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(54) **HEAT TREATMENT OF POLYSULPHIDE CONTAINING WHITE LIQUORS**

WÄRMEBEHANDLUNG VON POLYSULFID ENTHALTENDEN WEISSLAUGEN

PATE A PAPIER KRAFT AMELIOREE PRODUITE AU MOYEN DU TRAITEMENT THERMIQUE DE
LIQUEURS DE POLYSULFURE PRODUITES PAR OXYDATION

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(56) References cited:
WO-A-97/42372 **US-A- 4 024 229**
US-A- 5 082 526

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INSTITUTE OF PAPER SCIENCE AND
TECHNOLOGY, ATLANTA, GA, US; DATABASE
ACCESSION NUMBER AB4701536, RINGLEY, M.
B: "LABORATORY POLYSULFIDE COOKING OF
LOBLOLLY PINE" retrieved from DIALOG
XP002219846 & SOUTHERN PULP PAPER MFR.
39, NO. 1: 24-26, 28, 30-31 (JAN. 1976).,

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Description

TECHNICAL FIELD

[0001] The present invention relates to an improvement in any process which generates polysulphide by the oxidation of white liquor ; the invention also relates to a method of increasing the yield of pulp in Kraft pulping with an oxidized white liquor.

BACKGROUND ART

[0002] In Kraft pulping operations, where the goal is to remove lignin while retaining carbohydrates, yield is increased by minimizing carbohydrate (i.e., cellulose and hemicellulose) degradation. This degradation occurs through the "peeling" reaction in which sugar units are sequentially removed from the reducing end group of the polysaccharide chains. One way to prevent this reaction is to convert aldehyde groups on the wood polysaccharides to a form which is relatively inert to further "peeling". This conversion is achieved by either oxidizing the aldehyde to its corresponding carboxylic acid (Alfredsson, B., Samuelson, O. and Sandstig, B. Carboxyl end groups in sulfate and polysulphide pulps. *Svensk Papperstidn.* 66(18):703 (1963).), (Holton, H. H. Delignification of lignocellulosic material with an alkaline liquor in the presence of a cyclic keto compound. US patent No. 4,012,280, C.I.L. (1977).), or, alternatively, reducing it to its alcohol form (Hartler, N. Sulphate cooking with the addition of reducing agents. Part 1. Preliminary report on the addition of sodium borohydride. *Svensk Papperstidn.* 62(13):467 (1959).), (Pettersson, S. E. and Rydholm, S. A. Hemicelluloses and paper properties of birch pulps. Part 3. *Svensk Papperstidn.* 64(1):4 (1961).). The two methods that are applied in the pulp and paper industry involve the oxidation process and use anthraquinone (Holton, H. H. Delignification of lignocellulosic material with an alkaline liquor in the presence of a cyclic keto compound. US patent No. 4,012,280, C.I.L. (1977).), or polysulphide (Clayton, D. W. and Sakai, A. Multi-stage polysulphide pulping processes. Part I. Basic ideas and low-temperature impregnation studies on black spruce heartwood. *Pulp Pap. Mag. Can.* 68(12):619 (1967).), (Landmark, P. A., Kleppe, P. J. and Johnsen, K. Cooking liquor oxidation and improved cooking technique in polysulphide pulping. *Tappi J.* 48(5):56 (1965).), (Sanyer, N. and Laundrie, J. F. Factors affecting yield increase and fiber quality in polysulphide pulping of loblolly pine, other softwoods, and red oak. *Tappi J.* 47(10):640 (1964).), (Teder, A. Some aspects of the chemistry of polysulphide pulping. *Svensk Papperstidn.* 72(9):294 (1969).), or both as oxidizing agents. Anthraquinone is a catalytic additive while polysulphide is generated from white liquor by oxidation of sodium sulfide in one of several processes (Dorris, G. M. Process of producing Kraft pulping liquor by the oxidation of white liquor in the presence of lime mud. US patent No. 5,082,526, Paprican (1992)), (Smith, G. C. and Sanders, F. W. Production of polysulphide with PTFE coated catalyst. US patent No. 4,024,229 (1977).).

[0003] WO-A-97/42372 discloses a method for making an oxidised white liquor containing polysulfide.

[0004] Polysulfide cooking is described in an Article by M.B. Ringley "Laboratory polysulfide cooking of Loololly Pine", Southern Pulp Paper MRT. 39, no.1, pages 24-26,28,30,31; Jan 1976.

[0005] Accordingly the present invention seems to improve the process which generates polysulphide by the oxidation of white liquor, and increase the yield of pulp in kraft pulping with a white liquor.

[0006] In particular the present invention seeks to increase the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of polysulphide liquors generated by the oxidation of white liquor without substantial loss of polysulphide charge.

[0007] The present invention also seeks to increase the yield of pulp from wood particles by cooking the wood particles in a polysulphide liquor having a high concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio, generated by the oxidation of white liquor.

[0008] Still further, the invention seeks to increase the content of active polysulphide in a polysulphide liquor generated by the oxidation of white liquor.

[0009] The present invention also seeks to increase the yield of pulp from wood particles by cooking wood particles in a polysulphide liquor generated by the oxidation of white liquors and which have been thermally treated.

DISCLOSURE OF THE INVENTION

[0010] In accordance with one aspect of the invention, there is provided a method which comprises exposing an oxidized white liquor to a temperature effective to increase the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of polysulphide in the oxidized white liquor, in which the liquor is exposed to a temperature of 20°C to 95°C for a time of 1 to 72 hours.

[0011] In accordance with yet another aspect of the invention, there is provided a method of producing an oxidized white liquor containing polysulphide comprising: oxidizing a white liquor to produce an oxidized white liquor containing polysulphide and having a first PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR}

or PS_{VIS}/PS_{GR} ratio, and heating or cooling if necessary and then storing said liquor at a temperature between 20°C and 95°C for a time of 1 to 72 hours, to produce an oxidized white liquor having a second PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio, wherein said second ratio is greater than said first ratio.

[0012] In accordance with still another aspect of the invention, there is provided a method of increasing the yield of pulp in Kraft pulping with a white liquor containing polysulphide comprising: oxidizing a white liquor to produce an oxidized white liquor containing polysulphide, ii) heating or cooling if necessary and then storing said oxidized white liquor at a temperature between 20°C and 95°C for a time of 1 to 72 hours and in a subsequent step: iii) delignifying pulp with the oxidized white liquor from step ii).

[0013] The invention relates to the heat treatment of a polysulphide liquor generated by the oxidation of white liquor. This heat treatment is at a temperature between 20°C and 95°C, and most preferably between 50 and 95°C, for a time of 1 to 72 hours, preferably 1 to 48 hours, more preferably 6 to 30 hours, even more preferably 12 to 24 hours.

[0014] In one preferred embodiment of the invention, there is provided a method which comprises exposing an oxidized white liquor produced by oxidation of white liquor in the presence of lime mud, or MnO_2 or both lime and MnO_2 to a temperature effective to increase the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of polysulphide in the oxidized white liquor. Preferably the temperature, in this latter preferred embodiment, is between 20°C and 95°C and the period of exposure is for a time of 1 to 72 hours; more preferably the temperature is between 50°C and 95°C, for an exposure time up to 48 hours.

[0015] In another preferred embodiment of the invention, there is provided a method of increasing the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of a polysulphide liquor generated by oxidation of white liquor in the presence of lime mud or MnO_2 or both lime mud and MnO_2 ; which method comprises heat treating the oxidized white liquor at a temperature between 50°C and 95°C for a time of 1 to 72 hours, and preferably up to 48 hours.

