⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number. **0 010 451**
A1

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: **79302316.9**

㉒ Date of filing: **24.10.79**

(51) Int. Cl.^{3}: **D 21 C 1/00**
D 21 C 3/22, C 07 C 49/00

㉚ Priority: **25.10.78 GB 4185678**

㊸ Date of publication of application:
30.04.80 Bulletin 80/9

㊹ Designated Contracting States:
AT BE DE FR GB IT SE

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(54) Process for the delignification of lignocellulosic material and products thereof.

(57) There is disclosed a process for the delignification of lignocellulosic material by treatment with an alkaline liquor in the presence of a cyclic keto compound such as anthraquinone. The lignocellulosic material in subdivided form is first impregnated with the alkaline liquor containing a suitable amount of the cyclic keto compound whereafter any excess liquor is drained. The impregnated material is then cooked by heating. The delignified products are suitable for the manufacture of paper.

Croydon Printing Company Ltd

DESCRIPTION

"PROCESS FOR THE DELIGNIFICATION OF LIGNOCELLULOSIC MATERIAL AND PRODUCTS THEREOF".

This invention relates to a process for the delignification of lignocellulosic material such as wood, straw, bagasse, etc. and in particular relates to an improved vapour phase alkaline pulping process for the production of a chemical cellulosic pulp.

The processing of lignocellulosic material to produce cellulose suitable for the manufacture of paper products involves the removal of lignin and other non-cellulosic components such as gums. Reagents that attack lignin without appreciably affecting the cellulose component are preferred for this purpose. It is still a general practice today to use these reagents in the form of aqueous solutions and to effect the cooking of lignocellulosic material in such solutions under conditions of temperature and pressure chosen to provide an acceptable lignin to cellulose ratio. Depending upon the nature of the reagents used, this liquid phase process is known as the soda process wherein the reagent is sodium hydroxide alone, the kraft process wherein the reagents are sodium hydroxide and sodium sulphide, the polysulphide process wherein the reagents are sodium hydroxide, sodium sulphide and polysulphides, or the neutral sulphite semichemical process in which the reagents are an alkali metal base such as sodium hydroxide and an alkali metal sulphite such as sodium sulphite. All these reagents have in common that they give alkaline aqueous solutions and thus constitute alkaline cooking liquors.

In attempts to improve on the above liquid phase process, certain modifications have been proposed. One such modification, known as the vapour phase process, consists in impregnating lignocellulosic material in a suitably divided form with an alkaline cooking liquor, withdrawing any excess of cooking liquor and then cooking the impregnated material under the same time and temperature conditions as in conventional liquid phase pulping. An example of this process wherein kraft liquor is used as the impregnating liquor is described by Kleinert in United States Patent No. 3,215,588 issued on 2nd November, 1965. As compared with the liquid phase process, the vapour phase process affords an increased pulping rate and lower chemical requirements.

Another recently proposed modification is described in British application No. 5374/77 filed on 9th February, 1977 (United States Patent No. 4,012,280, issued on 15th March, 1977) as well as in United States application Serial No. 750,441, filed on 14th December, 1976, and United States Patent Nos. 4,036,680 and 4,036,681, issued on 19th July, 1977. In these applications, it is taught to effect the cooking of lignocellulosic material in a liquid phase process with an alkaline pulping liquor, there being present in said liquor from 0.001% to 10.0% by weight based on the lignocellulosic material of a cyclic keto compound selected from the group consisting of naphthoquinone, anthraquinone, anthrone, phenanthrenequinone, the alkyl, alkoxy and amino derivatives of these compounds, 6,11-dioxo-1H-anthra[1,2-c] pyrazole, anthraquinone-1,2-naphthacridone, 7,12-dioxo-7,12-dihydroanthra[1,2-b]pyrazine, 1,2-benzanthraquinone, 10-methylene anthrone and the unsubstituted and lower alkyl substituted Diels Alder adducts of naphthoquinone and benzoquinone. As compared with the conventional liquid phase process, this modification which consists in the addition to the cooking liquor of any one of the above cyclic keto compounds results in a increased rate of cooking as well as in a better pulp yield. One great advantage of this modification when applied to the soda process is that it makes the latter as efficient as the conventional kraft process in the pulping of soft wood.

