(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 311 356**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **88309239.7**

(51) Int. Cl.[4]: **D21C 9/10**

(22) Date of filing: **04.10.88**

(30) Priority: **05.10.87 US 104607**

(43) Date of publication of application:
12.04.89 Bulletin 89/15

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

(71) Applicant: **FMC Corporation**
2000 Market Street
Philadelphia Pennsylvania 19103(US)

(72) Inventor: **Hills, William Avery**
5 Pine Knoll Drive
Lawrenceville New Jersey 08648(US)
Inventor: **Richards, Joseph Charles**
49 Robbinsville-Edinburg Road
Robbinsville New Jersey 08691(US)

(74) Representative: **Beresford, Keith Denis Lewis et al**
BERESFORD & Co. 2-5 Warwick Court High Holborn
London WC1R 5DJ(GB)

(54) **Process for bleaching mechanical pulp.**

(57) A two-stage process for bleaching mechanical pulp is claimed incorporating a first reductive stage followed by a second peroxygen stage.

EP 0 311 356 A1

PROCESS FOR BLEACHING MECHANICAL PULP

The present invention is a process for bleaching mechanical pulp.

Mechanical pulps are formed by physically abrading wood into fibers containing cellulose and lignin rather than chemically dissolving the lignin in the wood to leave only a fibrous cellulosic residue. Because essentially all of the wood is converted into pulp suitable for manufacturing paper products, the mechanical pulping methods are considered desirable, both because of the high yield of pulp based on the wood employed as a raw material, and because there is substantially little waste generated for disposal.

Mechanical pulps may be made by grinding logs against a "stone" wheel (groundwood pulp) or by milling wood with a metal refiner blade either cold (refiner pulp) or hot (thermomechanical pulp).

The raw material used for refiner mechanical pulping and for thermomechanical pulping is usually inferior to the logs that are used in the production of groundwood. A large part of the wood used for refiner and thermomechanical pulping comes from chips from sawmill slabs, and this raw material contains more bark (and dirt) than debarked logs. Even if the bleachability of the pulp is not affected by these impurities, the brightness of both the unbleached and the bleached pulp will suffer.

There are two principal methods used for the bleaching of mechanical pulps: reductive and oxidative bleaching. These two methods can be used singly or combined in a two-stage bleaching sequence with oxidative bleaching in the first stage and reductive in the second stage. The reductive bleaching agents are bisulfite, hydrosulfite and borohydride. The principal oxidative bleaching agent is hydrogen peroxide. Hydrosulfite bleaching is the reductive bleaching method that is most used. Sodium hydro sulfite ($Na_2S_2O_4$) is the preferred form. Zinc hydrosulfite is used to some extent. It is more stable than the sodium form and can be produced at the mill site, but it has the drawback of being toxic to fish. Hydrosulfite bleaching is usually carried out at low consistency. Maximum bleach response is obtained at about 4% consistency. Maximum brightness is usually obtained between pH 5 and pH 6. Hydrosulfite can be produced by reducing a sulfite with sodium borohydride (available commercially as a solution "Borol").

All percentages reported herein are as percent by weight. Consistency is the percent oven dry weight of pulp in an aqueous slurry. Additives are reported as the weight percent based on the oven dry weight of pulp unless specifically stated otherwise.

Sodium borohydride is a strong reducing agent, but the bleaching effect is surprisingly low compared with hydrosulfite. The borohydride salt forms an alkaline solution, but this alkalinity is not sufficient to keep the pH above the critical range for self-decomposition of borohydride during bleaching. Somewhat better results are obtained with higher alkalinity and high consistency. The presence of a sequestering agent (DTPA) and sodium silicate also seems to improve the bleaching. Sodium borohydride is usually too expensive to be used, as such, for bleaching of pulp but often used for on-site production of sodium hydrosulfite.

Oxidative bleaching with a peroxide has certain advantages over hydrosulfite reductive bleaching. The brightness gain obtained with oxidative bleaching can be much higher than with hydrosulfite bleaching and the corrosion problems are less for peroxide than for hydrosulfite bleached pulp. Several oxidizing agents have been tried for bleaching of mechanical pulp, but peroxide is the only one used in bleaching mechanical pulp, primarily as hydrogen peroxide.

A simple mixture of hydrogen peroxide and alkali will not give the best bleaching results. One or more additional chemicals usually are added in order to improve the result. The most common chemical used is sodium silicate; others include magnesium sulfate and sequestering agents, such as DTPA and phosphates.