[0016] In still another preferred embodiment of the invention, there is provided a method of increasing the yield of pulp in Kraft pulping with a white liquor containing polysulphide comprising: i) oxidizing a white liquor in the presence of lime mud, MnO_2 or both lime mud and MnO_2 to produce an oxidized white liquor containing polysulphide, ii) heat treating the oxidized white liquor to increase the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of polysulphide in the oxidized white liquor, and storing the oxidized white liquor at a temperature between 20°C and 95°C for a time of 1 to 72 hours. and iii) cooking wood chips with the oxidized white liquor from step ii) to produce pulp.

BRIEF DESCRIPTION OF DRAWINGS

[0017]

FIG. 1 illustrates graphically the yield benefit in pulp delignification with increase in PS_{UV}/PS_{GR} ratio; FIG. 2 illustrates graphically the relationship between polysulphide decomposition and temperature; and FIGS. 3 and 4 show the relationship between pulp yield and permanganate number for polysulphide liquors of the invention at different temperatures; and conventional white liquors for different pulps.

DETAILED DESCRIPTION OF THE INVENTION

i) Oxidized White Liquor

[0018] The oxidized white liquor in this invention is one produced by oxidizing sodium sulphide in the white liquor to sodium polysulphide.

[0019] The invention is not confined to any particular oxidation procedure for producing the polysulphide or oxidized white liquor. The invention thus extends to oxidized white liquors in which the oxidation is carried out with oxygen or oxygen-containing gases such as air, in the presence of a catalyst, for example, wet-proofed activated carbon in the MOXY (trademark of The Mead Corporation) process; lime mud in the PAPRILOX (trademark of Pulp and Paper Research Institute of Canada) process, lime mud spiked with manganese dioxide; or with oxygen or oxygen containing gas in the presence of a metal oxide, such as oxides of manganese, iron, cobalt, zinc, aluminum, nickel or chromium, which metal oxide functions as a catalyst for polysulphide formation.

[0020] An especially preferred or advantageous oxidized white liquor for use in the invention is that produced by oxidation of a white liquor produced by causticizing green liquor and containing the lime mud generated in the causticization process.

[0021] Green liquor is produced from the smelt derived from black liquor in chemical recovery of a conventional Kraft liquor cycle. The green liquor comprises sodium carbonate and sodium sulphide and the causticization involves addition of lime, calcium oxide, to the green liquid. The lime reacts with the sodium carbonate to produce sodium hydroxide with

precipitation of insoluble calcium carbonate. The suspended solids comprising the calcium carbonate, unreacted calcium oxide and other insoluble solids present in the smelt, is referred to as lime mud.

[0022] This lime mud is thus a by-product of the white liquor formation.

[0023] The white liquor suspension containing lime mud, can be employed directly in the production of the oxidized white liquor, as outlined in U.S. Patent 5,082,526. Especially advantageously, a catalytic amount of manganese dioxide is added to the white liquor suspension to further enhance the oxidation. Suitable catalytic amounts of manganese dioxide comprise 0.1 to 2.0 g/l of a white liquor.

[0024] In such case, the resulting oxidized white liquor contains the lime mud and, where applicable, the added manganese dioxide catalyst, as suspended solids.

ii. Heat Treatment

[0025] The process of this invention for increasing the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of polysulphide liquors generated by the oxidation of white liquor is a process in which the polysulphide liquor is heat treated within a range of temperatures and times without substantial loss of polysulphide charge.

[0026] Increasing the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio increases the active polysulphide content in the liquor. The oxidized white liquor is separated from the oxidation catalysts such as lime mud and manganese oxide prior to the heat treatment.

[0027] In particularly advantageous embodiments, the liquors generated by the oxidation of white liquor in the presence of MnO_2 lime mud or both MnO_2 and lime mud are heat treated at a temperature below 95°C for a time up to 72 hours to increase the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio.

[0028] The temperature of the polysulphide liquor for the heat treatment can be adjusted using a heat exchanger. The temperature of the polysulphide liquor can also be adjusted by evaporative cooling with an oxygen-containing gas. Normal practice is to remove the heat generated by the reactions between sodium sulphide and oxygen, to prevent the oxidized liquor temperature from rising to or above the liquor boiling point (Uloth, V., Dorris, G., Thring, R., Hogikyan, R., Tench, L., and Ayton, J. Production of Polysulphide Liquor in a Kraft Mill's Causticizers. *Tappi J.* 80(10): 223 (1997). Tench, L., Uloth, V., Dorris, G., Hornsey, D., and Munro, F. Mill Scale Implementation of Paprican's Process for Polysulphide Liquor Production in Kraft Mill's Causticizers, Part 1: Batch Trials and Process Optimization. *Tappi J.* 82 (10): 120 (1999).). Storage may be provided by existing tankage provided both for liquor clarification and flow buffering or by new tankage. The target storage temperature and storage time can be optimized to ensure that the maximum charge of active polysulphide in the polysulphide liquor, is delivered to the pulp digester.

[0029] The heat treatment is preferably carried out by maintaining the oxidized liquor at a temperature of 50°C to 90°C for a time of 1 to 48 hours.

iii) Polysulphide PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio

[0030] Polysulphide can be generated from sodium sulphide in a white liquor by various methods including the direct addition of sulphur to the white liquor. However, this method cannot be used industrially without a bleed of sulphur from the Kraft recovery cycle, which is expensive to provide. Having different methods of polysulphide generation, however, allows comparisons of the form of the polysulphide that is generated by each of the different methods. These comparisons have shown that there are differences in what is measured as polysulphide when polysulphide liquor is generated by the direct addition of sulphur to the white liquor and when it is generated by the oxidation of white liquor.

[0031] Polysulphide can be measured in many ways but two of the most simple and effective are measurement by gravimetry (PS_{GR}) and by UV or VIS absorption (PS_{UV} or PS_{VIS}). The two methods can be used to give a PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio. Polysulphide generated by direct sulphur addition has a PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio very close to 1, but polysulphide generated by oxidation of white liquor has a ratio that varies depending on the way that it has been made.

[0032] The differences in the form of polysulphide in the white liquor change the degree to which the yield of pulp is increased by the application of a given polysulphide charge. Polysulphide liquors that have a PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of 1 deliver the full yield expected from the application of a given polysulphide charge in the Kraft pulping process. In such polysulphide liquors, the polysulphide content may thus be considered to be active polysulphide i.e. polysulphide which oxidizes aldehyde groups on wood polysaccharides to inhibit carbohydrate degradation during delignification of pulp.

[0033] Oxidized liquors that have lower ratios are found to deliver diminishing amounts of the expected yield (Figure 1).

[0034] The lower the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio, the lower is the content of active polysulphide in the polysulphide of the liquor, and conversely, the higher is the content of inactive polysulphide.

[0035] It is therefore desirable in industrial application that the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of the polysulphide liquor be as high as possible, or as close to 1 as possible.

[0036] The heat treatment of the invention does result in some loss in the total polysulphide content, determined as both active and inactive. The loss depends on the treatment temperature and time.

[0037] It will be recognized that the heat treatment parameters are desirably selected to establish a satisfactory content of active polysulphide for the protective oxidation of the carbohydrate aldehyde groups. As such, a balance is to be achieved between PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio and the actual concentration of active polysulphide. A PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio close to 1 will not be beneficial if the heat treatment has decreased the total polysulphide content to a level where the active polysulphide content is inadequate for the protective oxidation reaction.