It has now been found that there are advantages to be gained by using the above cyclic keto compounds as additives in the vapour phase process. It is thus proposed according to the present invention to delignify lignocellulosic material by impregnating the lignocellulosic material in subdivided form with an alkaline pulping liquor containing a suitable amount of a cyclic keto compound as hereinabove defined, withdrawing any excess of liquor and finally heating to a temperature and for a time sufficient to obtain the desired degree of pulping. In producing pulps of equivalent residual lignin levels under equivalent cooking schedules (time/temperature profile), this novel vapour phase process, as compared with the above-mentioned liquid phase process utilizing cyclic keto compounds, results in higher pulp yields while at the same time requiring lesser amount of caustic and cyclic keto compounds and retaining the advantages of the conventional vapour phase process.

The process of the present invention comparises the steps of:

1. impregnating lignocellulosic material in subdivided form with an alkaline pulping liquor containing from 0.001% to 10.0% by weight, based on the lignocellulosic material, of a cyclic keto compound selected from the group consisting of naphthoquinone, anthraquinone, anthrone, phenanthrenequinone, the alkyl, alkoxy and amino derivatives

of these compounds, 6,11-dioxo-1H-anthra[1,2-c]pyrazole, anthraquinone-1,2-naphthacridone, 7,12-dioxo-7,12-dihydro-anthra[1,2-b]pyrazine, 1,2-benzanthraquinone, 10-methylene anthrone and the unsubstituted and lower alkyl substituted Diels Alder adducts of naphthoquinone and benzoquinone,

2. removing any excess of liquor from the impregnated material, and

3. cooking said impregnated material by heating to a temperature in the range of 150°C to 200°C for a period of 0.5 to 480 minutes.

The cooked lignocellulosic material produced by the above third step is then washed as in the conventional processes with water or an aqueous liquor inert to the lignocellulosic material to obtain a delignified cellulosic material which may be used without further treatment or may be subjected to conventional bleaching steps.

When the lignocellulosic material employed is wood, it is first converted into the form of chips. Of course, this step is not required when the lignocellulosic material is of fibrous form.

The process of this invention can be used to delignify either coniferous or deciduous species of wood. By coniferous is meant species such as pine, spruce and balsam fir. By deciduous is meant species such as birch, aspen, eastern cottonwood, maple, beech and oak. When treating a high density deciduous wood such as birch, it is preferable to employ a longer time to reach maximum cooking temperature in the third step.

Pulping liquors suitable for use in the first step of the process are the soda, kraft, polysulphide and alkaline sulphite liquors. However, the soda liquor is much preferred because it does not contain any sulphur compounds and is therefore considerably less polluting than the three other liquors.

The soda liquor contains from 8% to 20% by weight of alkali metal base expressed as percent effective alkali, based on the weight of the lignocellulosic material, and normally also contains alkali metal carbonate.

The kraft liquor contains from 8% to 15% by weight of alkali metal base expressed as percent effective alkali (TAPPI T-1203 S-6) and from 5% to 40% by weight of alkali metal sulphide expressed as percent sulphidity (TAPPI T-1203 OS-61), based on lignocellulosic material. This pulping liquor will normally contain alkali metal sulphate and alkali metal carbonate.

The polysulphide liquor is essentially a kraft liquor as defined immediately above, containing excess sulphur, i.e. polysulphides. The presence of polysulphides results in an improved yield and an amount of 1.0% to 5.0%, preferably 2% thereof (expressed as sulphur and based on weight of lignocellulosic material) in the liquor is therefore a definite advantage.

The alkaline sulphite liquor is a liquor which contains an alkali metal hydroxide preferably sodium hydroxide and an alkali metal sulphite preferably sodium sulphite.

Effective alkali is the sum of all alkali hydroxide in solution expressed as Na_2O including that formed by hydrolysis of the alkali sulphide, also expressed as Na_2O.

Sulphidity is the total sulphide, expressed as Na_2O, calculated as a percentage of total titrable alkali, including that formed by hydrolysis.

