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(54) **Steam explosion pulping process for papermaking.**

(57) A pulping process includes a short saturated steam cooking of wood chips impregnated with alkaline solutions of sulphites and carbonates, chlorides, sulfates or bicarbonates in the temperature range of 180 to 210°C followed by explosive decompression and fibre refining.

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This invention relates to a steam explosion pulping process for papermaking.

Ingruber et al., *Pulp and Paper Manufacture*, Volume 4, TAPPI, CPPA, p. 160 (1985) lay down that conventional ultra-high-yield chemithermomechanical or chemimechanical pulping (CTMP/CMP) is preferably conducted at a pH level between 4 and 9, and involves either liquid or vapor phase cooking with sodium sulphite-bisulphite solutions for about 10 to 30 minutes at a temperature between 60 and 175 °C. It is generally accepted that the chemical treatment is mainly responsible for permanent fibre softening, increase in long fiber content, fibre specific surface and conformability, as demonstrated by Heitner et al., *Pulp and Paper Can.*, (84)11: T252-T257 (1983).

There is another softening approach which consists of a steam treatment of chips at high temperatures followed by explosive decompression.

The production of pulp using high-pressure and high steam chip softening well above glass transition temperatures of lignin should theoretically lead to lower energy consumption in subsequent refining stages.

The initial research in the field of high-pressure steam cooking, followed by defibration by explosion, was made by Mason, US-A-1 824 221; 2 645 623; 2 494 545; 2 379 8290. The masonite pulp obtained according to a two stage Sprout-Waldron refining procedure showed weak physical strength, dark color and yield loss of 16% to 20%, and revealed itself simply unsuitable for the production of paper according Koran et al., *Pulp and Paper Can.*, 79(3): T107-T-113 (1978). Mamers and al., TAPPI, 64(7): 93-96 (1981); APPITA, 29(5): 356-362 (1976) investigated explosion pulping of pinus eliotti wood chips with the help of high pressure carbon dioxide solutions and bagasse of wheat straw explosion pulping under high pressure of nitrogen. Paper properties which were obtained were similar to that of CTMP/CMP pulps, but at the expense of brightness. The major problem to overcome is oxidation, as well as hydrolytic degradation of fibers leading to brightness and yield loss.

It has been suggested by Vit et Kokta, CA-A-1 212 505 (1986) that the ultra-high-yield (90%+) pulp suitable for papermaking can be produced by vapor phase steam explosion cooking. The initial properties of papers made from exploded softwood chips were similar to those of TMP. However, refining energy was about 20% to 25% lower. Recently, a pulping process entitled "Process for Preparing Pulp for Paper Making", Kokta B.V., CA-A-1 230 208; US-A-4 798 651; Can. Pat. Appl. #542 643 (May 1987), referred to as "Steam Explosion Pulping Process" or "S-pulping" has been proposed both for softwoods and hardwoods. In this process,

impregnation and cooking conditions were aimed at minimizing yield and brightness loss, maximizing resulting paper properties and decreasing specific refining energy. The steam explosion pulping process consists of the chemical impregnation of chips, short duration saturated steam cooking at temperatures varying from 180 °C to 210 °C, pressure release, refining and bleaching (if necessary).

Kokta et al., *Paperi Ja Puu - Paper and Timber*, 9, 1044-1055 (1989), have shown that the specific refining energy of aspen explosion pulps is at least 50% lower than that of CMP pulp of similar yield and ionic content level, while paper strength increases by up to 50%. Compared at similar CSF levels, explosion hardwood pulps (i.e. aspen, maple, hardwood mixtures, eucalyptus) at 90% yield provide similar or better paper properties than commercial low yield (=50%) bleached hardwood pulps.

The object of this invention is to provide a process in which additional yield saving and brightness level increase and cost decrease are obtained when compared to the previous invention of Kokta, CA-A-1 230 208 by substituting sodium hydroxide with milder swelling agents like: sodium carbonate, sodium bicarbonate, magnesium carbonate, magnesium chloride, etc.

The major problems accompanying previous processes using explosive decompression are believed to have been degradation due to the oxidation of wood and acid hydrolysis leading to loss in brightness, deterioration of fiber and paper properties and loss of yield. The approach adopted by this invention is thereto to attempt to curtail hydrolytic and oxidative wood degradation and thereby to protect against loss of yield, brightness and fiber strength. The loss of fiber strength will be particularly great if the degree of polymerisation of the cellulose falls below the critical value which is about 500-600. Hydrolytic degradation will also cause yield loss due mainly to degradation of hemi-cellulose.

The process of this invention tries to achieve a positive improvement in the strength of the paper that will be produced from the fibers by increasing the number of hydrophilic groups on the fiber surfaces thereby adding to the potential sites for hydrogen bonding.