[0038] On the other hand, a low PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio will be beneficial where the total polysulphide content remains high such that the ratio signifies an adequate active polysulphide content for the protective oxidation reaction.

[0039] In general, an active polysulphide concentration of at least 4 g/l, and preferably at least 6 g/l, in the oxidized white liquor, is required for effective oxidation of the carbohydrate aldehyde groups in the wood chips.

[0040] The PS_{UV} can be measured at, for example, at 285nm, 286 nm or a 416 nm wavelength.

EXPERIMENTAL

[0041] The liquors used to generate the results in Figure 1 were obtained as follows. White liquors of varying concentrations and compositions (800 mL; preheated to 70 °C in a microwave oven) were brought to 90 °C (in an oil bath) in a stainless steel reactor (1 L) equipped with a condenser (5 °C) and ports for adding gas and MnO_2 and for withdrawing samples. During the rise to temperature, the liquor was stirred mechanically (600 rpm; Eurostar Power Digi-Visc-trademark) under a nitrogen flow (50 mL/min; 2 μ m stainless steel sparger (Supelco-trademark)). The impeller type used was a Rushton disk turbine with 6 flat blades (48 mm diameter). Finely powdered MnO_2 (1 g/L; Brickox 6807-trademark of Prince Manufacturing Company) was added to the reactor when the liquor reached 90 °C. PS_{OWL} was generated by bubbling air (450 mL/min) into the liquor at a constant stirring rate of 1000 rpm. The generation of polysulphide was monitored with a UV spectrometer at 286 nm (HP Vectra QS/165-trademark; 1 mm path-length cells; oxygen-free NaOH (1N) used for dilution and blanks). An absorptivity of 43.48 $Lg^{-1}cm^{-1}$ was used to calculate the concentration of PS_{UV} . Samples were removed from the reactor using a plastic syringe, immediately filtered on a ceramic Buchner funnel, and stored in polyethylene containers under argon prior to their analysis. The stainless steel sparger was cleaned with HCl (3N) prior to subsequent use. The PS_{GR} charge used in all the pulping experiments was 1.58% on wood (oven dried basis).

[0042] The PS_{UV} measurement for the ratios shown in Figure 1 were obtained at 286 nm, a wavelength at which all polysulphide species absorb with the same absorptivity. The PS measurement, however, could also have been made at 416 nm with a similar relationship between PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio and yield being found.

[0043] Figure 2 presents the % decomposition of polysulphide determined by gravimetry and by UV spectrophotometry (286 nm) of a typical liquor produced by catalytic oxidation with manganese dioxide as it is heated at 1.8°C per minute; this corresponds to the conventional rise to temperature used in Kraft cooking of 90 min to 170°C. It is very clear from this figure that, at temperatures above 100°C, polysulphide decomposes rapidly.

[0044] Similar results can be generated by using liquors that are produced by oxidizing white liquor with air in the presence of a wet-proofed activated carbon catalyst. At the industrial scale, this is done in a single oxidation step with compressed air blown into a fixed bed of the carbon black catalyst Smith and Sanders (US Patent 4,024,229) have presented some details on the production of PTFE-coated catalyst. Industrially the MOXY (trademark of The Mead Corporation) and Chiyoda processes both use carbon as the oxidation catalyst. These liquors also produce liquors that have PS_{UV}/PS_{GR} ratios of less than 1 and which can be improved by the heat treatment of the invention. Heat treatment increases the concentration of PS_{UV} , measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of these liquors and, therefore, the fibre yield when using them for pulping.

EXAMPLES

EXAMPLE 1

[0045] Oxidized white liquor was produced by causticizing 0.75 L of green liquor with 45 g reburned lime, spiked with 0.6 g MnO_2 . The manganese content of clarified green liquor samples is typically 0.3 to 6.0 mg/L. The amount of manganese added in the MnO_2 in this example (504 mg/L) is about a hundred times that normally found in green liquor. After 100 min causticizing time at 90°C, oxygen was sparged into the causticized slurry at a rate of 0.1 L/min for 30 min. After oxidation, the resulting $CaCO_3$ lime mud with added MnO_2 was separated from the oxidized white liquor. Samples of the clarified white liquor were then stored in a thermostated bath held at a desired temperature. At regular time intervals, small samples of liquor were withdrawn for determination of polysulphide concentration by UV spectrometry.

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(PS_{UV}) and by gravimetry (PS_{GR}).

[0046] Example 1 illustrates the increase in the PS_{UV}/PS_{GR} ratio when a freshly oxidized white liquor is treated at 73°C for up to 48 hours.

[0047] Table I shows that by heat treatment at 73°C for 48 hours, the PS_{UV}/PS_{GR} ratio was changed from 0.45 to 0.86 while the polysulphide concentration (PS_{GR}) was only decreased from 9.3 g/L to 7.1 g/L. Over 48 hours at 73°C, the PS_{UV} concentration increased by 44 %, from 4.23 to 6.08 g/L as sulphur. As can be seen from Figure 1, such an increase in ratio will allow the yield increase from a given concentration of polysulphide to be increased from zero to almost the full potential of that concentration.

Table 1-Stability at 73°C

Sample Time (h)	286 abs	PS concentration (UV) g/L	PS concentration (gravimetry) g/L	PS _{UV} /PS _{GR} Ratio
0	0.73	4.23	9.34	0.45
1	0.78	4.54	8.12	0.56
2	0.81	4.71	8.36	0.56
3	0.85	4.92	8.30	0.59
20	1.05	6.08	7.06	0.86
24	1.06	6.13	7.60	0.81
48	1.05	6.08	7.10	0.86

EXAMPLE 2

[0048] Example 2 illustrates the change in the ratio when the same liquor is heat treated at 95°C. At this temperature the activation of the liquor, as measured by the change in ratio, is very rapid. Within an hour the ratio has increased to a useful 0.74. Long times of treatment (>3 hours) are less useful at this temperature because of the increasing loss of polysulphide concentration measured either by UV spectrometry or gravimetry.

Table 2-Stability at 95°C

Sample Time (h)	286 abs	PS concentration (UV) g/L	PS concentration (gravimetry) g/L	PS _{UV} /PS _{GR} Ratio
0	0.73	4.23	9.34	0.45
1	0.80	4.65	6.32	0.74
2	0.83	4.81	5.86	0.82
3	0.85	4.91	5.36	0.92
20	0.71	4.11	5.00	0.82
24	0.70	4.07	5.30	0.77
48	0.57	3.31	4.20	0.79

EXAMPLE 3

[0049] Example 3 illustrates the change in the ratio and polysulphide concentration at an intermediate temperature of 85°C. At this temperature, it takes between 2 and 3 hours for the activation of the liquor. Again longer times of treatment are less useful because of the increasing loss of polysulphide charge.

Table 3-Stability at 85° C

Sample Time (h)	286 abs	PS concentration (UV) g/L	PS concentration (gravimetry) g/L	PS _{UV} /PS _{GR} Ratio
0	0.78	4.52	9.78	0.46
0.83	0.82	4.74	8.08	0.59
2	0.83	4.80	6.98	0.69
3	0.89	5.14	6.32	0.81
4	0.86	4.99	6.16	0.81

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(continued)

Sample Time (h)	286 abs	PS concentration (UV) g/L	PS concentration (gravimetry) g/L	PS _{UV} /PS _{GR} Ratio
10	0.73	4.22	5.18	0.81
22	0.74	4.28	4.66	0.92
26	0.66	3.85	4.28	0.90
50.42	0.53	3.05	3.70	0.82

EXAMPLE 4

[0050] Example 4 illustrates the change in the ratio and polysulphide charge at 78°C but with the liquor having been pre-activated over 4 days at ambient temperature. The ambient temperature treatment increased the ratio from 0.46 to 0.55 without any loss of polysulphide concentration.