As mentioned above, the compounds which are suitable for use as additives, in the process of the invention are the cyclic keto compounds selected from the group consistings of naphthoquinone, anthraquinone, anthrone, phenanthrenequinone, the alkyl, alkoxy and amino derivatives of these compounds, 6,11-dioxo-1H-anthra[1,2-c]pyrazole, anthraquinone-1,2-naphthacridone, 7,12-dioxo-7,12-dihydro-anthra[1,2-b]pyrazine, 1,2-benzanthraquinone, 10-methylene anthrone, 1,2,3,4,5,6,7,8-octahydroanthraquinone and the unsubstituted and lower alkyl substituted Diels Alder adducts of naphthoquinone and benzoquinone. By alkyl derivatives of these compounds, it is meant to include any of the four compounds naphthoquinone, anthraquinone, anthrone and phenanthrenequinone, substituted with one or two alkyl groups containing 1 to 4, preferably 1 to 2, carbon atoms. Among the alkoxy derivatives of the same four compounds which are suitable for use as additives, are those which have at least one alkoxy substituent containing 1 to 4, preferably one, carbon atoms. Among these alkyl, alkoxy and amino derivatives, those of anthraquinone are preferred and examples thereof are 1-methyl anthraquinone, 2-methyl anthraquinone, 2-ethyl anthraquinone, 2,6-dimethyl anthraquinone, 2,7-dimethyl anthraquinone, 2,3-dimethylanthraquinone, 1-methoxy anthraquinone and 2-amino anthraquinone.

The unsubstituted Diels Alder adducts suitable for use as additives in the process of this invention are those obtained by reacting 1 or 2 moles of butadiene with naphthoquinone and benzoquinone respectively. By lower alkyl-substituted adducts it is meant the adducts obtained where in the above reaction either one or both of the reactants are substituted with the appropriate lower alkyl groups. Such lower alkyl groups may range in number from 1 to 4, may each contain from 1 to 4 carbon atoms and may be the same or different. Examples of Diels Alder adducts are 1,4,4a,5,8,8a,9a,10a-octahydroanthraquinone, 2,3,6,7-tetramethyl-1,4,4a,5,8,8a,9a,10a-octahydroanthraquinone, 1,4,4a,9a-tetrahydroanthraquinone, 2-ethyl-1,4,4a,9a-tetrahydroanthraquinone, 2,3-dimethyl-1,4,4a,9a-tetrahydroanthraquinone and 1,3-dimethyl-1,4,4a,9a-tetrahydroanthraquinone.

The cyclic keto compound as above defined is added to the pulping liquor prior to impregnation of the lignocellulosic material and is employed in proportions of from 0.001% to 10.0%, preferably 0.01% to 1.0% by weight based on the lignocellulosic material.

Where the alkaline pulping liquor is the soda liquor, it has been found advantageous to use as a second additive in combination with any of the above cyclic keto compounds, a nitro aromatic compound selected from the group consisting of mono and dinitrobenzenes and the amino, carboxy, hydroxy, and methyl derivatives thereof. Examples of these compounds are nitrobenzene, 2-nitroaniline, 4-nitroaniline, 4-nitrobenzaldehyde, 4-nitrobenzoic acid, 2-nitroresorcinol, 4-nitrostyrene, 2-nitrotoluene, 4-nitrotoluene, 1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,4-dinitrotoluene, 3,5-dinitrobenzoic acid, 4,6-dinitro-o-cresol and 2,4-dinitroresorcinol. Among the above compounds, nitrobenzene is particularly preferred because of its favourable cost:benefit ratio. The nitro aromatic compound is employed in proportions of from 0.01% to 10.0%, preferably 0.10% to 2.0%, by weight, based on the lignocellulosic material.

It should be well understood that the use of nitro aromatic compound as second additives in combination with cyclic keto compounds is optional and only applicable to the case where the pulping liquor is soda liquor. All combinations formed from any one of the above defined cyclic keto compounds with any one of the above defined nitro aromatic compounds are suitable for use in this particular embodiment of the invention. Preferred, however, is the combination comprised of anthraquinone and nitrobenzene.

The alkali metal base employed as reagent in the alkaline pulping liquors may be sodium hydroxide, potassium hydroxide, sodium carbonate or potassium carbonate.

The process of the invention is carried out in a closed vessel to which lignocellulosic material in subdivided form, pulping liquor containing the above-defined additive or additives, and, if necessary, dilution water are fed in the amounts required to give the desired effective alkali. Impregnation is effected under gas or mechanical pressure and at a temperature of 25°C or higher. Once full impregnation has taken place, excess pulping liquor, if any, is drained off and the impregnated lignocellulosic material is heated either directly with steam or indirectly by e.g. electrical heating to a temperature of 150°C to 200°C for a period of 0.5 to 480 minutes.

The material resulting from step (3) of the process may be bleached by any conventional bleaching process. A conventional sequence comprising chlorination, alkaline extraction, chlorine dioxide treatment, alkaline extraction, chlorine dioxide treatment (C-E-D-E-D) will provide a product having a brightness of approximately 85-90 units (Elrepho).

