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(54) **SULPHUR-FREE PROCESS FOR PRODUCING CHEMICAL PULP**

SCHWEFELFREIES VERFAHREN ZUR HERSTELLUNG EINES CHEMISCHEN ZELLSTOFFS

PROCEDE EXEMPT DE SOUFRE POUR LA PRODUCTION D'UNE PATE CHIMIQUE

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(73) Proprietor: **KVAERNER PULPING AB**
651 15 Karlstad (SE)

(72) Inventors:
• **GUSTAVSSON, Sören**
S-652 23 Karlstad (SE)

- **FAHLGREN, Christer**
S-654 59 Karlstad (SE)
- **BODER, Bo**
S-660 50 Valberg (SE)
- **WESTLUND-JOHANSSON, Ewa**
S-652 22 Karlstad (SE)

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EP-A- 0 010 451 **WO-A-95/02726**
AU-A- 3 537 578 **US-A- 4 181 565**

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Description

TECHNICAL FIELD:

[0001] The present invention relates to a process for producing chemical pulp from comminuted cellulose-containing material without using sulphur-containing cooking liquids. The process according to the invention includes at least one impregnation stage followed by at least one cooking stage, with a delignification-accelerating compound, such as an anthraquinone, being supplied to at least one of the said stages. In the process according to the invention, a first cooking liquid which has been extracted from a position downstream of the impregnation stage is supplied to the impregnation stage, with the said first cooking liquid primarily containing OH⁻ ions as the active substance. The returning of extracted cooking liquid makes it possible to achieve a higher concentration of OH⁻ ions in the cooking stage which succeeds the said impregnation stage than is possible in the case of conventional soda-anthraquinone cooking. According to a preferred embodiment, a metal-complexing agent is supplied to the impregnation stage or to another stage located upstream of the cooking stage.

[0002] The process according to the invention is suitable for producing chemical pulp from essentially all the generally available raw materials for cellulose production. Examples of suitable raw materials are softwood chips derived from fir and pine and hardwood chips derived from birch, aspen and eucalyptus. The process according to the invention is also suitable for producing pulp from non-Scandinavian raw materials such as southern pine or loblolly pine and can also be used for producing pulp from straw, reed-grass, esparto grass and other alternative raw materials.

[0003] The process according to the invention is suitable both for producing pulp which is intended for ECF or TCF bleaching and for producing unbleached high-yield pulp.

STATE OF THE ART:

[0004] Recently, techniques for producing pulp have to an ever greater extent been directed by the environmental demands imposed by authorities, environmental organizations and customers. This trend has led to pulp manufacturing processes in which there is a reduced use of chlorine chemicals during bleaching, an increased degree of closure and a decreased consumption of energy.

[0005] A familiar problem associated with producing pulp by the sulphate method or the sulphite method is the problem of troublesome smells in the vicinity of the pulp mill and, in certain cases, even at a distance of several tens of kilometres. These smell problems are principally caused by various sulphur compounds which are produced when pulp is cooked using sulphur-containing cooking liquids. Examples of such malodorous compounds are hydrogen sulphide (H₂S) and methylmercaptan (CH₃SH). Various solutions, such as purifying exhaust gases and improving the sealing of the pulp manufacturing process, have been proposed for remedying the smell problems.

[0006] A disadvantage of using sulphur-containing cooking liquids for cooking pulp is that a relatively complicated chemical recovery system is required in order to be able to recirculate the chemicals.

[0007] The presence of sulphur also impedes efforts, which have been in progress for a long time now, to close the pulp manufacturing process.

[0008] Another disadvantage of sulphur-containing pulp cooking is that sulphur discharges from the pulp manufacturing process contribute to the ever increasing acidification of the environment.

[0009] It is very clear, therefore, that it would be advantageous to completely eliminate the use of sulphur in pulp production.

[0010] For this reason, various processes which do not make use of sulphur-containing cooking liquids have already been proposed.

[0011] For example, patent specification SE-C2-502 667, corresponding to WO-A-95/02726 previously disclosed a method for producing chemical pulp from comminuted cellulose-containing material, which method comprised cooking the fibre material with a cooking liquid. The object of the invention which is described is stated as being that of producing a chemical pulp which, after the cooking, already has a substantially reduced content of transition metals and at the same time has considerably improved properties, especially, but not exclusively, with regard to tear resistance, viscosity, yield, kappa number and brightness.

[0012] According to the abovementioned patent specification SE-C2-502 667, these advantages are achieved by means of a pretreatment, prior to the cooking, with a compound which has the ability to complex with metals which are naturally present in the fibre material. The pretreatment with complexing agents is stated to give, within the same kappa number interval, a lower content of metals such as manganese, a tear resistance which is at least 10% higher, a viscosity which is at least 5% higher and a yield which is at least 1% higher as compared with the corresponding parameters for a pulp produced without the said pretreatment. The method which is described for producing chemical pulp is stated to be suitable for any method for producing chemical pulp, including anthraquinone/hydroxide pulp (NaOH/KOH) as well. No cooking liquids containing sulphur are used in a pulp manufacturing process of this nature.

[0013] It is thus previously known to pretreat chips with complexing agents and then carry out isothermal cooking using a cooking liquid which principally contains OH^- as the active substance in the cooking, and using anthraquinone as a delignification-accelerating additive.

[0014] However, it is not evident from the said patent specification, SE-C2-502 667, how this abovementioned cooking without sulphur chemicals should be carried out in practice.

[0015] It is a previously known fact that conventional soda-anthraquinone cooking requires a high cooking temperature in order to achieve satisfactory lignin dissolution, i.e. to reach a relatively low kappa number. The high temperature gives rise to a high consumption of energy and to a serious risk of carbohydrate breakdown.

[0016] In this context it should be mentioned that AU-A-35 37578 does disclose a method for the production of pulp wherein cooking is carried out without sulphur chemicals and at relatively low temperatures, by the use of anthraquinone as a delignification-accelerating additive. However, this latter method does not provide for satisfactory lignin dissolution and accordingly such a method is not suited for producing market pulp, i.e. intended for bleaching to high brightness, nor does it provide a pulp having desired strength properties for high yield pulps.

ACCOUNT OF THE INVENTION:

[0017] An object of the present invention is therefore to provide a process for producing chemical pulp from comminuted cellulose-containing material, which process yields a perfectly satisfactory pulp quality at a competitive cost without any sulphur-containing cooking liquid having to be used.

[0018] This object of the invention is achieved by a continuous sulphur-free process for producing chemical pulp from comminuted cellulose-containing fibre material, comprising at least one impregnation stage followed by at least one cooking stage with at least one concurrent cooking zone and at least one countercurrent cooking zone and, as the conclusion to the cooking stage, at least one extended displacement zone, with a delignification-accelerating compound being supplied to at least one of the said stages, wherein a first cooking liquid, which has been extracted from a position downstream of the impregnation stage, is supplied to the said impregnation stage, with the said first cooking liquid essentially containing OH^- ions as the active substance, and wherein the concentration of OH^- ions in the said concurrent cooking zone is at least 20% higher than in the said impregnation stage, preferably at least 50% higher and wherein the quantity of delignification-accelerating compound which is added to the impregnation stage is less than 50% by weight of the total amount added of said delignification-accelerating compound

[0019] The concentration of OH^- ions at the beginning of the concurrent cooking zone of the cooking stage must exceed 0.5 mol/l, and preferably 0.7 mol/l. Most preferably, the concentration of OH^- ions must exceed 1.0 mol/l.

[0020] Under certain circumstances, it can be advantageous to make a further addition of OH^- ions to the previously mentioned first cooking liquid before it is supplied to the said impregnation stage.

[0021] As previously mentioned, a delignification-accelerating compound, for example anthraquinone, is supplied when the process according to the invention is being implemented.

[0022] It would be evident to the skilled person that several types of unsubstituted or substituted quinones or hydroquinones can also be used as the delignification-accelerating compound, such as anthraquinone, benzoquinone or naphthoquinone, or salts of these or other similar compounds, since such compounds have been found to give a similar effect.

[0023] 1,4-Dihydro-9,10-dihydroxyanthracene has been found to be especially suitable for use as the delignification-accelerating compound when the invention is being implemented.

[0024] When the process according to the invention is being implemented, the best results have been obtained when the major part of the delignification-accelerating compound is added to the previously mentioned concurrent cooking zone.

[0025] In this connection, the total delignification-accelerating compound added should exceed 1 kg per tonne of bone dry wood and preferably exceed 1.5 kg per tonne of bone dry wood. The optimum amount to be added is between 1.8 and 2.5 kg per tonne of bone dry wood.

[0026] The quantity of delignification-accelerating compound which is added to the impregnation stage should be less than 30% by weight of the total amount added. The best results are obtained if less than 10% by weight of the total amount of the delignification-accelerating compound added is added to the impregnation stage.

[0027] It has also been found that the total quantity of delignification-accelerating compound which is added must exceed 0.5% by weight of the total quantity of effective alkali (EA), calculated as NaOH, which is added to the process. Preferably, the total quantity of delignification-accelerating compound should exceed 1% by weight, and most preferably be from 1.1 to 1.5% by weight, of the total quantity of effective alkali (EA) which is added.

[0028] The fact that the abovementioned first cooking liquid is returned to the impregnation stage makes it possible to achieve a higher concentration of OH^- ions in the cooking stage, especially at the beginning of the said concurrent cooking zone, as compared with conventional soda-anthraquinone cooking. Furthermore, returning the cooking liquid means that the heat energy losses are minimized.

[0029] Taken together, this provides a more efficient delignification process, thereby making it possible to achieve a second main object of the invention, namely that of providing a process for producing chemical pulp, which process requires a lower temperature during cooking than do previously known processes for producing pulp without sulphur-containing cooking liquids, for example soda-anthraquinone cooking in accordance with the state of the art.

