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(54) Title: PROCEDURE FOR PREBLEACHING CHEMICAL CELLULOSE PULPS (57) Abstract Procedure for prebleaching cellulose pulp obtained by a chemical process. The cellulose pulp is treated with a phenol solution at elevated temperature, whereafter the cellulose pulp is, possibly after washing, bleached by single or multiple step bleaching known in itself in the art. For phenol solution is used an aqueous solution containing in addition acid catalyst, advantageously hydrochloric acid, 0.2-0.5 % of the water quantity. The treatment with phenol solution is carried out at a temperature between 98 and 102°C.		

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1 Procedure for prebleaching chemical cellulose pulps

5 The present invention relates to a procedure for prebleaching cellulose pulp that has been obtained by a chemical process.

Conventional prebleaching of cellulose pulps comprises a treatment with gaseous chlorine. However, no one has been able to solve the recovery and sensible use of the chlorine compounds which are produced in the bleaching process, and therefore the chlorine has unavoidably been emitted as wastes into the environment. Thus evidently remarkable need exists to substitute for chlorine bleaching other methods which impose less stress on the environment. The known replacing methods include oxygen bleaching, which presents the drawback of high oxygen consumption, and nitrogen bleaching, which is hampered by the fact that nitrogen compounds are emitted into the environment.

20 In the present invention it has been unexpectedly found that the chlorine treatment, as the first step in the bleaching process for chemical pulps, can be replaced with a phenol treatment. The phenol treatment affords numerous advantages over the use of chlorine. Firstly, the phenol can be recovered and reused, whereby there will be no emission of bleaching residues detrimental to the environment. The procedure of the invention renders possible also recovery of the residual lignin that has been detached from the cellulose in the bleaching process, in addition to the phenol.

30 The use of phenol furthermore endows the cellulose pulp with useful extra properties. No one of these advantages can be gained when using conventional chlorine prebleaching.

35 The use of phenol in treating substances containing cellulose is not novel in itself. For instance, cellulose pulp has been made from wood by treating wood chips with a phenol solution containing

1 a strong acid, e.g. hydrochloric acid, acting as a catalyst. As
examples may be mentioned the DE Patents No. 2 229 673 and
326 705. However, said patents relate to solubilizing lignocellu-
lose, such as wood, not to cellulose bleaching. The use of phenol
5 in prebleaching cellulose manufactured by chemical methods is not
known in the art. In contrast, it has been found with the aid of
NMR examinations that when wood is treated with a mixture of phenol
and hydrochloric acid there occurs condensation between the native
lignin in the wood and phenol and, consequently, darkening of the
10 pulp; this suggests that phenol would not be suitable at all for
use as a cellulose-bleaching chemical.

The procedure of the invention is characterized in that said cellu-
lose pulp is treated with phenol at elevated temperature, whereafter
15 said cellulose pulp, possibly after washing, is bleached by single
or multiple-step bleaching known in itself in the art.

The other characteristic features of the procedure of the invention
are stated in claims 2-6.

20 In the procedure of the invention a phenol treatment is applied in
the prebleaching of chemical pulp. In this case pulp is concerned
which has already been defibrated and in which the residual lignin
that is present has changed under effect of the digesting chemicals
25 so that condensation with phenol no longer occurs. Therefore a
substantially lower catalyst content and lower temperature suffice
for detaching the lignin from the defibrated cellulose. In addition,
the digesting process proper, a sulphate process for instance, may
be discontinued earlier than conventionally usual without detriment
30 to the quality characteristics of the ultimate pulp, and hereby
the digesting capacity can be substantially increased.

It is a further advantage of the prebleaching procedure of the
invention that phenol also dissolves extractible substances con-
35 tained in the cellulose pulp. This is of significance particularly
regarding the quality of hardwood cellulose because extractible

1 substances cause yellow discolouration of the cellulose and impairment of the absorptivity, which is important in view of the fluff pulp, and quality impairment of the soluble cellulose.

5 The procedure of the invention may be applied in prebleaching chemical cellulose pulps. Chemical pulps are here understood to be those pulps which have been obtained by chemical digestion methods. These methods include e.g. the sulphate process, various sulphite processes, and the soda process.