The invention is illustrated by the following

Examples but its scope is not limited to the embodiments shown therein.

In the Examples, the kappa number and viscosity determinations were carried out by the following methods.

Kappa number	TAPPI method T-236 M-60
Viscosity	TAPPI method T-230 SU-66

EXAMPLE 1

16 samples a black spruce chips were subjected to pulping treatment employing kraft liquor (samples 1-8) or soda liquor (samples 9-16). Runs 1 to 4 and 9 to 12 illustrate pulping by the conventional liquid phase process with (runs 2, 4, 10 and 12) or without (runs 1, 3, 9 and 11) anthraquinone as an additive and are provided for comparison purposes. Runs 5 and 13 illustrate pulping by the conventional vapour phase process and are also provided for comparison purposes. Runs 6 to 8 and 14 to 16 illustrate pulping by the process of the present invention employing kraft or soda liquors containing varying amounts of anthraquinone as an additive. In runs 6 to 8 and 14 to 16 as well as in runs 5 and 13, the chips were impregnated with the pulping liquor for 30 minutes at about 25°C under a pressure of 75 pounds per square inch gauge of nitrogen gas. After impregnation, the excess liquor was drained off and saved for analysis of effective alkali, sulphidity and residual additive. The characteristics of the 16 pulping runs and the results obtained are shown in the following Table I.

TABLE I

VAPOUR PHASE PULPING WITH ANTHRAQUINONE AS PULPING ADDITIVE

Run No.	Impregnating Liquor			Volume of liquor removed ml.	Liquor Remaining on Wood after excess Draining				Maximum temp. (T-max) °C.	Time to T-max	Time at T-max	Pulp kappa No.	Pulp yield % on wood	Pulp viscosity cps
	Additive % on wood	Effective alkali % on wood	Liquor to wood ratio		Liquor to wood ratio	Effective alkali % on wood	Sulphidity %	Additive % on wood						
1					4:1	14	25	-	170	90	90	35.2	50.2	40.0
2					4:1	14	25	0.25	"	"	"	25.3	50.0	36.7
3					2:1	14	25	-	"	"	"	25.3	48.3	25.1
4					2:1	14	25	0.25	"	"	"	19.6	49.4	20.8
5	-	40.1	6,7:1	350	2:1	15.0	24.3	-	"	"	"	22.9	47.6	19.7
6	0.25	40.1	6,7:1	350	2:1	15.2	24.6	0.070	"	"	"	22.7	48.7	20.0
7	0.42	40.1	6,7:1	350	2:1	14.8	25	0.123	"	"	"	23.6	49.8	21.7
8	0.84	40.1	6,7:1	350	2:1	15.4	25	0.149	"	"	"	20.3	49.9	22.1
9					4:1	15.5	-	-	"	"	80	100.5	56.2	-
10					4:1	15.5	-	0.25	"	"	"	38.1	50.6	27.1
11					2:1	15.5	-	-	"	"	"	66.9	50.1	-
12					2:1	15.1	-	0.25	"	"	"	27.4	48.2	13.7
13	-	53.3	6,7:1	360	1,9:1	13.1	-	-	"	"	"	96.6	54.1	-

TABLE I cont'd.

VAPOUR PHASE PULPING WITH ANTHRAQUINONE AS PULPING ADDITIVE

Run No.	Impregnating Liquor			Volume of liquor re-moved ml.	Liquor Remaining on Wood after excess Draining				Max-imum temp. (T-max) °C.	Time to T-max	Time at T-max	Pulp kappa No.	Pulp yield % on wood	Pulp visco-sity cps
	Addi-tive % on wood	Effect-ive alka-li % on wood	Liquor to wood ratio		Liquor to wood ratio	Effect-ive al-kali % on wood	Sul-phi-dity %	Addi-tive % on wood						
14	0.25	53,3	6,7:1	360	1.9:1	13.1	-	0.10	170	90	80	39.4	50.4	17.9
15	0.42	53.3	6,7:1	360	1.9:1	13.1	-	0.15	"	"	"	34.1	50.6	17.7
16	0.84	53.3	6.7:1	360	1.9:1	13.1	-	0.32	"	"	"	28.9	50.3	16.5

EXAMPLE 2

In four runs, samples of black spruce chips were subjected to pulping treatment employing kraft liquor. In each run, two samples of the chips were treated, one by vapour phase cooking and the other, for purposes of comparison, by conventional liquid phase cooking. The results obtained are shown in Table II. As will be seen in said Table, no additive was used in the cooking of run 1 whereas in runs 2 to 4, the additive anthraquinone (AQ)* was used.