Table 4-Stability at 78°C

Sample Time (h)	286 abs	PS concentration (UV) g/L	PS concentration (gravimetry) g/L	PS _{UV} /PS _{GR} Ratio
0	0.92	5.33	9.62	0.55
0.83	0.87	5.02	8.86	0.57
2.5	0.87	5.05	7.86	0.64
3.5	0.87	5.02	7.78	0.65
4.5	0.88	5.08	6.56	0.77
10	0.83	4.80	6.04	0.79
24	0.84	4.84	5.34	0.91
48	0.59	3.43	5.00	0.69

EXAMPLE 5

[0051] Oxidized white liquor was produced by causticizing 0.75 L of green liquor with 53 g reburned lime, spiked with 1.5 g MnO₂. After 60 min causticizing time at 95°C, air was sparged into the causticized slurry at a rate of 0.55 L/min for 58 min. After oxidation, the resulting CaCO₃ lime mud with added MnO₂ was separated from the oxidized white liquor. Samples of the clarified white liquor were then stored in a thermostated bath held at a desired temperature. At regular time intervals, small samples of liquor were withdrawn for determination of polysulphide concentration by UV spectrometry (PS_{UV}) and by gravimetry (PS_{GRAV}).

[0052] Example 5 illustrates the increase in the concentration of PS_{UV} measured at 285 or 286 nm and PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} and PS_{VIS}/PS_{GR} ratio when a freshly oxidized white liquor is treated at 60°C for up to 20 hours.

[0053] The data in the table in this example shows that by heat treatment at 60°C for 20 hours, the PS_{UV}/PS_{GR} or PS₂₈₅/PS_{GR} ratio was changed from 0.44 to 0.60, and the PS_{VIS}/PS_{GR} or PS₄₁₆/PS_{GR} ratio increased from 0.18 to 0.40, while the gravimetric polysulphide concentration was only decreased from 8.4 g/L to 7.5 g/L. The PS₄₁₆ concentration in the oxidized liquor doubled from 1.5 to 3.0 gpl (as sulphur) during the 20 hours of storage at 60 C. As can be seen from Figure 1, such an increase in the PS_{UV}/PS_{GR} or PS₂₈₅/PS_{GR} ratio will allow the yield increase from a given concentration of polysulphide to be increased from zero to approximately a third of the full potential of that concentration.

Table 5-Stability at 60°C

Sample Time (h)	PS concentration (gravimetry) g/L	PS concentration (UV 285) g/L	PS concentration (Vis 416) g/L	UV 285/Grav ratio	Vis 416/Grav ratio
0	8.4	3.7	1.5	0.44	0.18
1	8.3	3.8	1.6	0.46	0.19
3	8.1	3.8	1.8	0.47	0.22
16	7.9	4.3	2.7	0.54	0.34

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(continued)

Sample Time (h)	PS concentration (gravimetry) g/L)	PS concentration (UV 285) g/L	PS concentration (Vis 416) g/L)	UV 285/Grav ratio	Vis 416/Grav ratio
20	7.5	4.5	3.0	0.60	0.40

EXAMPLE 6

[0054] Example 6 illustrates the change in the ratio when the same liquor is heat treated at 80°C. At this temperature the activation of the liquor, as measured by the change in ratio, is more rapid. Within 16 hours the ratio has increased to a useful 0.89.

[0055] The data in the table in this example shows that by heat treatment at 80°C for 20 hours, the PS_{UV}/PS_{GR} or PS_{285}/PS_{GR} ratio was changed from 0.44 to 0.93, and the PS_{VIS}/PS_{GR} or PS_{416}/PS_{GR} ratio increased from 0.18 to 0.86, while the gravimetric polysulphide concentration was decreased from 8.4 g/L to 4.6 g/L. As can be seen from Figure 1, such an increase in PS_{UV}/PS_{GR} or PS_{285}/PS_{GRAV} ratio will allow the yield increase from a given concentration of polysulphide to be increased from zero to almost the full potential of that concentration.

Table 6-Stability at 80°C

Sample Time (h)	PS concentration (gravimetry) g/L)	PS concentration (UV 285) g/L	PS concentration (Vis 416) g/L)	UV 285/Grav ratio	Vis 416/Grav ratio
0	8.4	3.7	1.5	0.44	0.18
1	7.7	3.8	1.9	0.49	0.25
3	6.6	4.0	2.6	0.60	0.39
16	4.8	4.3	3.9	0.89	0.81
20	4.6	4.3	4.0	0.93	0.86

EXAMPLE 7

[0056] Example 7 illustrates the change in the ratio when a similar liquor is heat treated at 70°C. At this temperature the activation of the liquor, as measured by the change in ratio, is less rapid than at 80°C, but more rapid than 60°C. Within 20 hours, the PS_{UV}/PS_{GR} or PS_{285}/PS_{GR} ratio has increased to a useful 0.72 and the PS_{VIS}/PS_{GR} or PS_{416}/PS_{GR} ratio increased from 0.21 to 0.57. Through. 20 hours of heat treatment at 70 C, the PS_{416} concentration was more than doubled from 1.8 to 3.8 gpl (as sulphur).

Table 7 Stability at 70°C.

Sample Time (h)	PS concentration (gravimetry) g/L)	PS concentration (UV 285) g/L	PS concentration (Vis 416) g/L)	UV 285/Grav ratio	Vis 416/Grav ratio
0	8.5	4.0	1.8	0.47	0.21
1	8.7	4.0	1.8	0.46	0.21
3	8.5	4.1	2.2	0.48	0.26
5	8.0	4.2	2.3	0.52	0.29
16	6.6	4.7	3.5	0.71	0.53
20	6.7	4.8	3.8	0.72	0.57

EXAMPLE 8

[0057] Example 8 illustrates the change in the ratio when the same liquor is heat treated at 90°C. At this temperature, the activation of the liquor, as measured by the change in ratio, is very rapid. Within 5 hours, the PS_{UV}/PS_{GR} or PS_{285}/PS_{GR}

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ratio has increased to a useful 0.84, and the PS_{VIS}/PS_{GR} or PS_{416}/PS_{GR} ratio increased from 0.21 to 0.74, while the gravimetric polysulphide concentration was decreased from 8.5 g/L to 4.3 g/L. Longer times at this temperature resulted in a lower PS_{GR} , PS_{UV} and PS_{VIS} concentrations with only a small gain in the ratios.