Sodium silicate has a buffering action in the pH range where peroxide is most active as a bleaching agent. Another effect of sodium silicate is to inactivate metal ions. Magnesium sulfate has a similar inactivation effect and is especially useful when the hardness of the water is low. Sodium silicate and magnesium seem to act synergistically, but the mechanism for this is not known. Calcium has an effect similar to that of magnesium. Rather large quantities of sodium silicate are used in peroxide bleaching of mechanical pulp. Usually a 40% solution of sodium silicate is used and about 5% by weight of this solution is added based on pulp weight (2.0% sodium silicate on pulp weight). Magnesium sulfate (Epsom salt) is used in small quantities, generally 0.05% to 0.2% based on the pulp.

The consistency in bleaching is dependent on the dewatering equipment and the equipment used for mixing the pulp and bleach. Consistencies between 10 and 20% are used and 15% is about average. The retention time is usually from 1.5 to 3 hours. At the bottom of the tower the pulp is diluted with water to a consistency between 3% and 4%. As the pulp is alkaline, the pH of the slurry must be reduced in order to avoid color reversion. Usually the pH is lowered to about 5.5, which is the same as for the unbleached pulp.

If sulfur dioxide or bisulfite is used for lowering the pH, the residual peroxide will also be consumed.

Chemical pulps are usually bleached in more than one stage and a multistage process is also employed for mechanical pulps if high-brightness values are required. Oxidative bleaching with peroxide followed by reductive bleaching with hydrosulfite is the method used commercially for multistage bleaching of mechanical pulps. Because peroxide bleaching is terminated before all the peroxide is consumed, the residual peroxide should be destroyed before the hydrosulfite is added. An adjustment of the pH of the pulp must also be made before the hydrosulfite is added. Sulfur dioxide and sulfite liquor are suitable for both purposes. The reductive/oxidative bleaching sequence, using hydrosulfite in the first stage and peroxide in the second stage is believed to be inferior to a bleach sequence with peroxide in the first stage. The reason given is that some of the chromophoric groups reduced by the hydrosulfite are subsequently oxidized with peroxide, thereby offsetting part of the benefit of the reductive bleaching.

Two-stage oxidative/reductive bleaching with either hydrosulfite or borohydride followed by peroxide will produce high-brightness values. Borohydride and peroxide can also be used together in a single-stage bleaching; it is rather surprising but these two chemicals do not react with each other under normal bleaching conditions. The effect is not as good as that obtained in two-stage bleaching with the same chemicals, but it is better than with peroxide alone. By bleaching in three stages with borohydride-peroxide-hydrosulfite, brightness values of 87% to 88% have been obtained.

The present invention is a process for bleaching a mechanical pulp in an aqueous slurry comprising (a) contacting an aqueous slurry of the mechanical pulp with a reductive bleaching agent in a first stage, (b) washing the slurry pulp from the first stage to substantially remove any remaining reductive bleaching agent, (c) adjusting the consistency of the washed pulp slurry to at least 10%, and (d) incorporating into the pulp slurry from step (d) a sufficient amount of a peroxygen bleach solution to provide a concentration of at least 1% hydrogen peroxide based on the oven dry weight of the pulp in the slurry, and maintaining the temperature of the pulp slurry at an elevated temperature for a sufficient time to increase the brightness of the pulp in the slurry.

The conditions of the hydrosulfite reductive bleaching step are desirably the usual conditions employed,. desirably at a pH between 5 and 6, at a low consistency desirably between 2% and 5%, preferably about 4%. The temperature should be above 40°C, desirably 50°C to 100°C, preferably 60°C to 100°C. Usually the bleach response is satisfactory after 10 minutes, however, a slow increase in brightness continues for about two hours.

Normally from 0.5% to 1% hydrosulfite is employed based on the dry pulp, although lesser amounts are effective. More than 1% does no harm but the bleach response decreases.

Sequestering agents may be employed to eliminate heavy metals from the pulp. Commonly salts of ethylenediamine tetraacetate (EDTA), pentasodium diethylenetriamine pentaacetate (DTPA), nitrillotriacetate (NTA), sodium tripolyphosphate, sodium citrate and the like are employed commercially.

For refiner pulp or thermomechanical pulp the bleach solution may be incorporated with the chips as feed to the refiner. For ground wood pulp it is desirable to add the bleach chemicals to the pulp slurry.

Sodium borohydride is best employed to form sodium hydrosulfite by reacting it with sulfur dioxide or a sulfite. However, it may be employed without forming the hydrosulfite at a pH of 10 to 11 at a consistency of 4% or more.