The conditions for the achievement of the foregoing objects in accordance with the process of this invention are as follows:

- 1) The wood fragments, having fibers suitable for paper making, such as chips, are in a form in which thorough chemical impregnation can be achieved in a reasonable time.
- 2) There is an initial thorough impregnation of the chips or other wood fragments by an alkaline aqueous liquor having at least one agent

acting to produce hydrophilic groups and as an antioxidant which is capable of protecting the chips against oxidation and develops hydrophilic groups during the cooking stage. The same chemical may act as both an agent to produce hydrophilic groups and as an antioxidant or these functions may be performed by separate chemicals. At the end of cooking the pH should not be lower than about 6.0, so that acids released during cooking will be neutralized. Preferably a swelling agent is also used in the case of high density wood.

3) The impregnated chips are cooked using saturated steam in the substantial absence of air at high temperature and pressure.

4) After cooking, the chips that have been steam cooked are subjected to explosive decompression to result in chips which are softened and mostly defibrated.

5) The defibrated chips are preferably washed and then, without undue delay, and preferably immediately, refined to provide pulp.

The steps of one process of this invention will now be considered in more detail.

The wood fragments

The starting material will normally be chips in which the fibers are of a length suitable for paper making. Shavings could also be used but sawdust would be undesirable except as a minor part of the total furnish as the fibers are partially cut.

The chips should also, as is well known, be suitable in the sense of being free from bark and foreign matter.

It is desirable for efficiency that coarse chips be avoided as otherwise the subsequent impregnation may deposit chemicals only on the chip surface, unless impregnation is carried out for a very long time. Another problem with coarse chips is that cooking would not be complete. It is best to use shredded or thin chips of a 4-8 mm thickness. It has been found that this process is applicable to hardwoods, jack pine and larch, black spruce, douglas fir giving stronger papers at lower refining energy compared with conventional chemo-thermo mechanical or chemi-mechanical pulping.

Impregnation

The purpose of impregnation is to protect the chips against oxidation during cooking and during transfer from the cooking vessel to the refiner. It is also an objective to provide a positive increase in strength by developing hydrophylic groups on the fiber surface during steam treatment. This will then provide additional sites for hydrogen bonding.

The preferred antioxidant is sodium sulphite

Na_2SO_3 which also forms hydrophilic groups, and which is available at a low cost. It is used to provide a concentration of absorbed chemical of about 1 to 16% by weight. Concentrations below 4% would be used where brightness protection is unimportant and high strength is not required. Where, however, brightness is important the sodium sulphite should be at least 4%. If physical properties are important these will be improved by using a concentration of at least 4% sodium sulphite and will be further improved as the concentration is further increased towards 16%. The concentration of the solution is preferably about the same as the percentage of chemical to be absorbed where there are equal quantities of chips and liquor. For example, a ton of chips of 50% consistency mixed with one ton of 8% solution will result in about 8% absorbed on the pulp. Thorough impregnation is important so as to distribute the antioxidant evenly rather than depositing it just on the surface. Other antioxidants that can be used are potassium sulphite or magnesium sulphite. Ammonium sulphite could be used if cooking conditions are not severe, or with a buffer. Complexing agents such as ethylene diamine tetracetic acid (EDTA), sodium diethylene triaminepentacetate (DTPA), sodium tripolyphosphate (TPP) and other complexing agents known in the art as being usable under alkaline conditions may be added to minimize the catalytic effect of metals such as iron on oxidative degradation.

It is desirable also to use a swelling agent to assist the antioxidant or hydrophilic agent in penetrating the wood and this contributes also to softening the chip. This is of particular value in the case of high density wood. Suitable swelling agents are ammonium hydroxide or sodium carbonate or sodium bicarbonate or magnesium carbonate or magnesium sulphate any of which will contribute also to providing hydrophilic groups. Other swelling agents that can be used and which may be desirable as auxiliary swelling agents for high density wood are zinc chloride, sodium chloride, sodium bromide, magnesium chloride, calcium isocyanate, Schweitzer's solution, cupriethylenediamine (C.E.D.) tetraethylammonium hydroxide or dimethyldibenzylammonium hydroxide. The concentration of swelling agent and conditions of swelling must be controlled in such a way as to avoid any dissolution of the hollocellulose. Thus the percentage of swelling agent in the impregnating solution will be in the range of about 1 to 4% depending on the agent and the conditions.

The impregnating solution must be alkaline and have enough free hydroxyl to be able to neutralize the liberated wood acids such as formic acid and acetic acid. Normally the starting pH is about 7.5 or higher and the final pH after steam cooking should

be at least 6 or higher.

The time of impregnation at atmospheric pressure in holding tanks typically ranges from about 12 hours to 24 hours at a temperature of about 30°C to 60°C. Approximately equal weights of chips and of aqueous impregnating solution can be used. For industrial purposes, however, the time may be shortened to an hour or to minutes by impregnating with steam under pressure and at a higher temperature. The pressure should be up to about 1 atmospheric extra pressure at a temperature of about 100°C to 110°C. To improve impregnation the chips should be compressed in advance of impregnation in cool solutions of chemicals. Under these conditions, penetration will be achieved in a shorter time. Penetration is what predominantly occurs; there is no significant cooking as evidenced by the fact that there is no significant sulphonic and carboxylic group increase.