Table 8-Stability at 90°C

Sample Time (h)	PS concentration (gravimetry) g/L	PS concentration (UV 285) g/L	PS concentration (V is 416) g/L	UV 285/Grav ratio	Vis 416/Grav ratio
0	8.5	4.0	1.8	0.47	0.21
1	6.9	3.7	2.2	0.53	0.31
3	4.8	3.6	2.9	0.74	0.61
5	4.3	3.6	3.2	0.84	0.74
16	3.8	3.3	3.1	0.86	0.80
20	3.6	3.3	3.1	0.91	0.84

EXAMPLE 9

[0058] Unclarified mill white liquor containing 100 g/L of lime mud was oxidized with air in the presence of 2.0 g/L MnO_2 at 85-90°C for 60 minutes, cooled quickly to room temperature (20°C) using a water bath and filtered to remove the lime mud and to give a clarified oxidized white liquor. One portion of the oxidized white liquor was treated at 70 °C for 20 hours. Another portion was stored at room temperature (20 °C) for 20 hours. The polysulphide concentrations in these two oxidized white liquors were determined by gravimetry to be PS_{GR} = 6.4 g/L and 7.7 g/L, respectively, and by UV to be PS_{UV} = 5.1 g/L and 3.8 g/L, respectively. The PS_{UV} / PS_{GR} of the oxidized white liquor treated at 70 °C for 20 hours (OWL-70 °C) was thus 0.80 and the PS_{UV} / PS_{GR} of the oxidized white liquor stored at 20 °C for 20 hours (OWL-20 °C) was 0.49. The same amounts of these two oxidized white liquors were then used for the pulping of mixed softwood chips (50/50 black spruce and pine) in a micro-digester using 50 g (OD weight) of the wood chips in each of four stainless steel laboratory bombs. A control Kraft cook using the white liquor (WL) was also carried out. The liquor to wood ratio and the maximum cooking temperature were 4.5 to 1 and 170 °C, respectively. The PS_{GR} charges were 1.3 and 1.5% (on wood) for the cook using OWL-70 °C and the cook using OWL-20 °C, respectively. Each bomb was cooked to a certain H-factor. Upon completion of each cook, the pulp from each bomb was well washed and screened through a laboratory flat screen plate (0.2 mm or 0.008" slot). The screened pulp yields were measured by weighing the oven-dried screened pulps and the permanganate numbers determined according to PAPTAC, Standard G. 17H. Figure 3 shows that the PS cook using the heat-treated oxidized white liquor (OWL-70 °C) at a ratio of PS_{UV} / PS_{GR} = 0.80 gives a higher yield gain over the Kraft reference than the cook using oxidized white liquor without the heat treatment (OWL-20 °C) at a ratio of PS_{UV} / PS_{GR} = 0.49.

EXAMPLE 10

[0059] Unclarified mill white liquor containing 100 g/L of lime mud was oxidized with air in the presence of 2.0 g/L MnO_2 at 85-90°C for 60 minutes, cooled quickly to room temperature (20°C) using a water-bath and filtered to remove the lime mud and to give a clarified oxidized white liquor. One portion of the oxidized white liquor was treated at 70°C for 20 hours. Another portion was stored at room temperature (20 °C) for 20 hours. The polysulphide concentrations in these two oxidized white liquors were determined by gravimetry to be PS_{GR} = 6.0 g/L and 7.6 g/L respectively. The same amounts of these two oxidized white liquors were then used for the pulping of maple chips in a micro-digester using 50 g (OD weight) of the wood chips in each of four stainless steel laboratory bombs. A control Kraft cook using the white liquor (WL) was also carried out. The liquor to wood ratio and the maximum cooking temperature were 4.0 to 1 and 165 °C, respectively. The PS_{GR} charges were 1.1 and 1.4% (on wood) for the cook using OWL-70 °C and the cook using OWL-20 °C, respectively. Each bomb was cooked to a certain H-factor. Upon completion of each cook, the pulp from each bomb was well washed and screened through a laboratory flat screen plate (0.2 mm or 0.008" slot). The screened pulp yields were measured by weighing the oven-dried screened pulps and the permanganate numbers determined according to PAPTAC, Standard G. 17H. Figure 4 shows that the PS cook using the heat-treated oxidized white liquor (OWL-70 °C) again gives a higher yield gain over the Kraft reference than the cook using oxidized white liquor without the heat treatment (OWL-20 °C).

EXAMPLE 11

[0060] This example summarizes the optimum storage time needed to maximize the PS_{UV} content of a polysulphide liquor generated by the oxidation of white liquor. The active polysulphide concentration (PS_{416}) at a given storage time is described by a curve which increases with time. The temperature at which the liquor is held in storage is described by a curve that decreases with time. At the lowest temperature evaluated (60°C), a storage time of 60 hours is needed to produce 6 g/L of active polysulphide from a liquor initially having a PS_{GR} concentration of 8.5 g/L. At the highest temperature evaluated (103°C) a storage time of 2 hours is needed to produce 2.3 g/L of active polysulphide from the same liquor.

EXAMPLE 12

[0061] In this example, a polysulphide liquor was made with MnO_2 but without lime mud. A synthetic white liquor was prepared from sodium hydroxide and sodium sulphide. A sample (750 mL) of this white liquor was oxidized using air at 450 ml/min with 0.4 grams of a commercial grade MnO_2 (0.53 g/L MuO_2). The composition of the synthetic white liquor and the product oxidized liquor are illustrated in Table 9. Table 10 shows that heat treatment at 77°C for 16.5 hours of this type of oxidized liquor is effective in increasing the PS_{UV}/P_{GR} ratio from 0.46 to 0.97 and increasing the PS_{416} concentration in the oxidized liquor from 1.4 to 3.3 gpl (as sulphur).

Table 9 - Composition of liquors used in this example.

	Synthetic White Liquor	60 minutes Oxidation
Na_2S , g/L as S	18.11	11.16
PS, g/L as S	0.24	7.14
% Selectivity	n/a	99

Table 10 - Effect of thermal treatment (storage at 77°C for 16.5 hours) with a polysulphide liquor generated with MnO_2 in the absence of lime mud.

	285nm PS, g/L S	416nm PS, g/L S	Gravimetric PS, g/L S	UV 285/grav ratio
Before Thermal treatment	3.3	1.4	7.14	0.46
After Thermal treatment	3.6	3.3	3.65	0.97

EXAMPLE 13

[0062] In this example, a polysulphide liquor was made with a wet-proofed activated carbon catalyst. Wet proofing was done by spraying a dry film lubricant (TFE in Freon-trademark) on activated carbon (50-200 mesh from Fisher Scientific Co. Ltd.). The resulting paste was dried in the fume hood under a flow of nitrogen.

Table 11 shows that heat treatment at 65°C , or aging at 25°C , over 60 hours of this type of oxidized liquor increases the active polysulphide from 2.15 g/L to 4.55-5.68 g/L.

[0063] The oxidation was done at room temperature by adding 5 g of wet-proofed carbon to about 300mL of artificial white liquor pre-heated to 85°C in a 500mL beaker. Oxidation was done for about 15h by letting air diffuse through the floating carbon into the white liquor. Samples of the oxidized liquor were then analyzed by gravimetry and by UV spectrophotometry, just after production . (fresh) and then after storage for 60 h at 25°C . Another aliquot of the fresh oxidized liquor was also stored at 65°C for 60 h and then analyzed again.

[0064] The effect of liquor aging on the change in active (PS^{act}), inactive (PS^{inact}) and total (PS^{tot}) concentrations of polysulphides is presented in Table 11.