Peroxygen bleaching should be at a consistency of 10% to 20% with the temperature desirably between 40°C and 60°C sufficient bleaching can be obtained by 1 1/2 to 3 hours. Normally about 1% to 3% sodium silicate and 0.05% to 0.2% magnesium sulfate based on pulp weight are incorporated into the bleach solution. Sequestering agents such as DTPA or 2-hydroxyethyl-ethylenediamine triacetate (HEDTA) may be employed to pretreat the pulp prior to the peroxygen bleach step.

The peroxide content of the bleach solution should be equivalent to at least 1% H_2O_2, desirably 3% to 10%. Any source of hydrogen peroxide may be employed, such as 35% to 70% H_2O_2, sodium peroxide, sodium carbonate peroxide or the like.

The best mode for practising the invention will be clear to one skilled in the art from the following nonlimiting examples.

Pulp was generally pretreated with 0.25% DTPA at 4% consistency. An equivalent of 50 grams pulp, oven dried (O.D.), was weighed out and its consistency adjusted as desired using 60°C (140°F) deionized water.

Sodium Hydrosulfite Bleaching

The pulp was adjusted to a consistency of 4% and was placed in a closed container. The pH was adjusted to 6 with a solution of sulfur dioxide in water just before adding the required amount of sodium hydrosulfite. The contact of sodium hydrosulfite with air was minimized by introducing the sodium hydrosulfite solution below the surface of the liquid level in the jar with a pipette. The jar was immediately sealed and shaken by hand for proper mixing. The treated pulp was maintained at 60 °C for one hour. Subsequently the pulp was filtered, washed and adjusted to the desired consistency for the next operation.

Sodium Borohydride Bleaching

Sodium borohydride bleaching was carried out similar to the above except that the pH was on the basic side (10-11) and the pulp was adjusted to a 4% consistency. The bleaching was also carried out for shorter times.

Hydrogen Peroxide Bleaching

After washing the pulp from a prior reductive step, if any, bleaching with hydrogen peroxide was carried out in the conventional manner. Samples were bleached at 12% consistency.

The pulp sample was heated to the desired temperature in a microwave oven and the bleach liquor (prepared by adding sodium silicate, caustic soda, magnesium sulfate and hydrogen peroxide) was added to the preheated pulp and mixed thoroughly. The pulp mixture was placed in a glass covered beaker and heated in a thermostatically controlled bath.

Samples were removed periodically for brightness determination.

Hand Sheet Preparation for Brightness Measurement

A sample of 6 O.D. grams of pulp was removed for each determination. The sample was diluted with deionized water about .75% consistency. The pH of this slurry was adjusted to 4.5 with an aqueous solution of sulfur dioxide. A Waring high speed mixer was used to remove fiber lumps before forming the test sheets in a 6.25 inch TAPPI sheetmold according to the Appendix of TAPPI Standard T218 05-69. The sheets were dried overnight and brightness determined on a Data Color Model 2000 reflectance meter. The units are expressed as % Elrepho or ISO Brightness.

EXAMPLE 1

A two-stage bleach sequence was employed using hydrogen peroxide in the first stage and sodium hydrosulfite in the second stage. The pulp was a 50/50 mixture of hardwood/softwood TMP. Conditions and results are shown as Table I.

EXAMPLE 2

The same batch of pulp used in Example 1 was bleached in the reverse sequence, a sodium hydrosulfite stage followed by a hydrogen peroxide stage. Results are presented as Table II.

For comparison a single hydrogen peroxide stage bleach was run with the same other conditions as Example 3. The brightness was 85% and all 7% of the hydrogen peroxide was used.

EXAMPLE 3

Sodium borohydride was employed as the reductive bleaching agent for a southern thermomechanical softwood pulp. In experiment 1, the oxidation stage was first followed by the reduction stage. In experiment 2, the reduction stage was first followed by the oxidation stage. Experiment 3 was the reduction stage alone employing sodium borohydride as the reducing agent.

It is unexpected that a two-stage bleaching sequence employing a reducing agent as a first stage would be superior to the usual oxidative/reductive sequence in view of the references in the prior art teachings to the contrary. Only one published example of a reductive/oxidative bleach sequence employing groundwood is reported in the literature, Barton, R.W., "Bleaching of Groundwood with Combinations of Peroxide and Hydrosulfite", TAPPI, Vol. 41(3), pages 161A-165A. The single example employed only 0.4% H_2O_2 (2% Na_2O_2).

