NF T 12.005 and given under the letters D.P.

The trials, the results of which are shown in the table of FIGS. 1 and 2, were done on three different pulps.

The trials given under the letter A were done on a French maritime pine sulphate pulp, unbleached brightness 21, permanganate number 22.

The trials given under the letter B were done on an American softwood sulphate pulp, unbleached brightness 19.5, permanganate number 24.6.

The trials given under the letter C were done on an American sulphite pulp, unbleached brightness 60, permanganate number 21.1.

FIG. 1 gives the initial sequential results from left to right and FIG. 2 gives the remaining sequential results from left to right for each trial.

For each of those pulps, two or three trials show the results obtainable by conventional bleaching; four to ten trials show the results obtainable by the oxygen-chlorine method; one trial on pulp A and one on pulp C demonstrate the effect of the chlorine-oxygen method.

In trials A₃-A₆, oxygen treatment was effected under 7.8 bars pressure at 100° C.; in trials A₇-A₁₂, under 7 bars pressure at 97° C.

In trial B₁, the initial chlorination was effected in an open vessel; in trials B₂ and B₃, in closed vessels.

With 0.5-1.25% concentrations, the sodium hydroxide treatment is a true alkaline extraction; in other cases, it is a neutralization before the chlorine consumption is completed.

Investigations of the results given by the conventional bleaching methods show that the pulps were hard-bleaching, thus underlining the commercial interest of the results obtained through the double delignification by oxygen and chlorine according to the invention.

What we claim is:

1. A method for the two-stage delignification of chemical cellulose pulp comprising contacting said pulp in an alkaline medium with oxygen at from 80-130° C. under less than 15 bars pressure for approximately 1 to 3 hours, and then contacting said alkaline pulp with chlorine at a concentration of about 2 to 4% by weight based on the bone dry oxygen treated pulp at room temperature for not more than one hour.

2. A method in accordance with claim 1 wherein said treatment with oxygen is carried out at from 80° C.-100° C.

3. A method in accordance with claim 1 wherein said alkaline medium containing oxygen further contains a delignification catalyst.

4. A method in accordance with claim 3 wherein said catalyst is magnesium carbonate.

5. A method in accordance with claim 4 wherein said catalyst is present in about 1% concentration.

6. A method of delignifying and bleaching chemical cellulose pulp comprising first contacting said pulp with oxygen in an alkaline medium at a temperature between 80 and 130° C. for approximately 1 to 3 hours to effect a first-stage delignification, next contacting said alkaline pulp at room temperature with chlorine at a concentration of about 2 to 4% by weight based on the bone dry oxygen treated pulp for no more than one hour to effect a second-stage delignification and bleaching, and then further contacting said pulp with a bath containing materials selected from the group consisting of alkaline compounds,

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hydrogen peroxide and chlorine dioxide to effect further bleaching.

7. A method in accordance with claim 6 wherein said contacting with chlorine is carried out for about 15 minutes.

References Cited**UNITED STATES PATENTS**

2,147,618 2/1939 Rawling ----- 162—65

6**FOREIGN PATENTS**

569,029 1/1959 Canada.
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5 HOWARD R. CAINE, *Primary Examiner*.

U.S. Cl. X.R.

8—109; 162—88