Table 11 - Effect of thermal treatment with a polysulphide liquor generated using a wet-proofed activated carbon catalyst

MOXY-type liquor	PS concentrations (g/L, as S)		
	PS ^{act}	PS ^{inact}	PS ^{tot}
Fresh	2.15	10.39	12.54
Aged 60 h at 25°C	4.55	3.07	7.62
Aged 60 h at 65°C	5.68	3.58	9.20

Claims

1. A method of exposing an oxidized white liquor to a temperature effective to increase the concentration of PS_{UV} measured at 285 or 286 nm or PS_{VIS} measured at 416 nm and the PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio of polysulphide in the oxidized white liquor,
characterised in that the liquor is exposed to a temperature of 20°C to 95°C for a time of 1 to 72 hours.
2. A method according to claim 1, **characterised in that** said oxidized white liquor is maintained at a temperature of 50°C to 90°C for 1 to 48 hours.
3. A method according to claim 1 or 2, **characterised in that** said oxidized white liquor is maintained at a temperature of 50°C to 90°C for 4 to 48 hours.
4. A method according to any of the preceding claims, **characterised in that** said method comprises the steps of heating or cooling if necessary and then storing said oxidized white liquor at a temperature between 20°C and 95°C for a time of 1 to 72 hours.
5. A method according to any of the preceding claims, **characterised in that** the oxidized white liquor is produced by oxidizing a white liquor with oxygen containing gas in the presence of lime mud, manganese dioxide or both.
6. A method according to any of the preceding claims, **characterised in that** the liquor is exposed for a time of 6 to 30 hours.
7. A method according to claim 6 **characterised in that** the liquor is exposed for a time of 12 to 24 hours.
8. A method of increasing the yield of pulp in Kraft pulping with a white liquor containing polysulphide comprising:
 - i) oxidizing a white liquor to produce an oxidized white liquor containing polysulphide,
 - ii) heating or cooling if necessary and then storing said oxidized white liquor in accordance with the method of claim 4, and in a subsequent step:
 - iii) delignifying pulp with the oxidized white liquor from step ii).
9. A method according to claim 8, **characterised in that** said oxidizing in step i) is carried out with oxygen containing gas in the presence of activated carbon as catalyst.
10. A method according to claim 8, **characterised in that** the white liquor is oxidised in step i) with oxygen containing gas in the presence of lime mud, manganese dioxide or both.
11. A method according to claim 10, **characterised in that** said oxidizing in step i) is in the presence of lime mud and a catalytic amount of manganese dioxide, and including a step of; separating said oxidized white liquor produced in step i) from said lime mud and manganese dioxide prior to said heating or cooling if necessary and storing in step ii).
12. A method according to claim 11, **characterised in that** the method comprises prior to step i):
causticizing a green liquor with lime in the presence of manganese dioxide to produce said white liquor and

lime mud containing said manganese dioxide.

13. A method according to any one of claims 8 to 12, **characterised in that** in step ii) the liquor is heated or cooled if necessary and then stored for a time of 6 to 30 hours.

14. A method according to claim 13, **characterised in that** in step ii) the liquor is heated or cooled if necessary and then stored for a time of 12 to 24 hours.

15. A method of producing an oxidized white liquor containing polysulphide comprising:

i) oxidizing a white liquor to produce an oxidized white liquor containing polysulphide and having a first PS_{UV} concentration measured at 285 or 286 nm or PS_{VIS} concentration measured at 416 nm or PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio, and

ii) heating or cooling if necessary and then storing said oxidized white liquor to produce an oxidized white liquor having a second PS_{UV} concentration measured at 285 or 286 nm or PS_{VIS} concentration measured at 416 nm or PS_{UV}/PS_{GR} or PS_{VIS}/PS_{GR} ratio, wherein said second concentration or ratio is greater than said first concentration or ratio, step ii) further comprises heating or cooling if necessary and then storing said oxidized white liquor in accordance with the method of claim 4.

16. A method according to claim 15, **characterised in that** said oxidizing in step i) is carried out with oxygen containing gas in the presence of activated carbon as catalysts.

17. A method according to claim 15, **characterised in that** the white liquor is oxidised in step i) with oxygen containing gas in the presence of lime mud, manganese dioxide or both.

18. A method according to claim 17, **characterised in that** the method comprises the step of prior to step i):

causticizing a green liquor with lime in the presence of manganese dioxide to produce said white liquor and lime mud containing said manganese dioxide.

19. A method according to any one of claims 15 to 18, **characterised in that** in step ii) the liquor is heated or cooled if necessary and then stored for a time of 6 to 30 hours.

20. A method according to claim 19, **characterised in that** in step ii) the liquor is heated or cooled if necessary and then stored for a time of 12 to 24 hours.

Patentansprüche

1. Ein Verfahren zur Behandlung einer oxidierten Weißlauge mit einer Temperatur, die wirksam ist, um die Konzentration an PS_{UV} , die bei 285 oder 286 nm gemessen wird, oder an PS_{VIS} , die bei 416 nm gemessen wird, und das Verhältnis von PS_{UV}/PS_{GR} oder PS_{VIS}/PS_{GR} (PS_{GR} , gravimetrisch gemessenes Polysulfid) des Polysulfids in der oxidierten Weißlauge zu erhöhen, **dadurch gekennzeichnet ist, dass** die Lauge einer Temperatur von 20 °C bis 95 °C für einen Zeitraum von 1 bis 72 Stunden ausgesetzt wird.

2. Ein Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet ist, dass** die oxidierte Weißlauge bei einer Temperatur von 50 °C bis 90 °C für 1 bis 48 Stunden gehalten wird.

3. Ein Verfahren gemäß Anspruch 1 oder 2, **dadurch gekennzeichnet ist, dass** die oxidierte Weißlauge bei einer Temperatur von 50 °C bis 90 °C für 4 bis 48 Stunden gehalten wird.

4. Ein Verfahren gemäß einem der vorangegangenen Ansprüche, **dadurch gekennzeichnet ist, dass** das Verfahren die Schritte des Heizens oder Kühlens, falls dies erforderlich ist, und dann des Lagerns der oxidierten Weißlauge bei einer Temperatur zwischen 20 °C und 95 °C für einen Zeitraum von 1 bis 72 Stunden umfasst.

5. Ein Verfahren gemäß einem der vorangegangenen Ansprüche, **dadurch gekennzeichnet ist, dass** die oxidierte

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Weißlauge durch das Oxidieren einer Weißlauge mit sauerstoffhaltigem Gas in der Gegenwart von Kalkschlamm, Mangandioxid oder beidem hergestellt wird.

6. Ein Verfahren gemäß einem der vorangegangenen Ansprüche, das **dadurch gekennzeichnet ist, dass** die Lauge für einen Zeitraum von 6 bis 30 Stunden behandelt wird.

7. Ein Verfahren gemäß Anspruch 6, das **dadurch gekennzeichnet ist, dass** die Lauge für einen Zeitraum von 12 bis 24 Stunden behandelt wird.

8. Ein Verfahren zur Erhöhung der Ausbeute von Zellstoff bei dem Kraft-Zellstoffaufschluss mit einer Weißlauge, die Polysulfid enthält, umfassend:

- i) das Oxidieren einer Weißlauge zur Herstellung einer oxidierten Weißlauge, die Polysulfid enthält,
- ii) das Erwärmen oder Kühlen, falls dies erforderlich ist, und dann das Lagern der oxidierten Weißlauge entsprechend dem Verfahren von Anspruch 4, und in einem anschließenden Schritt:
- iii) das Entfernen von Lignin aus dem Zellstoff mit der oxidierten Weißlauge aus Schritt ii).

9. Ein Verfahren gemäß Anspruch 8, das **dadurch gekennzeichnet ist, dass** das Oxidieren in Schritt i) mit sauerstoffhaltigem Gas in der Gegenwart von Aktivkohle als Katalysator durchgeführt wird.

10. Ein Verfahren gemäß Anspruch 8, das **dadurch gekennzeichnet ist, dass** die Weißlauge in Schritt i) mit sauerstoffhaltigem Gas in der Gegenwart von Kalkschlamm, Mangandioxid oder beidem oxidiert wird.