10 In practice, prebleaching as taught by the invention is simply carried out in that the chemical cellulose pulp from the digesting process is treated with a phenol solution a sufficiently long time and at high enough temperature, whereafter the pulp is conducted,
15 after removal of the treatment liquid, to further bleaching steps.

The phenol content in the aqueous solution may vary so that the water/phenol proportion is in the range from 3:7 to 1:1. The phenol solution preferably also contains a small quantity of an acid,
20 advantageously hydrochloric acid, of which the quantity may vary in the range of 0.1-1.0%, preferably 0.2-0.5%, referred to the water quantity in the solution. Excessive acid quantity causes hydrolysis of the cellulose and hemicelluloses.

25 The treatment temperature is not critical from the viewpoint of the invention, but since phenol forms an azeotrope with water, with boiling point about 100°C, it is advantageous to perform the treatment at this temperature. The appropriate treatment temperature is thus e.g. 98-102°C. The treatment time naturally depends on the
30 chemical concentrations and temperatures employed, but it is normally enough if the temperature is raised to treatment temperature within 30-60 min., and the treatment time at normal temperature may vary from 1 to 60 min.

35 According to an advantageous embodiment of the invention, the phenol treatment solution is removed from the cellulose pulp after

1 its temperature has been raised to treatment temperature, and it
is replaced with fresh solution. The prebleaching will then be
enhanced because a greater amount of lignin can be removed without
substantially affecting the viscosity characteristics.

5 The procedure of the invention is applicable both in the case of
hardwood and softwood celluloses. Especially in the case of hardwood
cellulose, the procedure of the invention has turned out to be
advantageous because it eliminates the problems which extractible
10 substances cause regarding the cellulose quality.

Subsequent to treatment, the cellulose is washed in standard manner
to be free of phenol compounds, these being returned to the begin-
ning of the process for reuse. The cellulose is further conducted,
15 possibly after washing, to further bleaching steps, which thus
need not be any chlorine or hypochlorite bleaching processes: they
may consist for instance of chlorine dioxide or peroxide bleaching
processes. The washing is advantageously done with water containing
phenol and with hot water.

20 The invention is described more closely in the following with the
aid of examples.

Example 1

25 Unbleached birch cellulose with characteristics as presented in
Table I was treated with phenol under the following conditions:

30	Cellulose:liquid	1:8
	Water:phenol	3:7
	HCl in the water (%)	0.2
	Treatment temperature (°C)	98-100
	Raised to treatment temperature in min.	45
35	Treatment time (min.)	10

In Table I is shown a comparison between the characteristics of

1 the cellulose before and after the phenol treatment mentioned above.

Table 1

5		Initial cellulose	Treated cellulose
	Chlorine number (KCl)	4.57	2.46
	Viscosity (SCAN), dm^3/kg	1190	1180
	DKM extract (%)	0.46	0.03
10	Ash content (%)	0.90	0.55
	Yield (%)		94.9
	Yield from wood (%)	52.8	50.1
	Lignin removed in prebleaching (%)	-	46.6
15	Fibre length, average (mm)	0.93	0.86

Table I reveals, among other things, that the viscosity of the cellulose is almost unchanged, implying that the low-molecular hemicellulose has not been dissolved and no cellulose chains have
20 been cleaved. The average fibre length is unchanged, indicating that acid hydrolysis has not cleaved any fibres.

Example 2

25 Example 1 was repeated, but the hydrochloric acid content was increased to 1.0%. The quantity of removed lignin rose then to 79%, but the viscosity went down to 480, indicating that there has been substantial cleaving of carbohydrates.

30 Example 3

Example 1 was repeated, changing the water:phenol proportion to be 1:1. Only 32% of the lignin could then be removed from the pulp. This indicates that a greater amount of water impairs the solu-
35 bilization of lignin and the efficiency of the prebleaching. The viscosity of the cellulose retained the value 1330.