[0030] The lower temperature level which can be used in the process according to the invention results in lower energy consumption and in there being less risk of carbohydrate breakdown.

[0031] It has been found that, while the temperature in the impregnation stage, when implementing the invention, may be within the interval 80-140°C, it should preferably be between 100 and 130°C, and should most preferably be between 120 and 127°C.

[0032] While the temperature in the subsequent cooking stage may, when cooking softwood, be within the interval 150-170°C, it should preferably be between 158 and 163°C.

[0033] When cooking hardwood, the temperature in the said cooking stage may be within the interval 140-165°C and should preferably be between 155 and 158°C.

[0034] It has been found to be especially advantageous if the cooking is carried out isothermally in at least two adjacent zones in the said cooking stage.

[0035] According to a preferred embodiment of the invention, a metal-complexing agent is supplied to the impregnation stage or to another stage upstream of the cooking stage. In this context, a metal-complexing agent is understood as being a compound which has the ability to bind metals which are harmful to the pulp production process in the form of metal complexes which can, if required, be removed from the process.

[0036] Thus, metal complex-containing extraction liquid which has been extracted from the impregnation stage can be removed from the process or conveyed to evaporation. In this connection, an excess of cooking liquid which has been extracted from the cooking stage can be conveyed to evaporation at the same time.

[0037] Examples of compounds which are suitable for use as metal-complexing agents are DTPA, diethyltriaminepentaacetic acid, and EDTA, ethylenediaminetetraacetic acid, but other similar compounds can also be used.

DTPA has been found to be most advantageous for use in the process according to the invention.

[0038] According to a preferred embodiment of the invention, a second cooking liquid, having a lower concentration of OH⁻ ions than is present in the said first cooking liquid, is supplied to the previously mentioned extended displacement zone.

[0039] When the process according to the invention is being implemented, the kappa number after the cooking stage is between 15 and 30, and preferably between 18 and 25, when softwood pulp which is intended for bleaching is being cooked.

[0040] The kappa number is between 9 and 25, and preferably between 12 and 18, when hardwood pulp which is intended for bleaching is being cooked.

[0041] The kappa number is between 50 and 85, when high-yield pulp which is not to be bleached is being cooked.

[0042] It has been found that pulp which has been produced by the process according to the invention and which has then been oxygen-delignified in a manner familiar to the skilled person can be bleached to a brightness exceeding 80% ISO both by means of ECF bleaching and TCF bleaching (ECF: elemental chlorine-free, TCF: totally chlorine-free).

[0043] When higher brightness levels are required, for example higher than 85% ISO, in certain cases higher than 88% ISO, it has been found that, while pulp which has been produced by the process according to the invention can indeed be bleached to such high brightness levels, the consumption of bleaching chemicals is then greater than is the case when bleaching conventional oxygen-delignified sulphate pulp.

[0044] When pulp which has been produced by the process according to the invention is being ECF-bleached, it has been found advantageous for the bleaching sequence to comprise the bleaching stages (DQ)(PO).

[0045] When carrying out TCF-bleaching, a bleaching sequence is advantageously used which comprises the bleaching stages (Q)(OP)(ZQ)(PO).

[0046] For the rest, the process according to the invention can be implemented using apparatus and equipment which are suitable for preparing pulp and which are familiar to the skilled person.

[0047] The process according to the invention makes it possible to achieve a more efficient cooking process as compared with sulphur-free cooking in accordance with the state of the art, together with the previously mentioned advantages arising from the ability to use lower process temperatures.

BRIEF DESCRIPTION OF THE FIGURES:

[0048] The attached Figures 1, 2, 3 and 4 show typical results from beating experiments which were carried out using unbleached pulps which were obtained by processes according to the invention (Nos. ITC 1666 and ITC 1668). For comparison, corresponding results are shown for pulps which were produced by conventional ITC sulphate cooking (No. ITC 1544) and by soda-anthraquinone cooking (ITC 1618) in accordance with the state of the art.

[0049] The attached Figures 5, 6, 7 and 8 show results from beating experiments using bleached pulps which were

produced by processes according to the invention and which, after oxygen-delignification, were bleached by ECF bleaching using the bleaching sequence (DQ)(PO) and by TCF bleaching using the bleaching sequence Q(OP)(ZQ)(PO), respectively. In this context,

- Fig. 1 shows the tensile index as a function of the number of revolutions when beating in a PFI beater,
- Fig. 2 shows the tear index as a function of the number of revolutions when beating in a PFI beater,
- Fig. 3 shows the tear index as a function of the tensile index,
- Fig. 4 shows the tensile index as a function of the density,
- Fig. 5 shows the tensile index as a function of the number of revolutions when beating in a PFI beater,
- Fig. 6 shows the tear index as a function of the number of revolutions when beating in a PFI beater,
- Fig. 7 shows the tear index as a function of the tensile index, and
- Fig. 8 shows the tensile index as a function of the density.

EXAMPLES:

[0050] In that which follows, the invention is illustrated using process data and results from a number of laboratory experiments. The experiments are reported in Tables 1 to 7 below. The tables record cooking experiments using processes according to the invention and experiments using conventional isothermal (ITC) sulphate cooking together with experiments using isothermal (ITC) soda-anthraquinone cooking in accordance with the state of the art. In addition, results are recorded from a number of oxygen-delignification and bleaching experiments.

[0051] In the experiments, softwood chips were cooked on a laboratory scale in a standardized manner as described below, thereby simulating a continuous cooking process.

Presteamming:

[0052] Scandinavian softwood chips corresponding to 1.8 kg of bone dry chips were added to a circulation digester and subjected to steaming at 110°C for 5 minutes under a pressure of 1.0 bar.

Impregnation:

[0053] Impregnation liquid was allowed to circulate through the digester at 125°C for 45 minutes at the same time as a nitrogen pressure of 10 bar was applied.

[0054] In the two experiments using the process according to the invention, cooking liquid which had been extracted, and returned, from the subsequent cooking phase was used for the impregnation. This gave a liquid:wood ratio of 5.5:1. In addition, a metal-complexing agent, DTPA, was added during the impregnation at the rate of 2 kg per tonne of bone dry wood.

[0055] In the experiment using isothermal (ITC) soda-anthraquinone cooking in accordance with the state of the art, an OH⁻ ion-containing impregnation liquid was used, with the liquid:wood ratio being 3.6:1. No metal-complexing agent was added to the impregnation in this experiment. However, a delignification-accelerating compound, 1,4-dihydro-9,10-dihydroxyanthracene, was added at the rate of 1 kg per tonne of bone dry wood.

[0056] Only conventional white liquor was added in the experiment using conventional isothermal (ITC) sulphate cooking, with the liquid:wood ratio being 3.6:1. As a consequence, neither a delignification-accelerating compound nor a metal-complexing agent was added in this experiment.

Concurrent cooking:

[0057] After the impregnation had been carried out, the nitrogen pressure was released from the digester and the temperature was raised to the cooking temperature at the same time as further cooking liquid was added. The dwell time during this phase was 60 minutes.

[0058] In the two experiments using cooking in accordance with the invention, all the free liquid was extracted after the impregnation and replaced with cooking liquid containing OH⁻ ions, such that a liquid:wood ratio of 4:1 was obtained. In addition, the previously mentioned delignification-accelerating compound was added during the concurrent cooking at the rate of 2 kg per tonne of bone dry wood.

[0059] In the experiment using isothermal (ITC) soda-anthraquinone cooking in accordance with the state of the art, further cooking liquid was added, such that the liquid:wood ratio became 4:1. In addition, the previously mentioned delignification-accelerating compound was added at the rate of 0.5 kg per tonne of bone dry wood.

[0060] In the experiment using conventional isothermal (ITC) sulphate cooking, only conventional white liquor was added, such that a liquid:wood ratio of 4:1 was obtained.

Countercurrent cooking:

[0061] After the concurrent cooking had been completed, a countercurrent cooking was initiated with 7.2 l of cooking liquid containing 25 g/l effective alkali (EA), calculated as NaOH, being pumped in gradually and being allowed to displace the corresponding quantity of used cooking liquid from the concurrent cooking. The temperature was the same as for the concurrent cooking except in experiment No. ITC 1668, where the temperature, after having been at a lower level during the concurrent cooking, was raised during the countercurrent cooking. The concentration of the cooking liquid in the countercurrent phase was adjusted such that approximately 15-25 g/l effective alkali (EA) remained when the countercurrent cooking had been completed.

[0062] In the experiment using isothermal (ITC) soda-anthraquinone cooking in accordance with the state of the art, the delignification-accelerating compound was additionally added during the countercurrent cooking at the rate of 0.5 kg per tonne of bone dry wood.

Extended displacement washing - Hi-Heat:

[0063] In the extended displacement phase, the exchange of chemicals between the exhausted cooking liquid and the supplied cooking liquid continued at the same temperature as during the concurrent cooking and the countercurrent cooking. A cooking liquid containing 10 g/l effective alkali (EA), calculated as NaOH, was added in this context. In this way, 10.3 l of cooking liquid were displaced over a period of 180 minutes.

[0064] Finally, the fully cooked chips were transferred to a propeller-equipped disintegrator for defibering for a period of 15 minutes. After the resulting, unscreened pulp had been washed and thickened, its yield was determined. After that, the pulp was screened in two stages, with the coarser rejects being separated off in a perforated screen basket having a hole diameter of 1.5 mm under a water pressure of 150 kPa. The remaining fine rejects were separated off on a vibrating diaphragm screen having a 0.15 mm gap-width.

[0065] Process conditions during the cooking and the results which were obtained using processes according to the present invention are given in the enclosed Table 1, see experiments No. ITC 1666 and ITC 1668. For comparison, the said Table 1 records the corresponding process parameters and results for a cooking experiment which was carried out using conventional isothermal (ITC) sulphate cooking, see experiment No. ITC 1544. The said Table 1 also records the corresponding process parameters and results for a cooking experiment which was carried out using isothermal (ITC) soda-anthraquinone cooking in accordance with the state of the art, see experiment No. ITC 1618.