Steam cooking

The impregnated chips are steam cooked at a high temperature and pressure.

Equipment and methods that can be used for preliminary compacting of the impregnated chips, for cooking the chips with steam and for the discharge of the chips under conditions of explosive decompression and described in CA-A-1 070 537 dated January 29 1980; 1 070 646 dated January 29 1980; 1 119 033 dated March 2 1982 and 1 138 708 dated January 4 1983, all of which were granted to Stake Technology Ltd. The equipment used in the examples was acquired from that company.

The temperature of cooking should be within the range of about 180°C to 210°C and preferably within the range 190-200°C, which is in excess of the temperatures considered possible according to the publications of Asplund and Higgins previously referred to. These temperatures correspond with a pressure of 10 atmospheres for 180°C and 15.5 atmospheres for 200°C. It is these high pressures and temperatures which make a very important contribution to ensuring excellent penetration of the chips by the cooking liquor and results in higher efficiency of ionic groups formation on fiber surface.

The cooking may be preceded by steam flushing under low pressure steam at 100°C for a short period such as one minute. This is a matter of convenience, in that with a batch reactor the cooking vessel is initially open to the atmosphere, to eliminate air. This air would be disadvantageous in that it would result in oxidation if it were trapped in the cooking vessel. Additional antioxidant may if desired be added at this stage. Steam flushing is desirable with a batch reactor but would not be necessary for a continuous reactor.

This preliminary treatment is then followed by cooking for about 30 seconds to 6 minutes and preferably about 1 to 4 minutes.

It has been found that within reasonable limits there is a property improvement as a function of the product of time (min) and temperature (°C), which is assigned an arbitrary number. By increasing this from 285 to 760 in the case of black spruce at about the same freeness (157-167) the burst index increased from 3.15 to 4.41 and breaking length from 6.3 to 7.6 and tear from 5.6 to 5.8. Refining energy dropped from 3.2 to 3.1 and brightness dropped from 59.7 to 55.5.

Explosive decompression

After cooking the pressure is instantaneously released and the chips are exploded into a release vessel. If there is to be a delay between release of the chips and refining it is important to cool the chips down by washing them. Washing may also be desirable for the purpose of chemical recovery.

It is desirable immediately to refine the chips after explosive decompression. Otherwise, if the chips are stored, some oxidation will occur with resultant loss of brightness. The rapidity with which this will occur depends on how much residual antioxidant is present at that time and on the temperature of the chips and the extent of exposure to oxygen. Preferably, therefore, refining is immediate so that it is unnecessary to incur the cost of excess antioxidant. In any event, undue delay should be avoided. Such delay is regarded as being undue if oxidation takes place to an extent that will materially affect brightness.

The chips resulting from the explosive decompression are softened and partially defibrated.

Refining

Refining in the experiments described below standards using an atmospheric laboratory refining was conducted at 2% consistency level using a blender coupled with an energy meter model EW 604.

According to A.C. Shaw "Simulation of Secondary Refining" Pulp and Paper Canada 85(6): T152-T155 (1984) the blender results closely match those obtained with industrial refiners. Properties were evaluated after preparing paper sheets according to standard CPPA testing methods.

Refining energies are usually low and can be expected to be in the range of 1.7 to 4 MJ/kg, hardwoods, CSF = 100 ml, which is considerably lower than that of conventional CMP and similar to that described in Kokta, CA-A-1 230 208 and US-A-4 798 651.

The present invention is described in the en-

closed example.

EXAMPLE

Chips

Freshly cut and naturally grown aspen trees from the Joliette region of Quebec were debarked, chipped and screened at La Station Forestière Duchesnay, Quebec. Average chip size after screening, was as follows: length 2.5 to 3.75 cm; width: 1 to 2 cm; thickness: 1 to 9 mm with maximum distribution at 5 mm.

Impregnation

150 g of chips (= 50% siccidity) were mixed in plastic bags along with 150 g of a solution made up of 8% Na_2SO_3 alone or with 1% of NaOH or MgCl_2 or NaHCO_3 or MgCO_3 . Time of impregnation: 24 hours; temperature of impregnation: 60 °C. Liquid/chip ratio during impregnation was equal to 3.

In addition, 0.5% DTPA was used in applied cooking liquors.

Cooking

Explosion pulps were prepared using vapor phase team cooking of chemically pretreated aspen wood chips at a cooking temperature of 190 °C and cooking time 4 minutes.

Cooking took place using saturated steam in a laboratory batch reactor built by Stake Tech. Co. Cooking was preceded by one minute steam flushing at atmospheric pressure. After cooking, the pressure was instantaneously released and chips which exploded into the release vessel were washed and cooled down with one liter of tap water, and subsequently refined after being stored in a cold room. The reported amount of steam used for cooking varied from 0.5 to 1 kg of steam for 1 kg of chips. Yield was measured as follows: exploded chips (75 g) were washed with one liter of tap water and subsequently defibrated for 90 seconds in a laboratory blender at 2% consistency. The pulp was washed again with one liter of water, dried at 105 °C to constant weight and the resulted weights were compared to the initial O.D. weight of chips.