11. Ein Verfahren gemäß Anspruch 10, das **dadurch gekennzeichnet ist, dass** das Oxidieren in Schritt i) in der Gegenwart von Kalkschlamm und einer katalytischen Menge von Mangandioxid durchgeführt wird und den folgenden Schritt umfasst:

das Abtrennen der oxidierten Weißlauge, die in Schritt 1) hergestellt wurde, von dem Kalkschlamm und dem Mangandioxid vor dem Erwärmen oder Kühlen, falls dies erforderlich ist, sowie vor der Lagerung in Schritt ii).

12. Ein Verfahren gemäß Anspruch 11, das **dadurch gekennzeichnet ist, dass** das Verfahren vor dem Schritt i) das Folgende umfasst:

das Beizen einer Grünlauge mit Kalk in der Gegenwart von Mangandioxid zur Herstellung der Weißlauge und des Kalkschlammes, der das Mangandioxid enthält.

13. Ein Verfahren gemäß einem der Ansprüche 8 bis 12, das **dadurch gekennzeichnet ist, dass** die Lauge in Schritt ii), falls dies erforderlich ist, erwärmt oder gekühlt wird und dann für einen Zeitraum von 6 bis 30 Stunden gelagert wird.

14. Ein Verfahren gemäß Anspruch 13, das **dadurch gekennzeichnet ist, dass** die Lauge in Schritt ii), falls dies erforderlich ist, erwärmt oder gekühlt wird und dann für einen Zeitraum von 12 bis 24 Stunden gelagert wird.

15. Ein Verfahren zur Herstellung einer oxidierten Weißlauge, die Polysulfid enthält, umfassende:

- i) das Oxidieren einer Weißlauge zur Herstellung einer oxidierten Weißlauge, die Polysulfid enthält, und eine erste bei 285 oder 266 nm gemessene PS_{UV} -Konzentration, eine erste bei 416 nm gemessene PS_{VIS} -Konzentration oder ein erstes Verhältnis von PS_{UV}/PS_{GR} oder PS_{VIS}/PS_{GR} aufweist, und
- ii) das Erwärmen oder Kühlen, falls dies erforderlich ist, und dann das Lagern der oxidierten Weißlauge zur Herstellung einer oxidierten Weißlauge mit einer zweiten bei 285 oder 286 nm gemessenen PS_{UV} -Konzentration oder einer zweiten bei 416 nm gemessenen PS_{VIS} -Konzentration oder einem zweiten Verhältnis von PS_{UV}/PS_{GR} oder PS_{VIS}/PS_{GR} , wobei die zweite Konzentration oder das zweite Verhältnis größer als die erste Konzentration oder das erste Verhältnis ist,

wobei Schritt ii) zusätzlich das Erwärmen oder Abkühlen, falls dies erforderlich ist, und dann das Lagern der oxidierten Weißlauge gemäß dem Verfahren von Anspruch 4 umfasst.

16. Ein Verfahren gemäß Anspruch 15, das **dadurch gekennzeichnet ist, dass** das Oxidieren in Schritt i) mit sauerstoffhaltigem Gas in der Gegenwart von Aktivkohle als Katalysator durchgeführt wird.

17. Ein Verfahren gemäß Anspruch 16, das **dadurch gekennzeichnet ist, dass** die Weißlauge in Schritt 1) mit sauerstoffhaltigem Gas in der Gegenwart von Kalkschlamm, Mangandioxid oder beidem oxidiert wird.

18. Ein Verfahren gemäß Anspruch 17, das **dadurch gekennzeichnet ist, dass** das Verfahren vor Schritt i) den folgenden Schritt umfasst:

das Beizen einer Grünlauge mit Kalk in der Gegenwart von Mangandioxid zur Herstellung der Weißlauge und des Kalkschlammes, der das Mangandioxid enthält.

19. Ein Verfahren gemäß einem der Ansprüche 15 bis 18, das **dadurch gekennzeichnet ist, dass** die Lauge in Schritt ii) erwärmt oder gekühlt wird, falls dies erforderlich ist. und dann für einen Zeitraum von 6 bis 30 Stunden gelagert wird.

20. Ein Verfahren gemäß Anspruch 19, das **dadurch gekennzeichnet ist, dass** die Lauge in Schritt ii) erwärmt oder gekühlt wird, falls dies erforderlich ist, und dann für einen Zeitraum von 12 bis 24 Stunden gelagert wird.

Revendications

1. Procédé d'exposition d'une liqueur blanche oxydée à une température se révélant efficace pour renforcer la concentration en PS_{UV} mesurée à 285 ou 286 nm ou en PS_{VIS} mesurée à 416 nm et le rapport PS_{UV}/PS_{GR} ou PS_{VIS}/PS_{GR} de polysulfure dans la liqueur blanche oxydée, **caractérisé en ce que** la liqueur est exposée à une température de 20 à 95 °C pendant une durée de 1 à 72 heures.

2. Procédé selon la revendication 1, **caractérisé en ce que** ladite liqueur blanche oxydée est maintenue à une température de 50 à 90 °C pendant 1 à 48 heures.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** ladite liqueur blanche oxydée est maintenue à une température de 50 à 90 °C pendant 4 à 48 heures.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit procédé comprend les étapes consistant à chauffer ou refroidir si nécessaire, puis à stocker ladite liqueur blanche oxydée à une température comprise entre 20 et 95 °C pendant une durée de 1 à 72 heures.

5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la liqueur blanche oxydée est produite par oxydation d'une liqueur blanche au moyen d'un gaz contenant de l'oxygène en présence de boues résiduelles de chaux, de dioxyde de manganèse ou des deux.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la liqueur est exposée pendant une durée de 6 à 30 heures.

7. Procédé selon la revendication 6, **caractérisé en ce que** la liqueur est exposée pendant une durée de 12 à 24 heures.

8. Procédé de renforcement du rendement de la pâte à papier dans la production de pâte kraft au moyen d'une liqueur blanche contenant du polysulfure, comprenant les étapes consistant à :

- i) oxyder une liqueur blanche pour produire une liqueur blanche oxydée contenant du polysulfure,
- ii) chauffer ou refroidir si nécessaire, puis stocker ladite liqueur blanche oxydée conformément au procédé de la revendication 4, et au cours d'une étape ultérieure :
- iii) délignifier la pâte à papier au moyen de la liqueur blanche oxydée de l'étape ii).

9. Procédé selon la revendication 8, **caractérisé en ce que** ladite oxydation de l'étape i) est mise en oeuvre au moyen d'un gaz contenant de l'oxygène en présence de charbon actif comme catalyseur.

10. Procédé selon la revendication 8, **caractérisé en ce que** la liqueur blanche est oxydée au cours de l'étape i) au moyen d'un gaz contenant de l'oxygène en présence de boues résiduelles de chaux, de dioxyde de manganèse ou des deux.

11. Procédé selon la revendication 10, **caractérisé en ce que** ladite oxydation de l'étape i) se fait en présence de

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boues résiduelles de chaux et d'une quantité catalytique de dioxyde de manganèse, et comprenant une étape consistant à :

séparer ladite liqueur blanche oxydée produite au cours de l'étape i) desdites boues résiduelles de chaux et dudit dioxyde de manganèse préalablement audit chauffage ou refroidissement si nécessaire, puis au stockage de l'étape ii).