Impregnating of the chips for the vapour phase cooking was made as follows:

a) the chips, chemicals and dilution water were added to a 600 ml volume microdigestor together with a predetermined amount of AQ in a 50% aqueous dispersion form;

b) the microdigestor was closed and the contents well mixed;

c) the contents were subjected to the following treatment:

- i) application of 20 mm Hg vacuum for 1 minute;
- ii) application of 75 psig nitrogen pressure for 2.5 minutes;
- iii) vacuum application - 20 mm Hg for 1 minute;
- iv) pressure application - 75 psig nitrogen for 2.5 minutes;
- v) vacuum application - 20 mm Hg for 1 minute;
- vi) pressure application - 75 psig nitrogen for 5 minutes;
- vii) vacuum application - 20 mm Hg for 1 minute;
- viii) pressure application - 75 psig nitrogen for 10 minutes;
- ix) release of pressure;
- x) mixing of contents.

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* trade mark

This treatment was intended to simulate mill scale processes of presteaming to remove air followed by pressure impregnation. The procedure was carried out at 22°C.

The excess liquor, not absorbed by the chips, was poured off and collected for analysis by automatic titrater, to determine the effective alkali and sulphidity levels of the withdrawn liquor, and by GC-MS (gas chromatography-mass spectroscopy) to measure its content of additive. Simple calculations were then carried out to determine the charges of chemicals and additive in the chips during the cooking process.

All other operations were carried out in the manner described in Example 1. For liquid phase cooks, the additives and chemicals were charged to the chips in the microdigestor followed by closure and cooking.

Liquid phase cooks were carried out with the effective alkali, sulphidity and additive levels listed in Table II under the heading "Impregnated Liquor".

TABLE II

VAPOUR PHASE KRAFT PULPING WITH ADDITIVES

Impregnating Liquor					Volume of Removed Liquor, ml	Impregnated Liquor			Max. temp. °C	Time to max.temp. min.	Time at max. temp. min.
Run No.	Addi-tive	% Additive on wood	% Eff. Alkali on wood	Liquor: Wood Ratio		Effective alkali, % on wood	Sulphidity %	Additive % on wood			
1	-	-	32.0	6.7:1	370	9.55	14.9	-	170	40	80
2	AQ	0.075	32.0	6.7:1	378	9.59	17.7	0.053	170	40	80
3	AQ	0.15	32.0	6.7:1	360	10.8	18.4	0.115	170	40	80
4	AQ	0.30	32.0	6.7:1	370	10.4	15.6	0.195	170	40	80

Volume of Impregnating Liquor = 505 ml

AQ = anthraquinone

Sulphidity of Impregnating Liquors = 25%

TABLE II cont'd.

Vapour Phase Results				Liquid Phase Results Liquor:Wood Ratio = 4:1		
PULP				PULP		
Kappa No.	Yield % on wood	Viscosity mPa.S.	Liquor:Wood Ratio	Kappa No.	Yield % on wood	Viscosity mPa.S.
59.1	54.2	-	1.8:1	116.5	60.8	-
51.8	53.4	-	1.7:1	88.4	54.8	-
30.9	50.9	-	1.9:1	55.8	53.5	-
29.0	51.5	-	1.8:1	62.7	54.7	-

EXAMPLE 3

In 8 runs, samples of black spruce chips were subjected to pulping treatment employing soda liquor. In each run, two samples of the chips were treated, one by vapour phase cooking and the other by conventional liquid phase cooking. The results obtained are shown in Table III. As will be seen in said Table, no additive was used in run 1 whereas there was used as an additive, anthraquinone (AQ) in runs 2, 3 and 4; 2-methyl anthraquinone (2-MeAQ) in runs 5 and 6; and 1,4,4a,9a anthroquinone (THAQ) in runs 7 and 8.

Impregnation of the chips for the vapour phase cooking was effected as follows:

In run 1, the chips were impregnated as per Example 2.

In runs 2, 3 and 4, the chips were impregnated as per Example 1.

In runs 5 and 6, the chips were impregnated essentially as per Example 2 except that the microdigestor contents were preheated at 80°C for 1 hour before impregnation at 80°C. This modification was necessary to allow the 2MeAQ to be reduced and pass into solution to achieve a superior penetration.