[0066] Enclosed Table 2 records process parameters from two oxygen-delignification experiments, in this case for pulp which was cooked by conventional ITC sulphate cooking and for pulp which was cooked by a process according to the invention. The other pulps were oxygen-delignified in a similar manner, after which the pulps were bleached.

[0067] Table 3 records process parameters and results from ECF bleaching experiments using the bleaching sequence (DQ)(PO). In this context, the abbreviation ECF stands for elemental chlorine-free and may, like the abbreviations used in the bleaching sequence, be regarded as being familiar to skilled persons in the field. In the experiments recorded in Table 3, pulp which was cooked by conventional ITC sulphate cooking, or pulp which was cooked by isothermal soda-anthraquinone cooking in accordance with the state of the art, was bleached after oxygen-delignification.

[0068] Table 4 likewise records corresponding process parameters and results from an ECF bleaching experiment using the bleaching sequence (DQ)(PO), but in this case for an oxygen-delignified pulp which was cooked by a process according to the invention.

[0069] Table 5 likewise records results from bleaching experiments with an oxygen-delignified pulp which was cooked in accordance with the invention; however, in this case, a TCF bleaching sequence, i.e. Q(OP)(ZQ)(PO), was used. In this context, the abbreviation TCF stands for totally chlorine-free, which, like the bleaching sequence, is probably familiar to skilled persons in the field.

[0070] Table 6 records the pulp properties of the unbleached pulps which were obtained by means of the cooking experiments recorded in Table 1.

[0071] Finally, Table 7 records the pulp properties of pulp which was cooked by a process according to the invention and which, after oxygen-delignification, was bleached by means of ECF bleaching, using the bleaching sequence (DQ)(PO), or by means of TCF bleaching using the bleaching sequence Q(OP)(ZQ)(PO).

CONCLUSIONS:

[0072] Based on that which is recorded in the enclosed figures and tables, the following conclusions can be drawn.

[0073] Unbleached softwood pulp which has been produced by the process according to the invention exhibits, at the same kappa number, yields and tear resistances which are of the same level as those for a sulphate pulp produced by conventional ITC sulphate cooking.

[0074] Pulp which has been produced in accordance with the invention exhibits a tear resistance which is clearly higher than that of pulp which has been produced by isothermal (ITC) soda-anthraquinone cooking in accordance with the state of the art.

[0075] It is also evident that processes in accordance with the invention make it possible to achieve the same kappa number as that obtained by conventional ITC sulphate cooking at an H factor of the same order of size.

[0076] It is evident from the experiment using isothermal soda-anthraquinone cooking in accordance with the state of the art that, in this case, a substantially higher H factor is required in order to achieve the same kappa number, as compared with cooking in accordance with the invention.

[0077] This means, therefore, that the process in accordance with the invention, unlike isothermal soda-anthraquinone cooking in accordance with the state of the art, makes it possible to lower the cooking temperature to the same level as for conventional ITC sulphate cooking, thereby ensuring substantial energy savings and reduced risk of carbohydrate breakdown.

[0078] Based on the beating experiments which were carried out in a PFI beater, it appears that unbleached pulp which has been cooked in accordance with the invention requires more beating revolutions than do the two reference pulps which were cooked in accordance with the state of the art.

[0079] The bleaching experiment using the (DQ)(PO) bleaching sequence (ECF bleaching) shows that a perfectly satisfactory brightness can be achieved for pulp which has been produced in accordance with the invention.

[0080] The bleaching experiment using the Q(OP)(ZQ)(PO) bleaching sequence (TCF bleaching) likewise shows that, in this case too, a perfectly satisfactory brightness can be achieved for pulp which has been produced in accordance with the invention.

[0081] In summary, the results obtained show that the process in accordance with the invention makes it possible to produce both unbleached and bleached pulps having perfectly satisfactory pulp properties without any use of sulphur-containing cooking liquids and at a substantially lower cooking temperature than in the case of isothermal soda-anthraquinone cooking in accordance with the state of the art.

[0082] In the foregoing text, the present invention has been illustrated with the aid of examples comprising process data and results from a number of experiments. However, the invention is in no way restricted to that which has been stated in this context and can naturally be varied within the scope of the attached patent claims.

Table 1

LABORATORY COOKING REPORT				
GENERAL PROCESS CONDITIONS				
Wood type	Scandinavian softwood, chips			
Presteam, min	5			
Temperature, °C	110			
Pressure, bar	1.0			
Liquid:wood ratio	4.0			
EXPERIMENT TYPE	IN ACCORDANCE WITH THE STATE OF THE ART		IN ACCORDANCE WITH THE INVENTION	
PROCESS TYPE	SULPHATE (ITC)	SODA-AQ (ITC)	MODIFIED SODA-AQ (ITC), impregnation with returned extraction liquor liquid:wood = 5.5:1	
EXPERIMENT NO. ITC	1544	1618	1666	1668
IMPREGNATION				
Time, minutes	45	45	45	45
Temperature, °C	125	125	125	125
AQ added, kg/BDMT	-	1	-	-
DTPA added, kg/BDMT	-	-	2	2
Alkali consumption, kg of EA/BDMT of wood	105	96	89	86

Table 1 (continued)

LABORATORY COOKING REPORT				
GENERAL PROCESS CONDITIONS				
EXPERIMENT TYPE	IN ACCORDANCE WITH THE STATE OF THE ART		IN ACCORDANCE WITH THE INVENTION	
PROCESS TYPE	SULPHATE (ITC)	SODA-AQ (ITC)	MODIFIED SODA-AQ (ITC), impregnation with returned extraction liquor liquid:wood = 5.5:1	
CONCURRENT COOKING				
Time, minutes	60	60	60	60
Temperature, °C	159	168	160	145
AQ added, kg/BDMT	-	0.5	2	2
Alkali consumption, kg of EA/BDMT of wood	31	42	77	60
COUNTERCURRENT COOKING				
Time, minutes	60	60	60	60
Temperature, °C	159	168	160	162
AQ added, kg/BDMT	-	0.5	-	-
Alkali consumption, kg of EA/BDMT of wood	20	17	18	29
EXT. DISPL. WASHING				
Time, minutes	180	180	180	180
Temperature, °C	159	168	160	162
Alkali consumption, kg of EA/BDMT of wood	11	22	5	14
RESULTS				
H factor	1867	3960	2024	2055
Alkali consumption, tot.kg of EA/BDMT of wood	167	177	189	189
Yield, % of wood	46.9	45.4	45.3	45.4
Rejects, % of wood	<0.1	<0.1	0.3	<0.1
Kappa number	23.8	25.1	22.8	23.8
Viscosity, dm ³ /kg	1326	940	1018	1022
Metal content:				
Mg/Mn, ppm	60-74	69/29	106/29	100/31
Ca/Cu, ppm	610/1.6	770/2.7	550/3.6	430/3.4
Fe, ppm	8.2	18	30	45
(AQ: delignification-accelerating compound)				

Table 2

OXYGEN-DELIGNIFICATION		
Laboratory-scale oxygen-delignification of pulp which has been cooked using conventional ITC sulphate cooking or in accordance with the invention.		
PULP FROM COOK NO., TYPE OF COOKING	ITC 1544, SULPHATE (ITC) IN ACCORDANCE WITH THE STATE OF THE ART	ITC 1666, SULPHUR-FREE COOKING IN ACCORDANCE WITH THE INVENTION
Oxygen-delignification No.	S-1429	S-1459
PRIOR TO OXYGEN-DELIGNIFICATION		
Kappa number	23.8	22.8
Viscosity, dm ³ /kg	1326	1018
OXYGEN-DELIGNIFICATION		
Dry substance content, %	10	10
Temperature, °C	95	95
Time, minutes	60	60
Initial pressure, bar	5	5
NaOH added, kg/BDMT	20	20
MgSO ₄ added, kg/BDMT	3	3
AFTER OXYGEN-DELIGNIFICATION		
Final pH	11.4	11.0
Kappa number	10.3	11.1
Viscosity, dm ³ /kg	1031	884

Table 3

BLEACHING REPORT (DQ)(PO)		
(DQ)(PO)-bleaching of oxygen-delignified softwood pulp which has been cooked using conventional ITC sulphate cooking and of softwood pulp which has been cooked using SODA-AQ cooking in accordance with the state of the art.		
PULP FROM COOK NO., TYPE OF COOKING	ITC 1544, SULPHATE (ITC) IN ACCORDANCE WITH THE STATE OF THE ART	ITC 1618, SODA-AQ (ITC) IN ACCORDANCE WITH THE STATE OF THE ART
Oxygen-delignification No.	S-1429	S-1444
Bleaching experiment No.	B-3054	B-3113
PRIOR TO BLEACHING		
Kappa number	10.3	10.3
Viscosity, dm ³ /kg	1031	810
(DO) -CHLORINE DIOXIDE STAGE	10	10

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Table 3 (continued)