TABLE I

OXIDATIVE/REDUCTIVE BLEACHING OF A THERMOMECHANICAL PULP				
Experiment	1	2	3	4
Peroxygen stage (stage 1) 60° C Consistency 12%				
% H_2O_2	3	5	10	5
% NaOH	3	5	6	5
% Na_2SiO_3	5	5	5	5
% $MgSO_4$	.05	.05	.05	.05
Hydrogen stage (stage 2) 60° C Consistency 4%				
% $Na_2S_2O_4$	1	1	1	-
Brightness				
2 hours	80.0	82.2	84.2	82.4
% H_2O_2 Used	2.37	3.79	4.14	4.00

TABLE II

REDUCTIVE/OXIDATIVE BLEACHING OF A THERMOMECHANICAL PULP			
Experiment	1	2	3
Peroxygen stage (stage 2) 60° C Consistency 12%			
% H_2O_2	3	5	10
% NaOH	3	5	7
% Na_2SiO_3	5	5	5
% $MgSO_4$	.05	.05	.05
Hydrosulfite stage (stage 1) 60° C Consistency 4%			
% $Na_2S_2O_4$	1	1	1
Brightness			
2 hour	81.2	84.1	86.2
% H_2O_2 Used	2.03	4.23	4.69

TABLE III

REDUCTIVE/OXIDATIVE BLEACHING OF A THERMOMECHANICAL PULP			
Experiment	1	2	3
Stages sequence*	O/R	R/O	R
Peroxygen stage 60° C Consistency 12%			
% H_2O_2	6	6	6
% NaOH	6	6	6
Borohydride stage 140° F Consistency 4%			
$NaBH_4$	1	1	-
% $MgSO_4$	.05	.05	.05
Brightness (gain)			
2 hours	64.3	66.1	60.5
4 hours	67.0 (31.7)	68.5 (33.0)	62.7 (27.2)
% H_2O_2 Used			
2 hours	4.22	3.95	5.22
4 hours	4.69	4.41	5.47

* O/R = oxidative stage, reductive stage
R/O = reductive stage, oxidative stage
R = reductive stage only

Claims

1. A process for bleaching a mechanical pulp contained in an aqueous slurry characterized by (a) contacting an aqueous slurry of the mechanical pulp with a reductive bleaching agent in a first stage, (b) washing the slurry pulp from the first stage to substantially remove any remaining reductive bleaching agent, (c) adjusting the consistency of the washed pulp slurry to at least 10%, and (d) incorporating into the pulp slurry from step (c) a sufficient amount of a peroxygen bleach solution to provide a concentration of at least 1% hydrogen peroxide based on the oven dry weight of the pulp in the slurry, and maintaining the temperature of the pulp slurry at an elevated temperature for a sufficient time to increase the brightness of the pulp in the slurry.

2. The process of claim 1 characterized in that the reductive bleaching agent is sodium hydrosulfite, zinc hydrosulfite or sodium borohydride.

3. The process of claim 1 characterized in that the reductive bleaching agent is present as an aqueous solution of 0.5% to 1% hydrosulfite as sodium hydrosulfite at a pH of 5 and 6.

4. The process of claim 1 characterized in that the reductive bleaching agent is sodium borohydride at a pH of 10 to 12.

5. The process of claim 1 characterized in that the reductive bleaching agent is an aqueous solution of 0.5 to 1% hydrosulfite as zinc hydrosulfite at a pH of 5 and 6.

6. The process of any preceding claim characterized in that the peroxygen bleach solution comprises a solution comprising an aqueous solution containing at least 1% hydrogen peroxide at a pH of 10 to 11 and containing 1% to 3% sodium silicate and 0.5% to 0.2% magnesium sulfate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 9239

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	ABSTRACTS BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 53, no. 2, August 1982, page 260, no. 2296, Appleton, Wisconsin, US; & JP-A-5 992/82 (MITSUBISHI GAS CHEMICAL CO., INC.) 12-01-1982 * Abstract *	1-3,5,6	D 21 C 9/10
X	US-A-2 290 601 (J.S. REICHERT et al.) * Whole document *	1-3,6	
X	DE-C- 834 808 (DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT) * Whole document *	1-3,6	
X	DE-B-1 171 723 (M.O. DOMSJö) * Whole document *	1,2,4	
P,X	EP-A-0 263 040 (ATOCHEM) * Claims 1-3,7,8,10-12 *	1-4,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D 21 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11-01-1989	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)