In runs 7 and 8, impregnation was effected as follows:

a) The chips were charged to the microdigestor, the latter closed and the contents subjected to 10 cycles of 75 psig nitrogen pressure for 1 minute followed by 20 mm Hg vacuum for 1 minute to remove air from the wood.

b) THAQ was added to dilution water in a flask, purged of air with nitrogen followed by the addition to the additive of part of the oxygen-free caustic soda charge for the cook.

c) The above was heated at 95°C under nitrogen until the THAQ passed completely into solution, forming an orange-red solution. This was cooled under nitrogen and finally the flask was sealed under nitrogen by means of stop-cocks.

d) The microdigestor, dissolved additive and remaining pulping chemicals were placed in a nitrogen-filled glove box followed by the assembly of the cook under nitrogen.

e) The treatment described in Example 2 (c) was then carried out on the contents of the microdigestor.

The excess liquor, not absorbed by the chips, was poured off and collected for analysis as in Example 2.

All other operations were carried out in the manner described in Example 1. For liquid phase cooks, the additives and chemicals were charged to the chips in the microdigestor followed by closure and cooking.

Liquid phase cooks were carried out with the effective alkali and additive levels shown in Table III under the heading "Impregnated Liquor".

TABLE III

VAPOUR PHASE SODA PULPING WITH ADDITIVES

Impregnating Liquor					Volume of Removed Liquor ml	Impregnated Liquor			Max. temp. °C	Time to max. temp. min.	Time at max. temp. min.
Run No.	Additive	% additive on wood	% Eff. alkali on wood	Liquor: wood ratio		Effective alkali % on wood	Sulphidity %	Additive % on wood			
1	-	-	41.6	6.7:1	355	13.0	-	-	170	40	80
2	AQ	0.35	41.6	6.7:1	364	13.5	-	0.115	170	40	80
3	AQ	0.25	53.3	6.7:1	360	13.1	-	0.100	170	90	80
4	AQ	0.42	53.3	6.7:1	360	13.1	-	0.150	170	90	80
5	2MeAQ	0.175	41.6	6.7:1	353	12.1	-	0.101	170	40	80
6	2MeAQ	0.35	41.6	6.7:1	354	12.2	-	0.178	170	40	80
7	THAQ	0.10	41.6	6.7:1	374	12.1	-	0.044	170	40	80
8	THAQ	0.20	41.6	6.7:1	363	13.8	-	0.087	170	40	80

Volume of Impregnating Liquor = 505 ml
AQ = anthraquinone
2MeAQ = 2-methylanthraquinone
THAQ = 1,4,4a,9a-tetrahydroanthraquinone

TABLE III cont'd.

Vapour Phase Results				Liquid Phase Results Liquor:Wood Ratio = 4:1		
PULP				PULP		
Kappa No.	Yield % on wood	Viscosity mP.S.	Liquor:Wood Ratio	Kappa No.	Yield % on wood	Viscosity mPa.S.
88.8	53.3	-	2:1	138.5	67.7	-
33.6	49.0	-	1.9:1	58.2	53.5	-
39.4	50.4	17.9	1.9:1	63.1	53.6	-
34.1	50.6	17.7	1.9:1	60.5	53.5	-
51.7	52.4	-	2:1	73.0	56.0	-
37.6	51.9	23.2	2:1	60.9	54.8	-
47.4	50.2	-	1.75:1	94.2	57.7	-
35.9	48.8	-	1.9:1	59.4	52.9	-

EXAMPLE 4

In two runs, samples of black spruce chips were subjected to pulping treatment employing a polysulphide liquor. In each run, two samples of the chips were treated, one by vapour phase cooking and the other, for purposes of comparison, by conventional liquid phase cooking. The results obtained are shown in Table IV. As will be seen in said table, no additive was used in run 1 whereas in run 2, the additive anthraquinone was used.

Impregnation of the chips for the vapour phase cooking was effected by the same technique as used for runs 5 and 6 of Example 3, except that the one hour preheating operation (to form the polysulphide solution) and the subsequent impregnation were carried out at 50°C instead of 80°C.

All other operations were carried out in the manner described in Example 1.