BLEACHING REPORT (DQ)(PO)						
(DQ)(PO)-bleaching of oxygen-delignified softwood pulp which has been cooked using conventional ITC sulphate cooking and of softwood pulp which has been cooked using SODA-AQ cooking in accordance with the state of the art.						
PULP FROM COOK NO., TYPE OF COOKING	ITC 1544, SULPHATE (ITC) IN ACCORDANCE WITH THE STATE OF THE ART			ITC 1618, SODA-AQ (ITC) IN ACCORDANCE WITH THE STATE OF THE ART		
Dry substance content, %	55/70*			55/70*		
Temperature, °C	30+60*			30+60*		
Time, minutes						
Chlorine multiple,	2.0			2.0		
kg of a. Cl/BDMT/kappa No.						
Active Cl added, kg/BDMT of pulp	20.6			20.6		
Remaining active Cl,	0			0		
kg/BDMT of pulp	4			4		
Initial pH (H ₂ SO ₄)	2*			2*		
EDTA added, kg/BDMT	10*			12		
NaOH added, kg/BDMT	2.0/4.9*			1.9/5.0*		
Final pH	3.7			3.7		
Kappa number	1044			786		
Viscosity, dm ³ /kg	140/0.7/190					
Mg/Mh/Ca, ppm	0.7/27					
Cu/Fe, ppm						
<u>(PO)</u> <u>-PEROXIDE</u> <u>STAGE</u>						
Dry substance content, %	10	10	10	10	10	10
Temperature, °C	110	110	110	110	110	110
Time, minutes	180	180	180	180	180	180
Mean pressure, bar (overpressure)	5	5	5	5	5	5
MgSO ₄ added, kg/BDMT	3	3	3	3	3	3
DTPA added, kg/BDMT	2	2	2	2	2	2

Table 3 (continued)

BLEACHING REPORT (DQ)(PO)						
(DQ)(PO)-bleaching of oxygen-delignified softwood pulp which has been cooked using conventional ITC sulphate cooking and of softwood pulp which has been cooked using SODA-AQ cooking in accordance with the state of the art.						
PULP FROM COOK NO., TYPE OF COOKING	ITC 1544, SULPHATE (ITC) IN ACCORDANCE WITH THE STATE OF THE ART			ITC 1618, SODA-AQ (ITC) IN ACCORDANCE WITH THE STATE OF THE ART		
H ₂ O ₂ added, kg/BDMT	20	30	40	20	30	40
NaOH added, kg/BDMT	20	25	30	20	25	30
H ₂ O ₂ consumption, kg/BDMT	12.6	21.6	31.3	14.3	21.9	31.7
Final pH	10.2	10.5	10.7	10.2	10.3	10.6
Kappa number	1.6	1.5	1.4	1.1	1.0	0.9
Viscosity, dm ³ /kg	859	736	637	712	669	574
Brightness, % ISO	90.5	91.1	91.6	84.2	85.7	87.9
Brightness reversion, % ISO	88.1	88.4	89.0			
Active Cl added, kg/ADMT	19	19	19	19	19	19
Peroxide added, kg/ADMT	18	28	37	18	28	37
Peroxide consumption, kg/ADMT	12	20	29	13	20	29

Table 4

BLEACHING REPORT (DQ)(PO)	
(DQ)(PO)-bleaching of oxygen-delignified softwood pulp which has been produced using the process in accordance with the invention.	
PULP FROM COOK NO., TYPE OF COOKING	ITC 1666, IN ACCORDANCE WITH THE INVENTION
Oxygen-delignification No.	S-1459
Bleaching experiment No.	B-3158
<u>PRIOR TO BLEACHING</u>	
Kappa number	11.1
Viscosity, dm ³ /kg	884
<u>(DO)-CHLORINE DIOXIDE STAGE</u>	
Dry substance content, %	10
Temperature, °C	55/55*
Time, minutes	30+60*
Chlorine multiple, kg of a. Cl/BDMT/ kappa No.	2.0

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Table 4 (continued)

BLEACHING REPORT (DQ)(PO)			
(DQ)(PO)-bleaching of oxygen-delignified softwood pulp which has been produced using the process in accordance with the invention.			
PULP FROM COOK NO., TYPE OF COOKING	ITC 1666, IN ACCORDANCE WITH THE INVENTION		
Active Cl added, kg/BDMT of pulp	22.2		
Remaining active Cl, kg/BDMT of pulp	0		
Initial pH(H ₂ SO ₄)	4		
EDTA added, kg/BDMT	2*		
NaOH added, kg/BDMT	12		
Final pH	1.9/5.0*		
Kappa number	4.4		
Viscosity, dm ³ /kg	880		
Mg/Mn/Ca, ppm	131/0.4/181		
Cu/Fe, ppm	2.3/9		
<u>(PO)-PEROXIDE STAGE</u>			
Dry substance content, %	10	10	10
Temperature, °C	110	110	110
Time, minutes	180	180	180
Mean pressure, bar (overpressure)	5	5	5
MgSO ₄ added, kg/BDMT	3	3	3
DTPA added, kg/BDMT	2	2	2
H ₂ O ₂ added, kg/BDMT	20	30	40
NaOH added, kg/BDMT	22	26	30
H ₂ O ₂ consumption, kg/BDMT	15.0	21.4	30.0
Final pH	10.5	10.6	10.6
Kappa number	1.0	0.9	0.9
Viscosity, dm ³ /kg	745	711	657
Brightness, % ISO	87.8	88.9	89.5
Brightness reversion, % ISO	85.7	86.7	87.2
Active Cl added, kg/ADMT	21	21	21
Peroxide added, kg/ADMT	19	28	37
Peroxide consumption, kg/ADMT	14	20	28

Table S

BLEACHING REPORT Q(OP)(ZQ)(PO)		
Q(OP)(ZQ)(PO)-bleaching of oxygen-delignified softwood pulp from cook No. ITC 1666 (IN ACCORDANCE WITH THE INVENTION).		
<u>PRIOR TO BLEACHING</u>	Kappa number	11.1
	Viscosity, dm ³ /kg	884
<u>O-STAGE</u>	Dry substance content, %	10
	Temperature, °C	70
	Time, minutes	60

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Table S (continued)

BLEACHING REPORT Q(OP)(ZQ)(PO)				
Q(OP)(ZQ)(PO)-bleaching of oxygen-delignified softwood pulp from cook No. ITC 1666 (IN ACCORDANCE WITH THE INVENTION).				
	H ₂ SO ₄ added, kg/BDMT	2		
	EDTA added, kg/BDMT	2		
	Final pH	4.9		
	Mg/Mn/Ca, ppm	249/0.6/131		
	Cu/Fe, ppm	2.5/2		
(OP)-STAGE	Dry substance content, %	10		
	Temperature, °C	100		
	Time, minutes	60		
	Initial pressure, bar (overpressure)	5		
	MgSO ₄ added, kg/BDMT	3		
	H ₂ O ₂ added, kg/BDMT	4		
	NaOH added, kg/BDMT	18		
	H ₂ O ₂ consumption, kg/BDMT	3.4		
	Final pH	11.0		
	Kappa number	6.2		
	Viscosity, dm ³ /kg	844		
(ZQ)-STAGE	Dry substance content, %	10		
	Temperature, °C	50/50*		
	Time, minutes	20s+45*		
	O ₃ added, kg/BDMT	3		
	H ₂ SO ₄ added, kg/BDMT	5.5		
	NaOH added, kg/BDMT	3*		
	EDTA added, kg/BDMT	2*		
	Final pH	3.2/4.9*		
	Kappa number	2.8		
	Viscosity, dm ³ /kg	739		
(PO)-STAGE	Dry substance content, %	10	10	10
	Temperature, °C	105	105	105
	Time, minutes	120	120	120
	Initial pressure, bar (overpressure)	5	5	5
	MgSO ₄ added, kg/BDMT	3	3	3
	DTPA added, kg/BDMT	2	2	2
	H ₂ O ₂ added, kg/BDMT	15	25	35
	NaOH added, kg/BDMT	19	23	26
	H ₂ O ₂ consumption, kg/BDMT	9.0	14.3	23.3
	Final pH	10.5	10.6	10.7
	Kappa number	1.2	1.1	0.9
	Viscosity, dm ³ /kg	691	674	644
	Brightness, % ISO	86.9	88.6	90.0

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Table S (continued)

BLEACHING REPORT Q(OP)(ZQ)(PO)				
Q(OP)(ZQ)(PO)-bleaching of oxygen-delignified softwood pulp from cook No. ITC 1666 (IN ACCORDANCE WITH THE INVENTION).				
	Brightness reversion, % ISO	85.0	86.5	88.1
	Peroxide added, kg/ADMT	18	27	36
	Peroxide consumption, kg/ADMT	12	16	25

Table 6

PULP PROPERTIES - UNBLEACHED PULP AFTER COOKING				
PULP TYPE	IN ACCORDANCE WITH THE STATE OF THE ART		IN ACCORDANCE WITH THE INVENTION	
Pulp No.	ITC 1544	ITC 1618	ITC 1666	ITC 1668
Kappa number	23.8	25.1	22.8	23.8
Viscosity, dm ³ /kg	1326	940	1018	1022
Weighted mean fibre length, mm	2.37	2.36	2.49	2.52
Fibre strength - zero span, Nm/g	149	137	145	148
<u>Interpolated pulp properties at a tensile index of 80 kNm/kg:</u>				
PFI beater, revolutions	900	1100	1400	1600
Schopper-Riegler number, °SR	15.5	16.5	16.5	17.0
Density, kg/m ²	630	640	620	620
Air resistance, sec/100 ml	3.0	4.0	3.0	4.0
Burst index, MN/kg	6.0	5.3	5.6	5.7
Tear index, Nm ² /kg	19.5	17.4	20.2	19.2

Table 7

PULP PROPERTIES - OXYGEN-DELIGNIFIED SOFTWOOD PULP PRODUCED BY THE PROCESS ACCORDING TO THE INVENTION, AFTER ECF BLEACHING AND AFTER TCF BLEACHING		
BLEACHING SEQUENCE	(DQ)(PO)	Q(OP)(ZQ)(PO)
Bleaching experiment No.	B-3158	B-3159
Kappa number	0.9	---
Viscosity, dm ³ /kg	721	661
Brightness, % ISO	89.1	88.9
Weighted mean fibre length, mm	2.16	2.22
Fibre strength - zero span, Nm/g	112	105
<u>Interpolated pulp properties at a tensile index of 80 kNm/kg:</u>		
PFI beater, revolutions	1300	1400