Refining

Laboratory refining was also done using a domestic blender Osterizer B-8614 at a consistency level of 2%. Defibration and refining energy was measured using a HIOKI model 3181-01 power-meter with an integrator. Relative specific refining

energy was calculated by subtracted blending energy of fully beaten pulp from the total energy needed to defibrate and blend the fiber suspension.

5 Property evaluation

10 Paper sheets were prepared and tested according to standard CPPA testing methods on 1.2 g sheets. Brightness (Elrepho) was evaluated on sheets made with deionized water. Ionic content (sulfonate and carboxylate ions) was determined by means of conductometric titration.

Bleaching

15 Bleaching was carried out using 2% of hydrogen peroxide, 2% NaOH; 0.05% of MgSO_4 ; 2% of sodium silicate; 0.5% DTPA; pulp concentration: 20%; bleaching time: 2 hours; bleaching temperature: 80 °C; neutralization with $\text{Na}_2\text{S}_2\text{O}_5$ to pH = 5.5; washing with de-ionized water.

20 In Figures 1 to 4, the paper properties of improved steam explosion process are compared to that of an explosion process as defined in Kokta, CA-A-230 208 (1987) and Kokta, US-A-4 798 651 (1989) using either 8% Na_2SO_3 or 8% Na_2SO_3 + 1% NaOH.

25 It is evident from Figure 1 that substituting 1% NaOH with 1% of MgCl_2 or 1% NaHCO_3 resulted in 3% pulp yield increase. Furthermore, this increment was 6% when 1% MgCO_3 was used.

30 The effect of chemical pre-treatment on brightness is shown in Figure 2. It shows, in the shaded blocks, that brown stock brightness increases from 59.9% of that obtained with 8% Na_2SO_3 + 1% NaOH to 64.3%; 65.4%; 64.5% when 1% NaOH is substituted either with 1% of MgCl_2 or NaHCO_3 or MgCO_3 . Values shown in outline blocks in that Figure are those of brightness after bleaching.

35 The increase of yield as well as brightness is obtained in the case of NaOH substitution by NaHCO_3 or MgCO_3 without any breaking length lost as demonstrated in Figure 3. On the other hand, a system with MgCl_2 gave lower strength.

40 The results in Figure 4 indicate also that substituting NaOH with either NaHCO_3 or MgCO_3 leads to the same low level of relative specific refining energy. The comparable physical strength as well as relative specific refining energy of the above indicated systems can be explained by similar ionic content as indicated in Figure 5.

45 Therefore the present invention, consisting in substituting NaOH by agents such as carbonates or bicarbonates results not only in the yield and brightness advantage but also in cost decrease.

Claims

1. A process for producing pulp suitable for making paper, which comprises the steps of impregnating wood fragments with an alkaline aqueous liquor including at least one soluble sulphite to provide hydrophylic groups and/or act as an antioxidant, steam cooking the impregnated wood fragments with saturated steam at superatmospheric pressure and at an elevated temperature; subjecting the cooked wood fragments to explosive decompression to partially defibrate same; and refining the softened and defibrated fragments to provide pulp, characterized in that the liquor comprises an alkali metal ammonium or alkaline earth metal carbonate or bicarbonate as a swelling agent. 5
10
15
2. A process according to claim 1 wherein the swelling agents are in an amount of 1-4% by weight absorbed by the wood fragments. 20
3. A process according to claim 1 or claim 2 wherein the steam cooking is conducted at a cooking temperature in the range of 180 °C to 210 °C, and the cooking pressure is about 10 atm to about 15.5 atm. 25
4. A process according to claim 3 wherein the cooling temperature is 190 °C to 200 °C. 30
5. A process according to any one of the preceding claims wherein the step of impregnation is preceded by the replacement of air with saturated steam. 35
6. A process according to any one of the preceding claims wherein the cooking time is in the range of 30 seconds to 6 minutes.
7. A process according to claim 6 wherein the cooking time is 1 minute to 4 minutes. 40
8. A process according to any one of the preceding claims wherein a small percentage of an auxiliary swelling agent is additionally present during the impregnation step. 45
9. A process according to claim 8 wherein the auxiliary swelling agent is zinc chloride, sodium chloride, sodium bromide, magnesium chloride, calcium isocyanate, Schweitzers solution, cupriethylenediamne (C.E.D.) tetraethylammonium hydroxide or dimethyldibenzylammonium hydroxide. 50
55

FIGURE 1

Yield as a function of chemical pre-treatment of chips.