T A B L E IV

VAPOUR PHASE POLYSULPHIDE PULPING WITH ANTHRAQUINONE

Impregnating Liquor					Volume of Removed Liquor, ml	Impregnated Liquor				Max. temp. °C	Time to max. temp. min.	Time at max. temp. min.
Run No.	% Sulphur on wood	% Additive on wood	% Eff. alkali on wood	Liquor: wood ratio		% Eff. alkali, on wood	Sulphidity %	Sulphur, % on wood	% Additive on wood			
1	7.5	0.10	33.1	6.7:1	374	10.9	12.9	0.7	0.026	170	30	80
2	7.5	0.20	33.1	6.7:1	365	11.4	13.9	1.9	0.056	170	30	80

Weight of Wood = 75 gm O.D./Run

Total Liquor Volume = 505 ml

Sulphidity of Impregnating Liquors = 25%

TABLE IV cont'd.

Vapour Phase Results				Liquid Phase Results Liquor:Wood Ratio = 4:1		
PULP				PULP		
Kappa No.	Yield % on wood	Viscosity mPa.S.	Liquor:Wood Ratio	Kappa No.	Yield % on wood	Viscosity mPa.S.
25.8	53.3	34.8	1.75:1	82.8	55.4	-
24.4	53.1	33.2	1.9 :1	50.3	56.0	-

EXAMPLE 5

In seven runs, samples of black spruce chips were subjected to pulping treatment employing an alkaline sulphite liquor. In each run, two samples of the chips were treated one by vapour phase cooking and the other, for comparison purposes, by conventional liquid phase cooking. The results obtained are showin in Table V. As will be seen in said table, no additive was used in run 1 whereas in the other runs a cyclic keto compound was used as an additive.

Impregnation of the chips for the vapour phase pulping was effected by the same technique as used for runs 5 and 6 of Example 3.

All other operations were carried out in the manner described in Example 1.

TABLE V

VAPOUR PHASE ALKALINE SULPHITE PULPING WITH ANTHRAQUINONE

Impregnating Liquor					Volume of Removed Liquor ml	Impregnated Liquor			Max. temp. °C	Time to max. temp. min.	Time at max. temp. min.
Run No.	% Additive on wood	% NaOH	% Na_2SO_3	Liquor: wood ratio		% NaOH on wood	% Na_2SO_3 on wood	% Additive on wood			
1	-	40	80	6.7:1	373	14.3	20.1	-	170	32	80
2	0.075	40	80	6.7:1	375	14.3	21.2	0.029	170	32	80
3	0.15	40	80	6.7:1	371	14.8	26.1	0.046	170	32	80
4	0.30	40	80	6.7:1	374	14.6	20.7	0.128	170	32	80
5	-	60	80	6.7:1	385	18.8	29.2	-	170	32	80
6	0.075	60	80	6.7:1	383	20.9	22.6	0.041	170	32	80
7	0.15	60	80	6.7:1	381	19.5	27.9	0.057	170	32	80

Weight of Wood = 75 gm O.D./Run

Toal Liquor Volume = 505 ml

TABLE V cont'd.

Vapour Phase Results				Liquid Phase Results Liquor:Wood Ratio = 4:1		
PULP				PULP		
Kappa No.	Yield % on wood	Viscosity mPa.S.	Liquor:Wood Ratio	Kappa No.	Yield % on wood	Viscosity mPa.S.
59.1	52.5	-	1.8:1	108.5	56.6	-
31.2	50.0	12.3	1.8:1	62.4	53.9	-
26.9	49.6	13.1	1.8:1	43.4	52.2	-
19.6	50.0	14.6	1.8:1	34.2	51.9	-
30.4	47.3	21.6	1.8:1	65.6	53.0	-
21.0	46.7	21.0	1.8:1	50.8	53.1	-
18.2	46.5	23.9	1.8:1	30.6	49.6	-

CLAIMS.

1. A process for the delignification of lignocelulosic material comprising the steps of:

i. impregnating lignocellulosic material in subdivided form with an alkaline pulping liquor containing from 0.001% to 10.0% by weight based on the lignocellulosic material, of a cyclic keto compound selected from the group consisting of naphthoquinone, anthraquinone, anthrone, phenanthrenequinone, the alkyl, alkoxy and amino derivatives of these four compounds, 6,11-dioxo-1H-anthra 1,2-c pyrazole, anthroquinone-1,2 naphthacridone, 7,12-dioxo-7,12 dihydroanthra 1,2-b pyrazine, 1,2-benzanthraquinone, 10-methylene anthrone and the unsubstituted and lower alkyl substituted Diels Alder adducts of naphthoquinone and benzoquinone,

ii. removing any excess of liquor from the impregnated material, and

iii. cooking said impregnated material by heating to a temperature in the range of 150°C to 200°C for a period of 0.5 to 480 minutes.