Table 7 (continued)

PULP PROPERTIES - OXYGEN-DELIGNIFIED SOFTWOOD PULP PRODUCED BY THE PROCESS ACCORDING TO THE INVENTION, AFTER ECF BLEACHING AND AFTER TCF BLEACHING		
BLEACHING SEQUENCE	(DQ)(PO)	Q(OP)(ZQ)(PO)
Schopper-Riegler number, °SR	17.5	19.5
Density, kg/m ²	660	660
Air resistance, sec/100 ml	4.0	4.6
Burst index, MN/kg	6.2	6.4
Tear index, Nm ² /kg	17.4	16.5

Claims

- Continuous sulphur-free process for producing chemical pulp from comminuted cellulose-containing fibre material, comprising at least one impregnation stage followed by at least one cooking stage with at least one concurrent cooking zone and at least one countercurrent cooking zone and, as the conclusion to the cooking stage, at least one extended displacement zone, with a delignification-accelerating compound being supplied to at least one of the said stages, wherein a first cooking liquid, which has been extracted from a position downstream of the impregnation stage, is supplied to the said impregnation stage, with the said first cooking liquid essentially containing OH⁻ ions as the active substance, **characterized in that**, the concentration of OH⁻ ions in the said concurrent cooking zone is at least 20% higher than in the said impregnation stage, preferably at least 50% higher and **in that** the quantity of delignification-accelerating compound which is added to the impregnation stage is less than 50% by weight of the total amount added of said delignification-accelerating compound.
- Process according to Patent Claim 1, **characterized in that** the temperature in the impregnation stage is within the interval 80-140°C, preferably between 100 and 130°C and most preferably between 120 and 127°C, and **in that** the temperature in the subsequent cooking stage, when cooking softwood is within the interval 150-170°C, preferably between 158 and 163°C, and **in that** the temperature in the said cooking stage, when cooking hardwood is within the interval 140-165°C, preferably between 155 and 158°C.
- Process according to Patent Claim 1 or 2, **characterized in that** a metal-complexing agent is supplied to the said impregnation stage or to another stage upstream of the said cooking stage.
- Process according to any one of the preceding patent claims, **characterized in that** a second cooking liquid, having a lower concentration of OH⁻ ions than is present in the first cooking liquid, is supplied to the said extended displacement zone.
- Process according to any one of the preceding patent claims, **characterized in that** the major part of the said delignification-accelerating compound is added to the said concurrent cooking zone.
- Process according to any one of the preceding patent claims, **characterized in that** the total quantity of the said delignification-accelerating compound added exceeds 1 kg per tonne of bone dry wood, preferably exceeds 1.5 kg per tonne of bone dry wood, and is most preferably between 1.8 and 2.5 kg per tonne of bone dry wood.
- Process according to any one of the preceding patent claims, **characterized in that** the quantity of delignification-accelerating compound which is added to the said impregnation stage is less than 30% by weight of the total quantity added, preferably less than 10% by weight of the total quantity of the said delignification-accelerating compound added.
- Process according to any one of the preceding patent claims, **characterized in that** the total quantity of delignification-accelerating compound which is added exceeds 0.5% by weight, preferably exceeds 1% by weight, and is most preferably between 1.1 and 1.5% by weight, of the total quantity of effective alkali (EA), calculated as NaOH, which is added.
- Process according to any one of the preceding patent claims, **characterized in that** the concentration of OH⁻ ions

at the beginning of the said concurrent cooking zone exceeds 0.5 mol/l, preferably exceeds 0.7 mol/l, and most preferably exceeds 1.0 mol/l.

- 5 10. Process according to any one of the preceding patent claims, **characterized in that** a further addition of OH⁻ ions is made to the said first cooking liquid before it is supplied to the said impregnation stage.
11. Process according to any one of the preceding patent claims, **characterized in that** the cooking is carried out isothermally in at least two adjacent zones in the said cooking stage.
- 10 12. Process according to any one of the preceding patent claims, **characterized in that** an excess of the said first cooking liquid which has been extracted from a position downstream of the impregnation stage, and a metal complex-containing extraction liquid which has been extracted from the impregnation stage, are conveyed to evaporation.
- 15 13. Process according to any one of the preceding patent claims, **characterized in that** the kappa number after the cooking stage is between 15 and 30, and preferably between 18 and 25, when cooking softwood pulp which is intended for bleaching.
- 20 14. Process according to any one of the preceding patent claims, **characterized in that** the kappa number after the cooking stage is between 9 and 25, and preferably between 12 and 18, when cooking hardwood pulp which is intended for bleaching.
- 25 15. Process according to any one of the preceding patent claims, **characterized in that** the kappa number after the cooking stage is between 40 and 85, when cooking high-yield pulp which is not to be bleached.
- 30 16. Process according to any one of the preceding patent claims, **characterized in that** pulp which is intended for ECF bleaching is bleached, after the cooking stage and most preferably after an intervening oxygen-delignification stage, to a brightness exceeding 80% ISO, preferably exceeding 85% ISO, and most preferably exceeding 88% ISO.
- 35 17. Process according to Patent Claim 16, **characterized in that** the said ECF bleaching comprises the bleaching stages (DQ)(PO).
- 40 18. Process according to any one of the preceding patent claims, **characterized in that** pulp which is intended for TCF bleaching is bleached, after the cooking stage and most preferably after an intervening oxygen-delignification stage, to a brightness exceeding 80% ISO, preferably exceeding 85% ISO, and most preferably exceeding 88% ISO.
- 45 19. Process according to Patent Claim 18, **characterized in that** the said TCF bleaching comprises the bleaching stages (Q)(OP)(ZQ)(PO).
- 50 20. Process according to any one of the preceding patent claims, **characterized in that** the said delignification-accelerating compound comprises unsubstituted or substituted quinones or hydroquinones, or salts of these compounds.
21. Process according to any one of the preceding patent claims, **characterized in that** the said delignification-accelerating compound comprises anthraquinones, benzoquinones or naphthoquinones, or salts of these compounds.
22. Process according to any one of the preceding patent claims, **characterized in that** the said delignification-accelerating compound comprises 1,4-dihydro-9,10-dihydroxyanthracene.

Patentansprüche

1. Kontinuierliches schwefelfreies Verfahren zur Herstellung von Zellstoff aus zerkleinertem cellulosehaltigem Fasermaterial mit mindestens einer Tränkstufe gefolgt von mindestens einer Kochstufe mit mindestens einer Gleichstromkochzone und mindestens einer Gegenstromkochzone und als Abschluß der Kochstufe mindestens einer

verlängerten Verdrängungszone, wobei mindestens einer der Stufen eine die Delignifizierung beschleunigende Verbindung zugeführt wird, bei dem eine erste Kochflüssigkeit, die von einer Stelle stromabwärts der Tränkstufe abgezogen worden ist, der Tränkstufe zugeführt wird, wobei die erste Kochflüssigkeit als Aktivsubstanz im wesentlichen OH⁻-Ionen enthält, **dadurch gekennzeichnet, daß** die Konzentration an OH⁻-Ionen in der Gleichstromkochzone mindestens 20% höher und vorzugsweise mindestens 50% höher ist als in der Tränkstufe und die der Tränkstufe zugesetzte Menge an die Delignifizierung beschleunigender Verbindung weniger als 50 Gew.-% der zugesetzten Gesamtmenge der die Delignifizierung beschleunigenden Verbindung beträgt.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** die Temperatur in der Tränkstufe im Bereich von 80 bis 140°C, vorzugsweise zwischen 100 und 130°C und ganz besonders bevorzugt zwischen 120 und 127°C liegt und die Temperatur in der nachfolgenden Kochstufe beim Kochen von Nadelholz im Bereich von 150 bis 170°C und vorzugsweise zwischen 158 und 163°C und beim Kochen von Laubholz im Bereich von 140 bis 165°C und vorzugsweise zwischen 155 und 158°C liegt.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** man der Tränkstufe oder einer anderen Stufe stromaufwärts der Kochstufe einen Metallkomplexbildner zuführt.

4. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** man der verlängerten Verdrängungszone eine zweite Kochflüssigkeit mit einer niedrigeren Konzentration an OH⁻-Ionen als in der ersten Kochflüssigkeit zuführt.

5. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** man den größten Teil der die Delignifizierung beschleunigenden Verbindung der Gleichstromkochzone zuführt.

6. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die zugesetzte Gesamtmenge der die Delignifizierung beschleunigenden Verbindung über 1 kg pro Tonne absolut trockenes Holz, vorzugsweise über 1,5 kg pro Tonne absolut trockenes Holz und ganz besonders bevorzugt zwischen 1,8 und 2,5 kg pro Tonne absolut trockenes Holz liegt.

7. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die der Tränkstufe zugeführte Menge an die Delignifizierung beschleunigender Verbindung weniger als 30 Gew.-% der zugesetzten Gesamtmenge und vorzugsweise weniger als 10 Gew.-% der zugesetzten Gesamtmenge der die Delignifizierung beschleunigenden Verbindung beträgt.

8. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die zugesetzte Gesamtmenge an die Delignifizierung beschleunigender Verbindung über 0,5 Gew.-%, vorzugsweise über 1 Gew.-% und ganz besonders bevorzugt zwischen 1,1 und 1,5 Gew.-% der zugesetzten Gesamtmenge an effektivem Alkali (EA), berechnet als NaOH, liegt.

9. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die Konzentration an OH⁻-Ionen am Anfang der Gleichstromkochzone über 0,5 mol/l, vorzugsweise über 0,7 mol/l und ganz besonders bevorzugt über 1,0 mol/l liegt.

10. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** man der ersten Kochflüssigkeit vor der Zuführung zur Tränkstufe weitere OH⁻-Ionen zusetzt.

11. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** man das Kochen isothermisch in mindestens zwei benachbarten Zonen in der Kochstufe durchführt.

12. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** man einen Überschuß der ersten Kochflüssigkeit, die von einer Stelle stromabwärts der Tränkstufe abgezogen worden ist, und eine metallkomplexbaltige Extraktionsflüssigkeit, die aus der Tränkstufe ausgeschleust worden ist, der Verdampfung zuführt.

13. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die Kappazahl nach der Kochstufe zwischen 15 und 30 und vorzugsweise zwischen 18 und 25 liegt, wenn zum Bleichen vorgesehener Nadelholzhalbstoff gekocht wird.

14. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die Kappazahl nach der Kochstufe zwischen 9 und 25 und vorzugsweise zwischen 12 und 18 liegt, wenn zum Bleichen vorgesehener Laubholzhalbstoff gekocht wird.

15. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die Kappazahl nach der Kochstufe zwischen 40 und 85 liegt, wenn nicht zu bleichender Hochausbeutehalbstoff gekocht wird.

16. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** zur ECF-Bleiche vorgesehener Halbstoff nach der Kochstufe und ganz besonders bevorzugt nach einer zwischengeschalteten Sauerstoffdelignifizierungsstufe auf einen Weißgrad von mehr als 80% ISO, vorzugsweise mehr als 85% ISO und ganz besonders bevorzugt mehr als 88% ISO gebleicht wird.

17. Verfahren nach Anspruch 16, **dadurch gekennzeichnet, daß** die ECF-Bleiche die Bleichstufen (DQ)(PO) aufweist.

18. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** zur TCF-Bleiche vorgesehener Halbstoff nach der Kochstufe und ganz besonders bevorzugt nach einer zwischengeschalteten Sauerstoffdelignifizierungsstufe auf einen Weißgrad von mehr als 80% ISO, vorzugsweise mehr als 85% ISO und ganz besonders bevorzugt mehr als 88% ISO gebleicht wird.

19. Verfahren nach Anspruch 18, **dadurch gekennzeichnet, daß** die TCF-Bleiche die Bleichstufen (Q) (OP) (ZQ) (PO) aufweist.

20. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** es sich bei der die Delignifizierung beschleunigenden Verbindung um gegebenenfalls substituierte Chinone oder Hydrochinone oder Salze davon handelt.

21. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** es sich bei der die Delignifizierung beschleunigenden Verbindung um Anthrachinone, Benzochinone oder Naphthochinone oder Salze davon handelt.

22. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** es sich bei der die Delignifizierung beschleunigenden Verbindung um 1,4-Dihydro-9,10-dihydroxyanthracen handelt.

Revendications

1. Procédé sans soufre, continu, pour produire une pâte chimique à partir d'un matériau fibreux broyé contenant de la cellulose, comprenant au moins une étape d'imprégnation suivie d'au moins une étape de cuisson avec au moins une zone de cuisson concurrente et au moins une zone de cuisson à contre-courant et, à la fin de l'étape de cuisson, au moins une zone de déplacement prolongée, un composé accélérant la délignification étant introduit dans au moins une desdites étapes, dans lequel un premier liquide de cuisson, qui a été extrait en une position en aval de l'étape d'imprégnation, est introduit dans ladite étape d'imprégnation, ledit premier liquide de cuisson contenant essentiellement des ions OH⁻ comme substance active, **caractérisé en ce que** la concentration en ions OH⁻ dans ladite zone de cuisson concurrente est supérieure d'au moins 20% à ce qu'elle est dans ladite étape d'imprégnation, de préférence supérieure d'au moins 50%, et **en ce que** la quantité de composé accélérant la délignification qui est ajoutée dans l'étape d'imprégnation représente moins de 50% en poids de la quantité totale ajoutée dudit composé accélérant la délignification.

2. Procédé selon la revendication 1, **caractérisé en ce que** la température, dans l'étape d'imprégnation, est dans l'intervalle de 80-140°C, de préférence entre 100 et 130°C et tout particulièrement entre 120 et 127°C, et **en ce que** la température dans l'étape de cuisson suivante, lors de la cuisson de bois tendre, est dans l'intervalle de 150-170°C, de préférence entre 158 et 163°C, et **en ce que** la température dans ladite étape de cuisson, lors de la cuisson de bois dur, est dans l'intervalle de 140-165°C, de préférence entre 155 et 158°C.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce qu'**un agent complexant les métaux est introduit dans ladite étape d'imprégnation ou dans une autre étape en amont de ladite étape de cuisson.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**un second liquide de

cuisson, ayant une concentration en ions OH^- inférieure à celle présente dans le premier liquide de cuisson, est introduit dans ladite zone de déplacement prolongée.

- 5 5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la majeure partie dudit composé accélérant la délignification est ajoutée dans ladite zone de cuisson concurrente.
- 10 6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la quantité totale dudit composé accélérant la délignification ajoutée dépasse 1 kg par tonne de bois sec absolu, de préférence dépasse 1,5 kg par tonne de bois sec absolu, et est tout particulièrement comprise entre 1,8 et 2,5 kg par tonne de bois sec absolu.
- 15 7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la quantité de composé accélérant la délignification qui est ajoutée dans ladite étape d'imprégnation est inférieure à 30% en poids de la quantité totale ajoutée, de préférence inférieure à 10% en poids de la quantité totale dudit composé accélérant la délignification ajoutée.
- 20 8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la quantité totale de composé accélérant la délignification qui est ajoutée dépasse 0,5% en poids, de préférence dépasse 1% en poids, et est tout particulièrement comprise entre 1,1 et 1,5% en poids de la quantité totale d'alcali efficace (EA), calculée en NaOH, qui est ajoutée.
- 25 9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la concentration en ions OH^- au début de ladite zone de cuisson concurrente dépasse 0,5 mol/l, de préférence dépasse 0,7 mol/l et tout particulièrement dépasse 1,0 mol/l.
- 30 10. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'on fait une addition supplémentaire d'ions OH^- dans ledit premier liquide de cuisson avant de l'introduire dans ladite étape d'imprégnation.
- 35 11. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la cuisson est réalisée de façon isotherme dans au moins deux zones adjacentes de ladite étape de cuisson.
- 40 12. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'un** excès dudit premier liquide de cuisson qui a été extrait en une position en aval de l'étape d'imprégnation, et un liquide d'extraction contenant un complexe métallique qui a été extrait dans l'étape d'imprégnation, sont envoyés vers l'évaporation.
- 45 13. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'indice kappa après l'étape de cuisson est compris entre 15 et 30, et de préférence entre 18 et 25, lors de la cuisson d'une pâte de bois tendre destinée à être blanchie.
- 50 14. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'indice kappa après l'étape de cuisson est compris entre 9 et 25, et de préférence entre 12 et 18, lors de la cuisson d'une pâte de bois dur destinée à être blanchie.
- 55 15. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'indice kappa après l'étape de cuisson est compris entre 40 et 85, lors de la cuisson d'une pâte à fort rendement qui n'est pas destinée à être blanchie.
16. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la pâte qui est destinée à être blanchie par blanchiment sans chlore élémentaire (ECF) est blanchie, après l'étape de cuisson et tout particulièrement après une étape de délignification à l'oxygène intermédiaire, jusqu'à un degré de blancheur dépassant 80% ISO, de préférence dépassant 85% ISO et tout particulièrement dépassant 88% ISO.
17. Procédé selon la revendication 16, **caractérisé en ce que** ledit blanchiment ECF comprend les étapes de blanchiment (DQ)(PO).
18. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la pâte qui est destinée à être blanchie par blanchiment sans chlore total (TCF) est blanchie, après l'étape de cuisson et tout particulière-