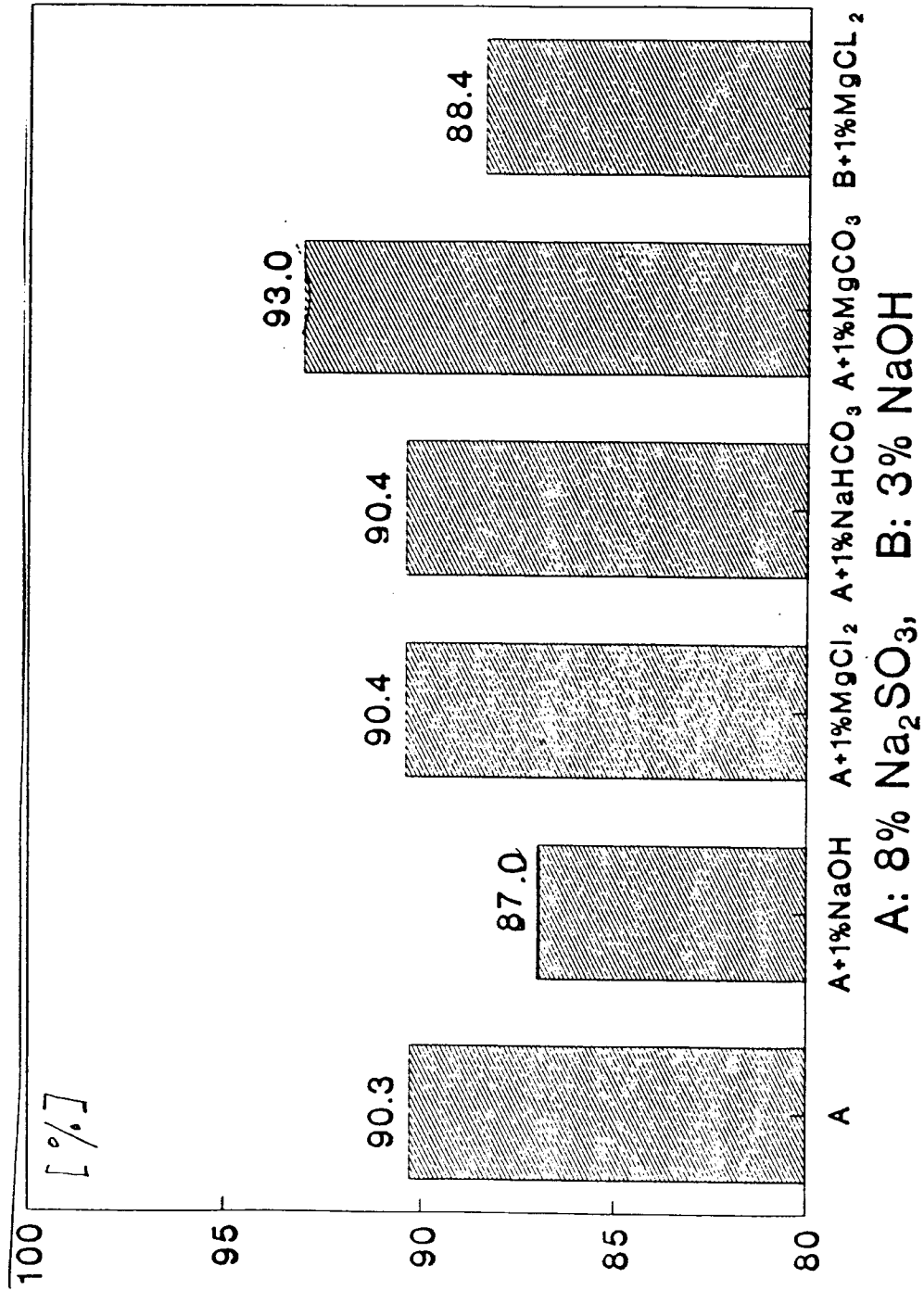


FIGURE 2

Effect of chemical pre-treatment of aspen chips on resulting brightness.