2. A process as claimed in claim 1 wherein the alkyl groups in the alkyl derivatives of the compounds naphthoquinone, anthraquinone, anthrone and phenanthrenequinone range from 1 to 2 in number and each have from 1 to 4 carbon atoms, and the alkoxy groups in the alkoxy derivatives of these same compounds are at least one in number and each have from 1 to 4 carbon atoms.

3. A process as claimed in claim 1, wherein the alkyl group in the alkyl substituted Diels Alder adducts range from 1 to 4 in number and each contain from 1 to 4 carbon atoms.

4. A process as claimed in claim 1 wherein the cyclic keto compound is anthraquinone.

5. A process as claimed in claim 1 wherein the cyclic keto compound is anthrone, anthraquinone, 2-methylanthraquinone, 2-ethylanthraquinone, 2,6-dimethylanthra-

quinone, 2,7-dimethylanthraquinone, 2,3-dimethylanthraquinone, 1-methoxyanthraquinone or 2-aminoanthraquinone.

6. A process as claimed in claim 1 wherein the cyclic keto compound is a Diels Alder adduct selected from the group consisting of 1,4,4a,5,8,8a,9a,10a-octahydroanthraquinone, 2,3,6,7-tetramethyl-1,4,4a,5,8,8a,9a,10a-octahydroanthraquinone, 1,4,4a,9a-tetrahydroanthraquinone, 2-ethyl-1,4,4a,9a-tetrahydroanthraquinone, 2,3-dimethyl-1,4,4a,9a-tetrahydroanthraquinone, 2,3-dimethyl-1,4,4a,9a-tetrahydroanthraquinone and 1,3-dimethyl-1,4,4a,9a-tetrahydroanthraquinone.

7. A process as claimed in any one of the preceding claims, wherein the alkaline pulping liquor contains from 0.01% to 1.0% by weight based on lignocellulosic material, of the cyclic keto compound.

8. A process as claimed in any one of the preceding claims, wherein the alkaline pulping liquor is a soda liquor.

9. A process as claimed in claim 8 wherein there is used in combination with the cyclic keto compound from 0.01% to 10.0% by weight based on the lignocellulosic material of a nitroaromatic compound selected from the group consisting of nitrobenzene, 2-nitroaniline, 4-nitroaniline, 4-nitrobenzaldehyde, 4-nitrobenzoic acid, 4-nitroresorcinol, 4-nitrostyrene, 2-nitrotoluene, 4-nitrotoluene, 1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,4-dinitrotoluene, 3,5-dinitrobenzoic acid, 4,6-dinitro-o-cresol, 2,4-dinitroresorcinol and the amino, carboxy, hydroxy and methyl derivatives of these compounds.

10. A process as claimed in claim 9 wherein the cyclic keto compound is anthraquinone and the nitroaromatic compound is nitrobenzene.

11. A process as claimed in any one of claims 1 to 7, wherein the alkaline pulping liquor is a kraft liquor.

12. A process as claimed in claim 11, wherein the kraft liquor contains from 1.0% to 5.0% by weight based on the weight of lignocellulosic material, of polysulphides expressed as sulphur.

13. A process as claimed in any one of claims 1 to 7 wherein the alkaline pulping liquor is an alkaline sulphite liquor.

14. A process as claimed in any one of the preceding claims, wherein the delignified cellulosic material is subjected to conventional bleaching.

15. Delignified lignocellulosic material whenever prepared by a process as claimed in any one of the preceding claims.

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 79 30 2316

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	CA - A - 986 662 (MacMILLAN BLOEDEL) * Claims 1-8,11,12; page 6, lines 8-26; page 8, lines 4-21 * --	1,8,15
D	US - A - 4 036 680 (H.H. HOLTON et al.) * Entire document * --	1,3,6-9,14,15
D	US - A - 3 215 588 (T.N. KLEINERT) * Entire document * --	1,11-15
P	US - A - 4 127 439 (J.S. FUJII et al.) * Column 1, lines 1-53; column 2, lines 1-65; column 3,line 11 to column 4, line 38 * ----	1,2,4,5,7,8,15

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

D 21 C 1/00
3/22
C 07 C 49/00

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

D 21 C 1/00
3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10-01-1980	NESTBY

EPO Form 1503.1 06.78