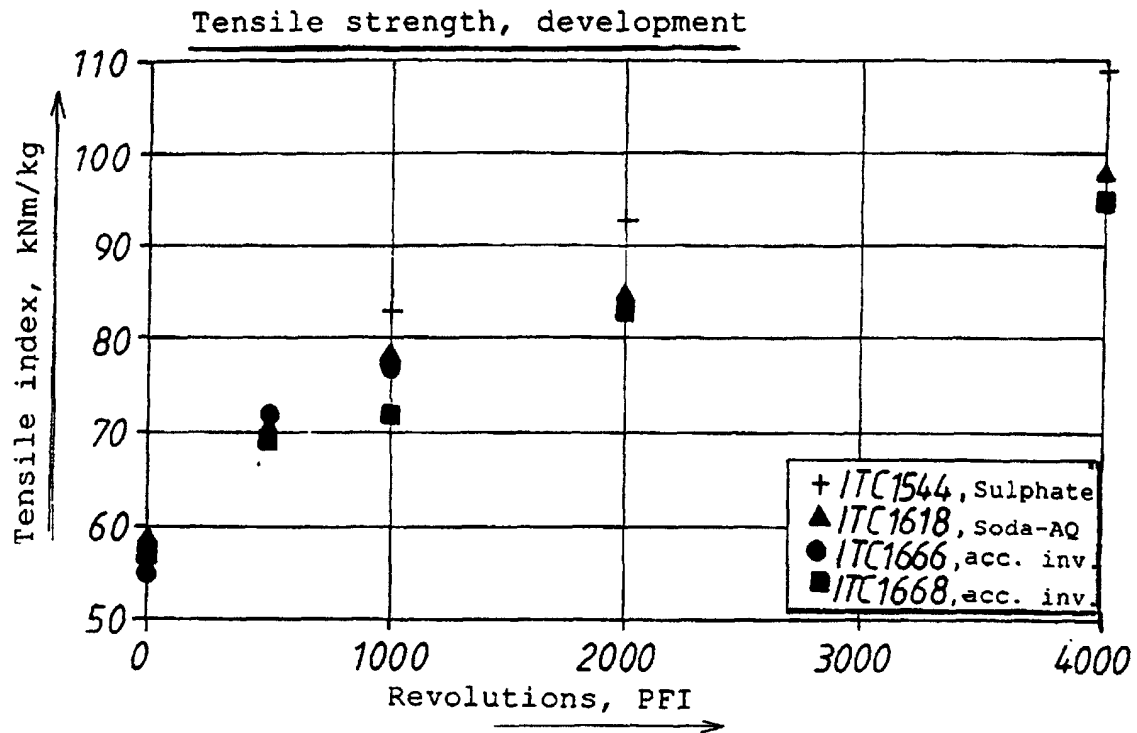
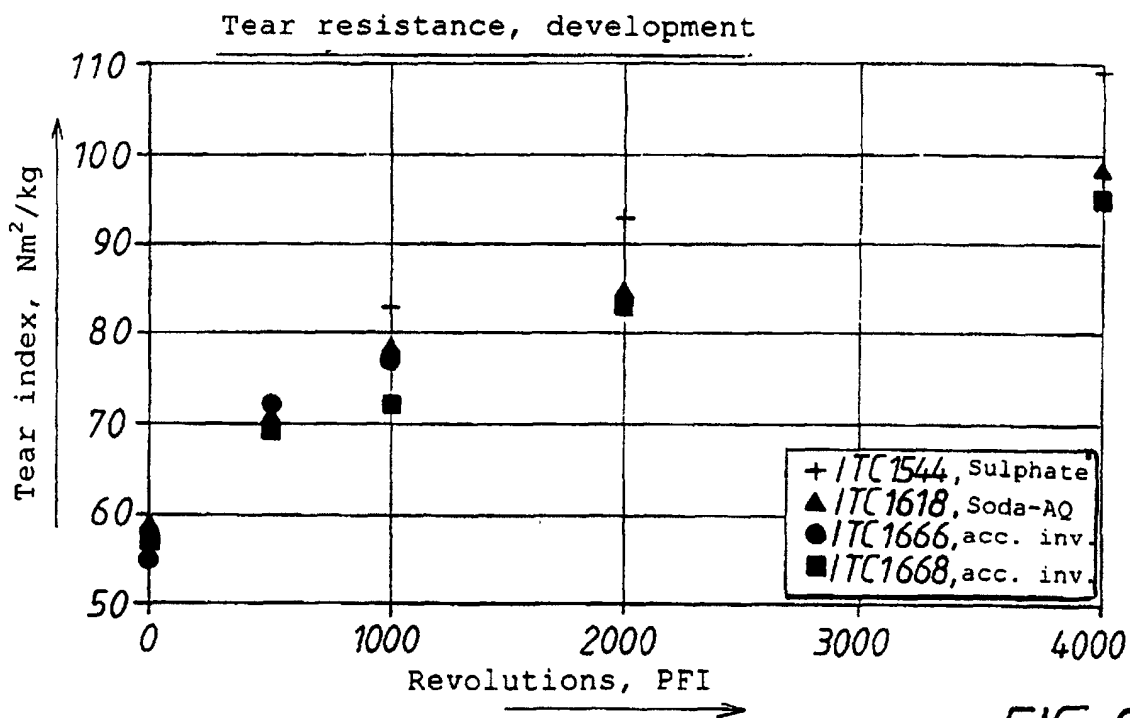
ment après une étape de délignification à l'oxygène intermédiaire, jusqu'à un degré de blancheur dépassant 80% ISO, de préférence dépassant 85% ISO et tout particulièrement dépassant 88% ISO.

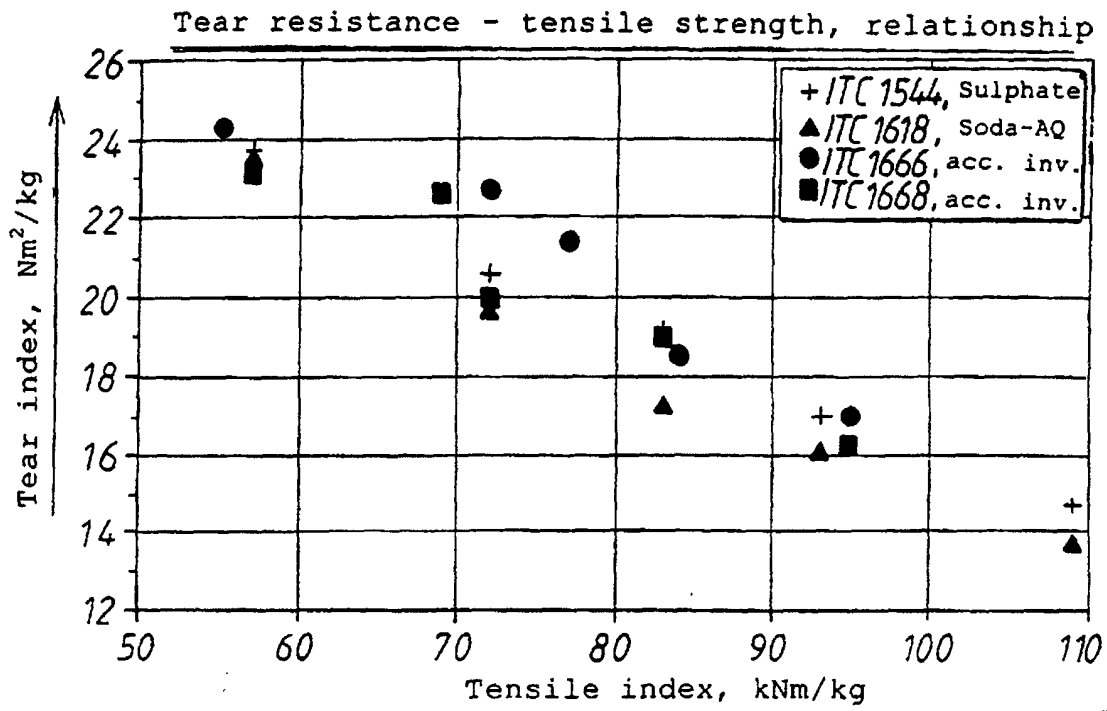
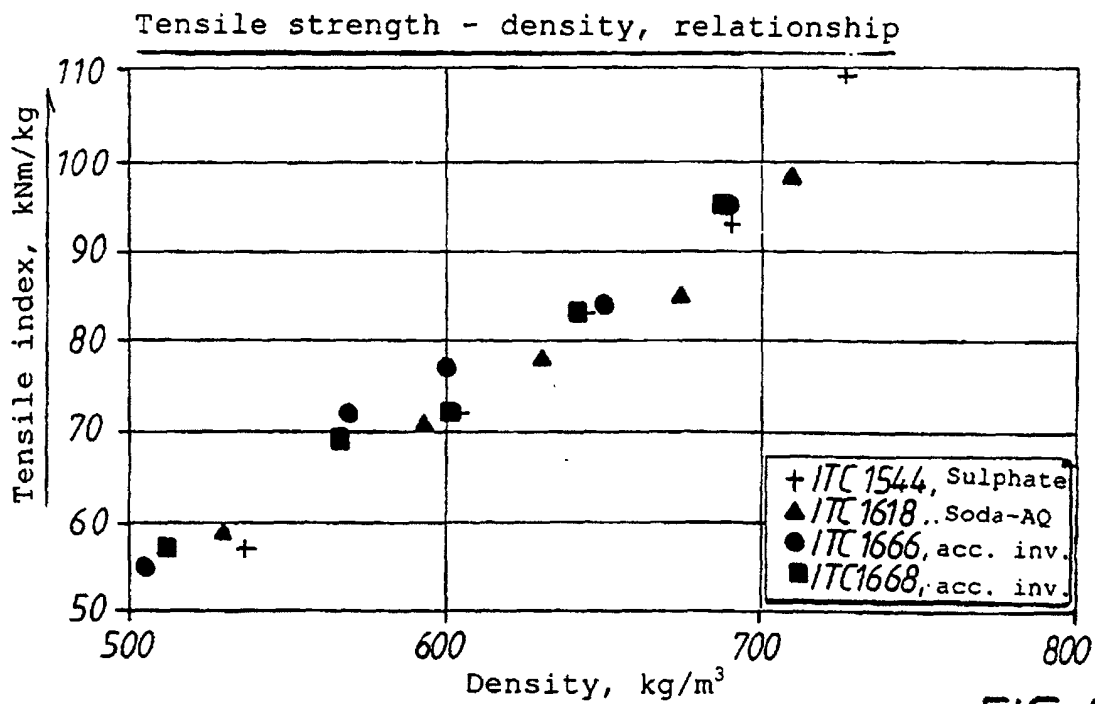
5 19. Procédé selon la revendication 18, **caractérisé en ce que** ledit blanchiment TCF comprend les étapes de blanchiment (Q)(OP)(ZQ)(PO).