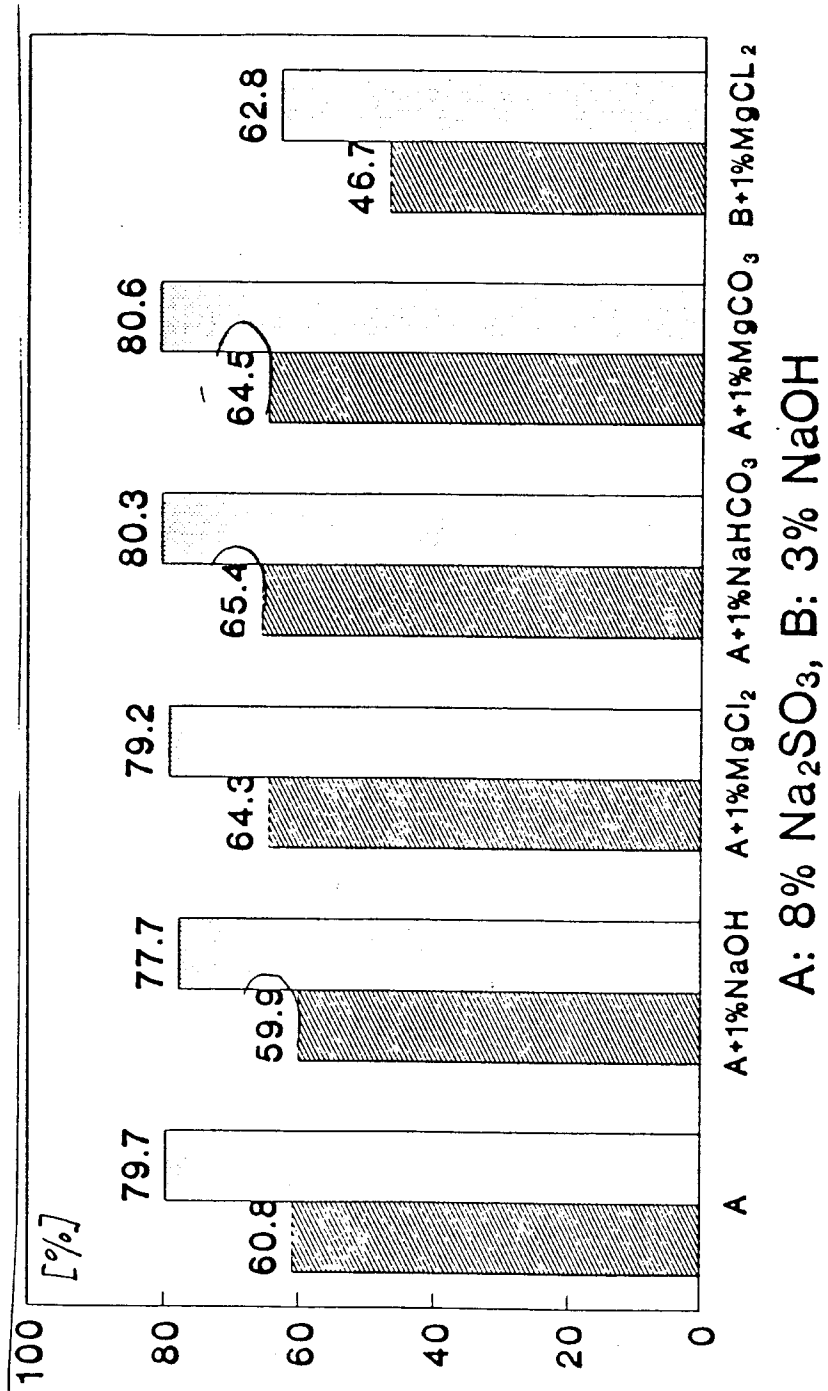


FIGURE 3
Effect of chemical pre-treatment and CSF on breaking length.