1 Example 4

Example 1 was repeated with the modification that the acid content was 0.12% of the water quantity. A cellulose product was then
 5 obtained which has chlorine number 3.27, viscosity 1330. The lignin quantity removed was only 29%.

Example 5

10 Unbleached birch sulphate cellulose having the characteristics shown in Table II was treated with phenol under the following conditions:

	Cellulose:liquid	1:12
15	Water:phenol	3:7
	HCl in the water (%)	0.2
	Treatment temperature (°C)	98-100
	Raised to treatment temperature in min.	45
	Treatment time (min.)	60

20

After the treatment, the characteristics of the cellulose were compared with those of the initial cellulose. The results are presented in Table II.

25

Table II

	Initial cellulose	Treated cellulose
30		
	Chlorine number (KCl)	5.23
	Viscosity (SCAN), dm ³ /kg	1340
	DKM extract (%)	0.41
	Yield (%)	96.6
	Yield from the wood (%)	53.2
35	Lignin removed in prebleaching (%)	-
	Fibre length, average (mm)	0.92

1 Example 6

Example 5 was repeated, replacing the treatment solution with
fresh solvent after the temperature had been raised to treatment
5 temperature. When the treatment time was 30 min., the chlorine
number was 2.46 and viscosity 1030, and removed lignin quantity 52%.
When the same experiment was repeated with treatment time 60 min.,
the chlorine number 1.85 and viscosity 910 were obtained, and
removed lignin quantity 65%. The results indicate that it is advan-
10 tageous to replace the treatment solution.

Example 7

Pine sulphate cellulose with characteristics as shown in Table III
15 was treated with phenol solution under the following conditions:

Cellulose:liquid	1:10
Water:phenol	3:7
HCl in the water (%)	0.16
20 Treatment temperature (°C)	98-100
Raised to treatment temperature in min.	45

After treatment, the characteristics of the cellulose were compared
with those of the initial cellulose. The results are presented in
25 Table III.

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35

1

Table III

	Initial cellulose	Treated cellulose
5		
Chlorine number (KCl)	6.2	4.50
Viscosity (SCAN), dm ³ /kg	1070	850
Yield (%)		97.8
Yield from the wood (%)	46.5	45.5
10 Lignin removed in prebleaching (%)	-	24.5
Fibre length, average (mm)	1.94	1.97

15 The example indicates that the procedure of the invention is also appropriate to be used in prebleaching softwood cellulose.

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1 Claims

1. A procedure for prebleaching cellulose pulp obtained by a chemical process, characterized in that said cellulose pulp is
5 treated with a phenol solution at elevated temperature, whereafter said cellulose pulp is, possibly after washing, bleached by single or multiple step bleaching known in itself in the art.
2. Procedure according to claim 1, characterized in that for phenol
10 solution is used an aqueous solution containing in addition acid catalyst, advantageously hydrochloric acid, 0.2-0.5% of the water quantity.
3. Procedure according to claim 1 or 2, characterized in that the
15 treatment with phenol solution is carried out at temperature 98-102°C.
4. Procedure according to any one of the preceding claims, characterized in that the phenol solution is replaced with fresh phenol
20 solution after its temperature has been raised to the treatment temperature.
5. Procedure according to any one of the preceding claims, characterized in that the washing is performed with an aqueous solution
25 containing phenol and with hot water.
6. Procedure according to any one of the preceding claims, characterized in that for cellulose is used cellulose digested by the
30 sulphate or sulphite or soda process.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI87/00071

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
D 21 C 9/10		4
II. FIELDS SEARCHED		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC 4 US C1	D 21 C 9/10, /12 <u>162:77</u>	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
SE, NO, DK, FI classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, 11 with Indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
X	FI, B, 69 131 (NESTE OY) 30 August 1985	1-6
X	US, A, 1 705 424 (OTTO C. STRECKER) 12 March 1929	1-6
A	SE, C, 103 962 (DYNAMIT-ACTIENGESSELLSCHAFT) 10 March 1942	
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
1987-07-15		1987-07-22
International Searching Authority		Signature of Authorized Officer
Swedish Patent Office		Bo Bergström