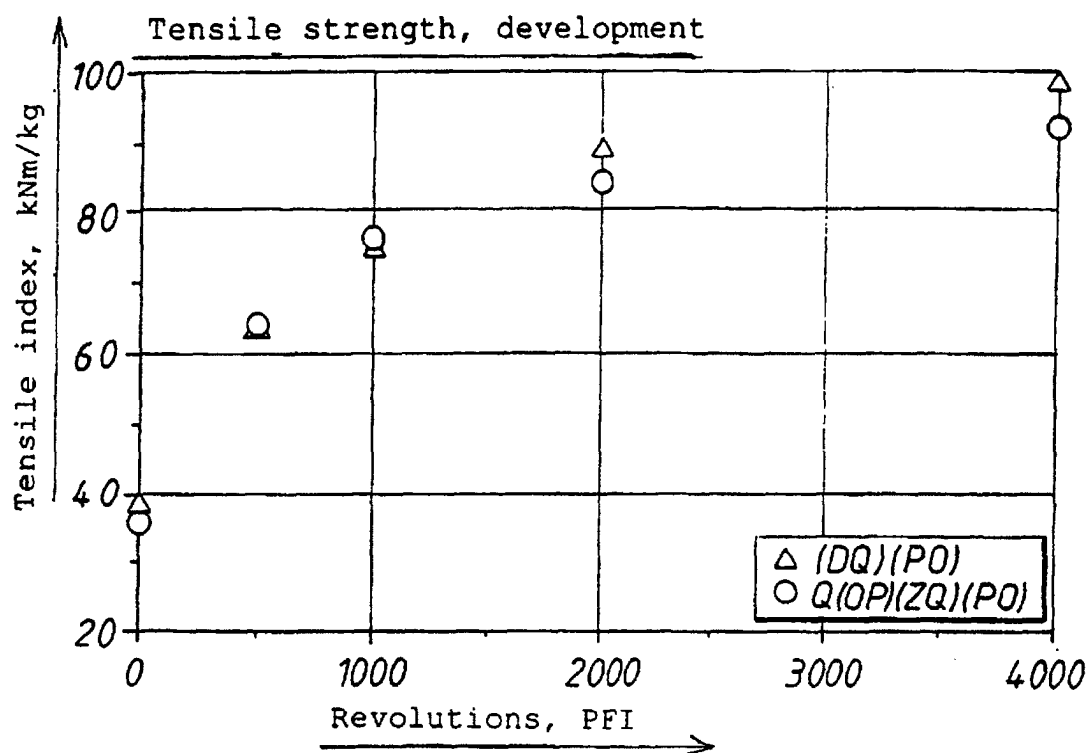
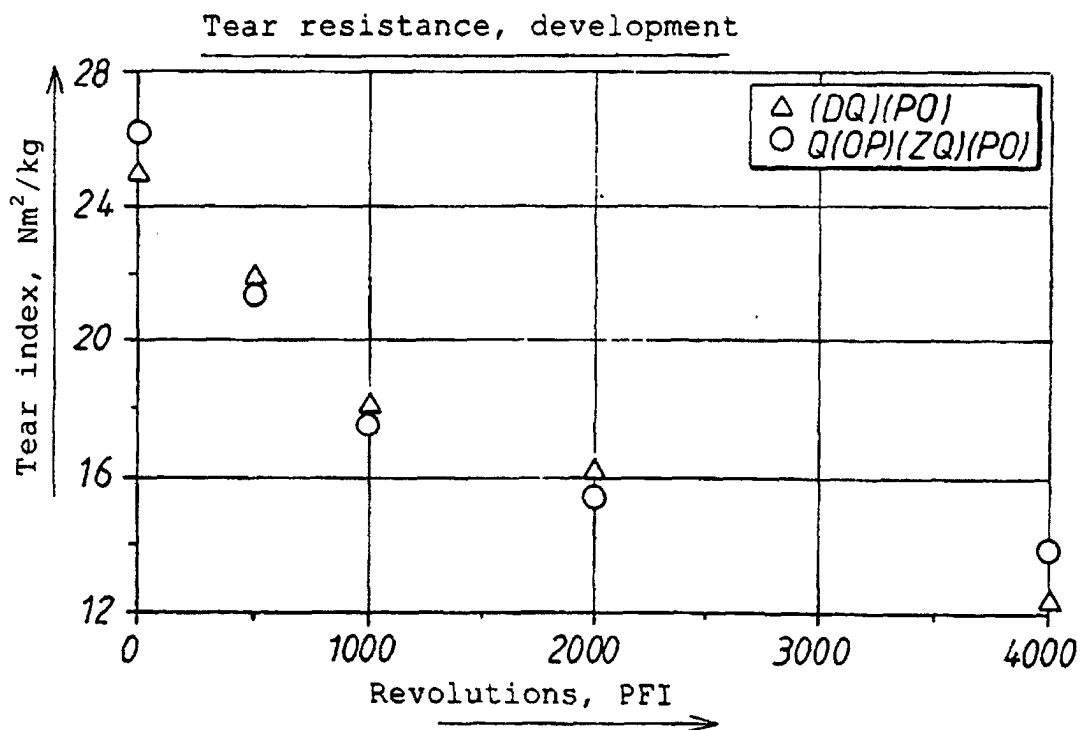
10 20. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit composé accélérant la délignification comprend des quinones ou hydroquinones non substituées ou substituées, ou des sels de ces composés.

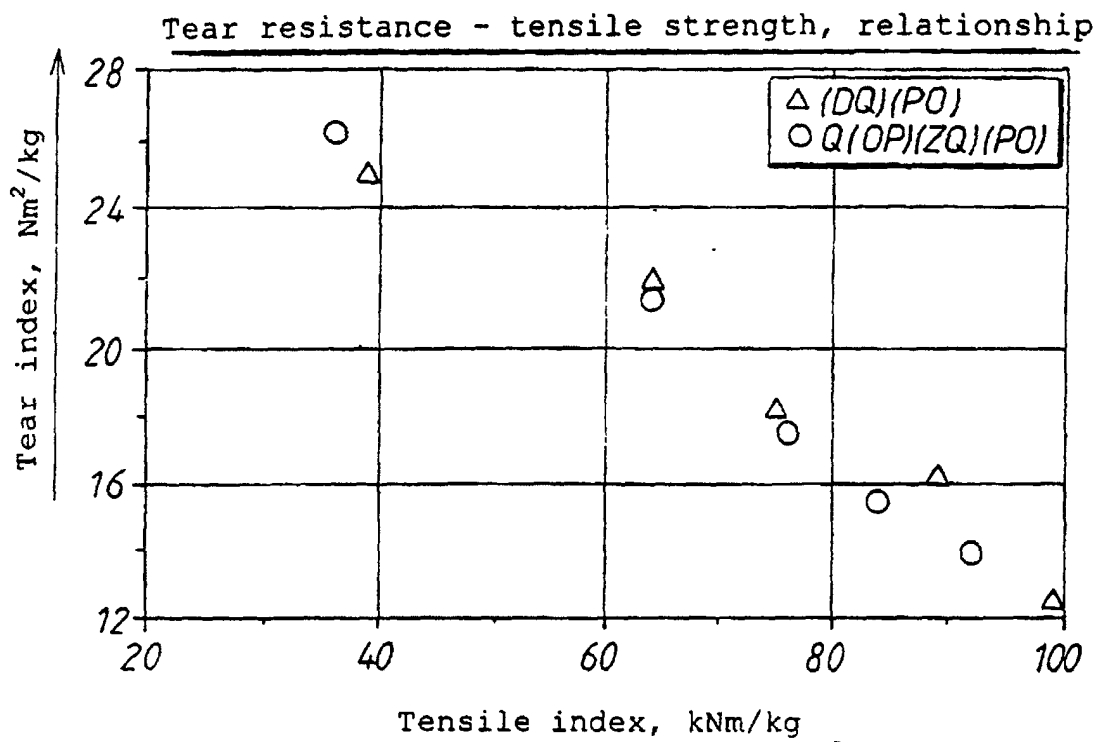
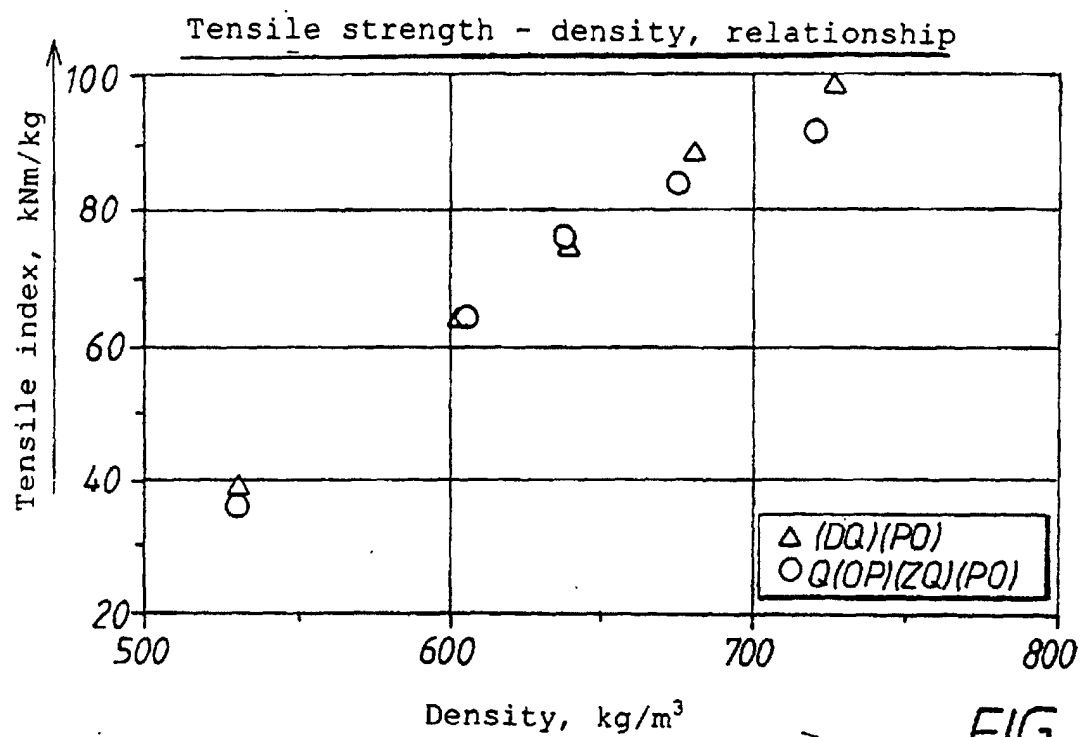
15 21. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit composé accélérant la délignification comprend des anthraquinones, des benzoquinones ou des naphthoquinones, ou des sels de ces composés.

20 22. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit composé accélérant la délignification comprend le 1,4-dihydro-9,10-dihydroxyanthracène.

FIG. 1FIG. 2

FIG. 3FIG. 4

FIG. 5FIG. 6

FIG. 7FIG. 8