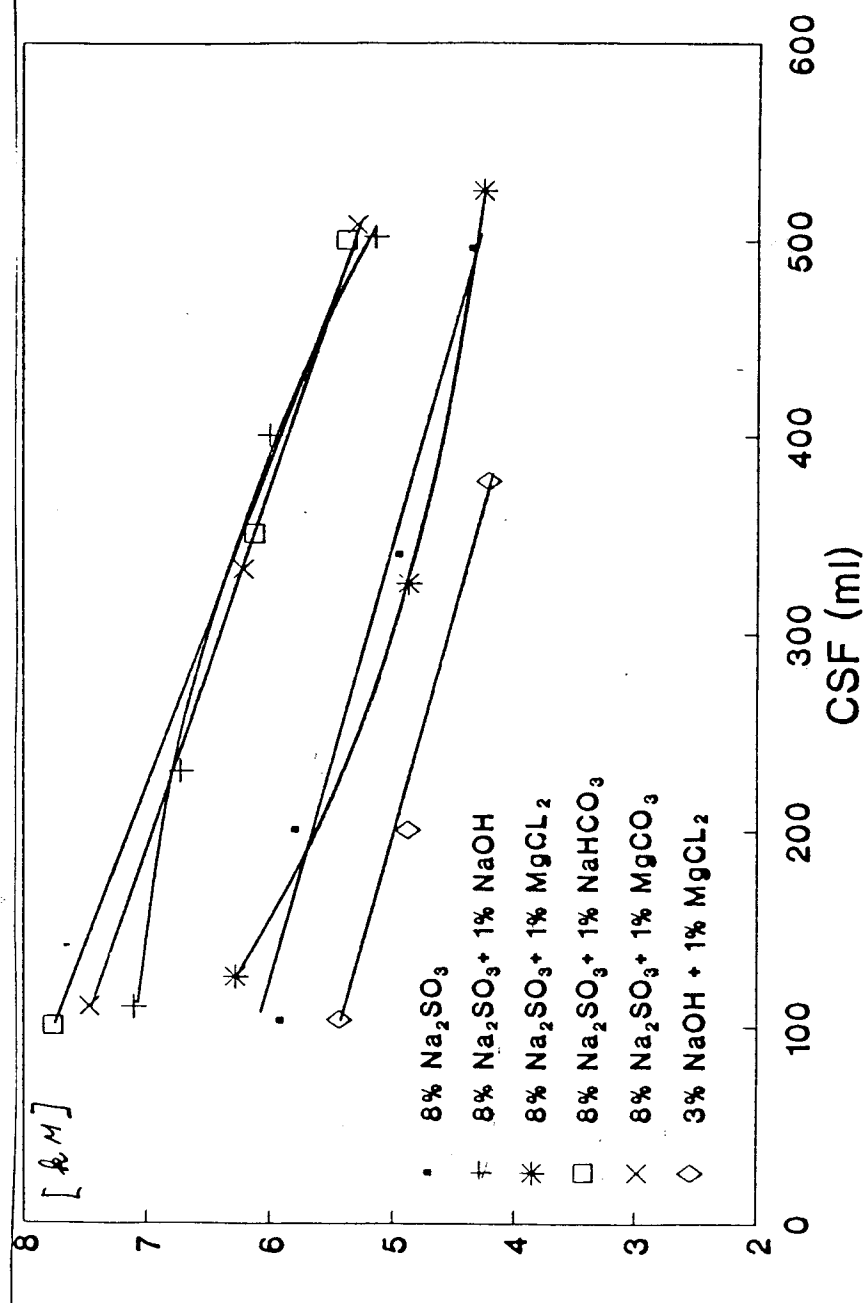


FIGURE 4
Relative specific energy as a function of canadian standard freeness (CSF)
and chemical pre-treatment of chips.

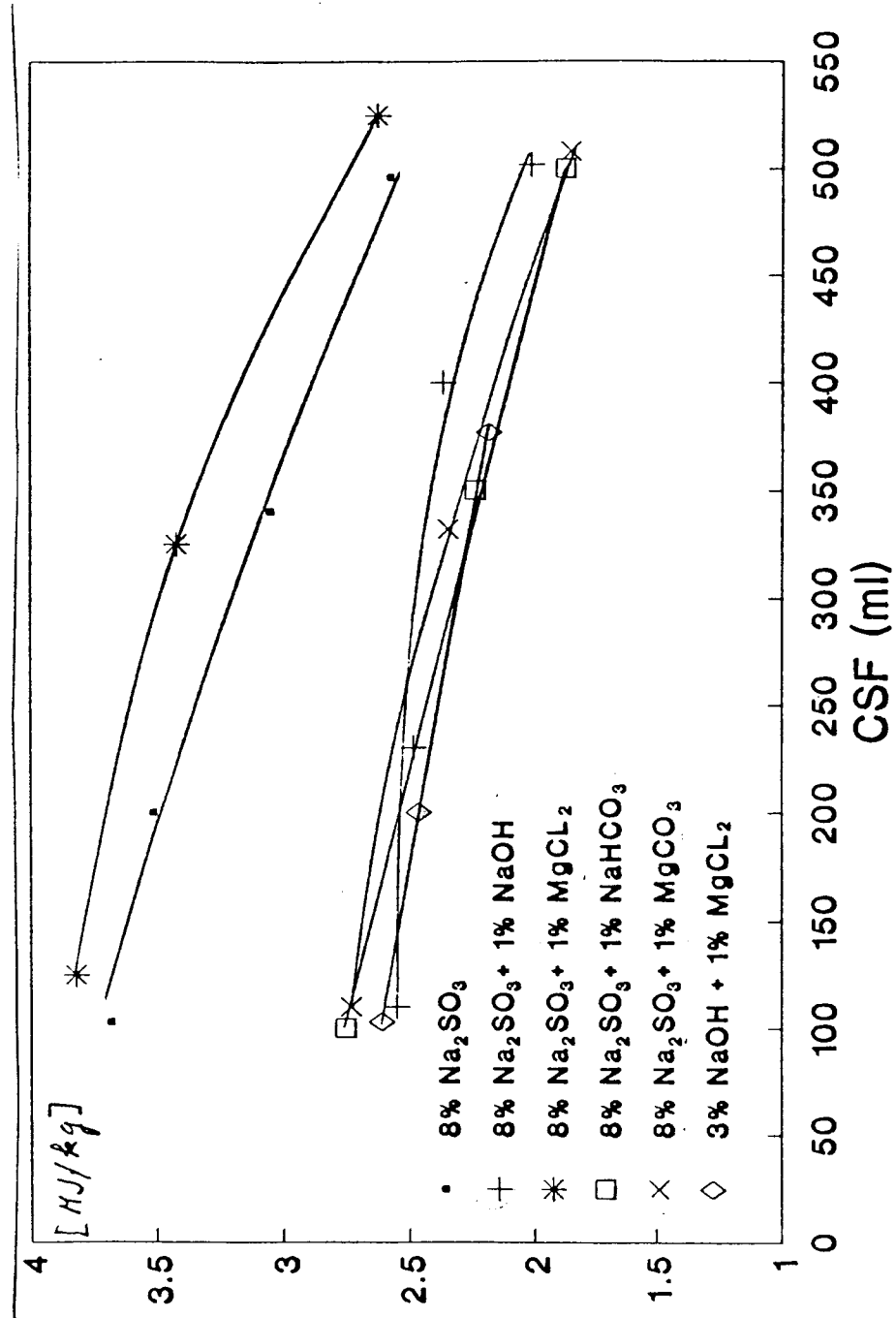
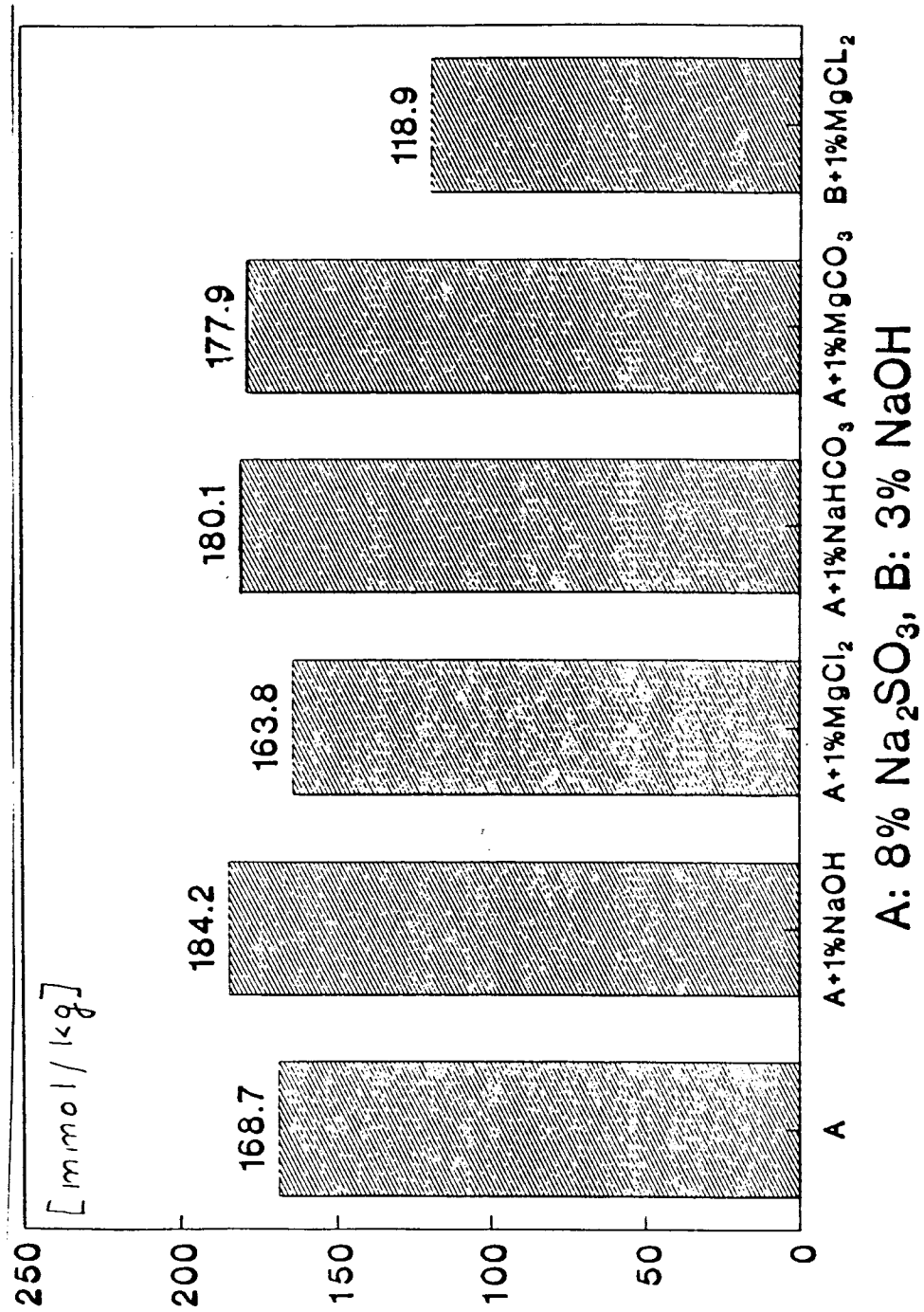


FIGURE 5
Effect of chemical pre-treatment on chips on total ionic content
(sulphonic + carboxylic ions)





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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 6166

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.5)
D,X	EP-A-0 284 585 (STAKE TECHNOLOGY LTD.) * page 3, line 60 - page 4, line 4 * ---	1-4,6-9	D21B1/36 D21C1/00
D,X	EP-A-0 172 135 (VIT, R. ET AL.) * claims 9,24,25 * -----	1-3,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21B D21C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 JUNE 1992	Examiner BERNARDO NORIEGA F.
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	