12. Procédé selon la revendication 11, **caractérisé en ce que** le procédé comprend, préalablement à l'étape i) :

la caustification d'une liqueur verte au moyen de chaux en présence de dioxyde de manganèse pour produire ladite liqueur blanche et lesdites boues résiduelles de chaux contenant ledit dioxyde de manganèse.

13. Procédé selon l'une quelconque des revendications 8 à 12, **caractérisé en ce qu'**au cours de l'étape ii), la liqueur est chauffée ou refroidie si nécessaire, puis stockée pendant une durée de 6 à 30 heures.

14. Procédé selon la revendication 13, **caractérisé en ce qu'**au cours de l'étape ii), la liqueur est chauffée ou refroidie si nécessaire, puis stockée pendant une durée de 12 à 24 heures.

15. Procédé de production d'une liqueur blanche oxydée contenant du polysulfure, comprenant :

i) l'oxydation d'une liqueur blanche en vue de la production d'une liqueur blanche oxydée contenant du polysulfure et présentant une première concentration en PS_{UV} mesurée à 285 ou 286 nm ou en PS_{VIS} mesurée à 416 nm ou encore un premier rapport PS_{UV}/PS_{GR} ou PS_{VIS}/PS_{GR} , et

ii) le chauffage ou le refroidissement si nécessaire, puis le stockage de ladite liqueur blanche oxydée pour produire une liqueur blanche oxydée présentant une seconde concentration en PS_{UV} mesurée à 285 ou 286 nm ou une concentration en PS_{VIS} mesurée à 416 nm ou encore un second rapport PS_{UV}/PS_{GR} ou PS_{VIS}/PS_{GR} , ladite seconde concentration ou ledit second rapport étant supérieur à ladite première concentration ou audit premier rapport,

l'étape ii) comprend, en outre, le chauffage ou le refroidissement si nécessaire, puis le stockage de ladite liqueur blanche oxydée conformément au procédé de la revendication 4.

16. Procédé selon la revendication 15, **caractérisé en ce que** ladite oxydation de l'étape i) est mise en oeuvre au moyen d'un gaz contenant de l'oxygène en présence de charbon actif en tant que catalyseur.

17. Procédé selon la revendication 15, **caractérisé en ce que** la liqueur blanche est oxydée au cours de l'étape i) au moyen d'un gaz contenant de l'oxygène en présence de boues résiduelles de chaux, de dioxyde de manganèse ou des deux.

18. Procédé selon la revendication 17, **caractérisé en ce que** le procédé comprend, préalablement à l'étape i) l'étape consistant à :

caustifier une liqueur verte au moyen de chaux en présence de dioxyde de manganèse pour produire ladite liqueur blanche et lesdites boues résiduelles de chaux contenant ledit dioxyde de manganèse.

19. Procédé selon l'une quelconque des revendications 15 à 18, **caractérisé en ce qu'**au cours de l'étape ii), la liqueur est chauffée ou refroidie si nécessaire, puis stockée pendant une durée de 6 à 30 heures.

20. Procédé selon la revendication 19, **caractérisé en ce qu'**au cours de l'étape ii), la liqueur est chauffée ou refroidie si nécessaire, puis stockée pendant une durée de 12 à 24 heures.

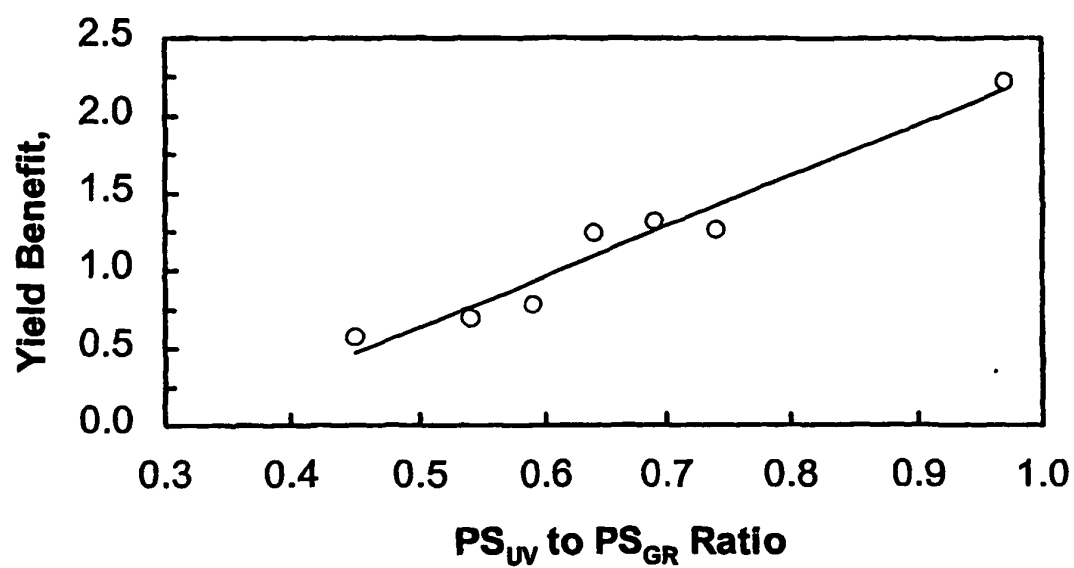


FIG. 1

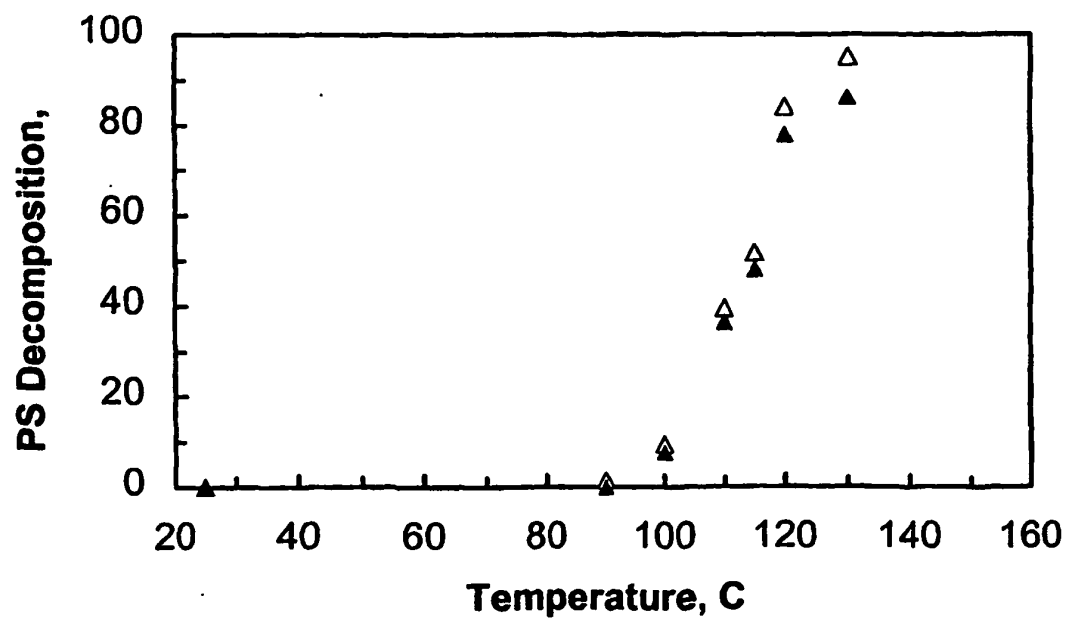


FIG. 2

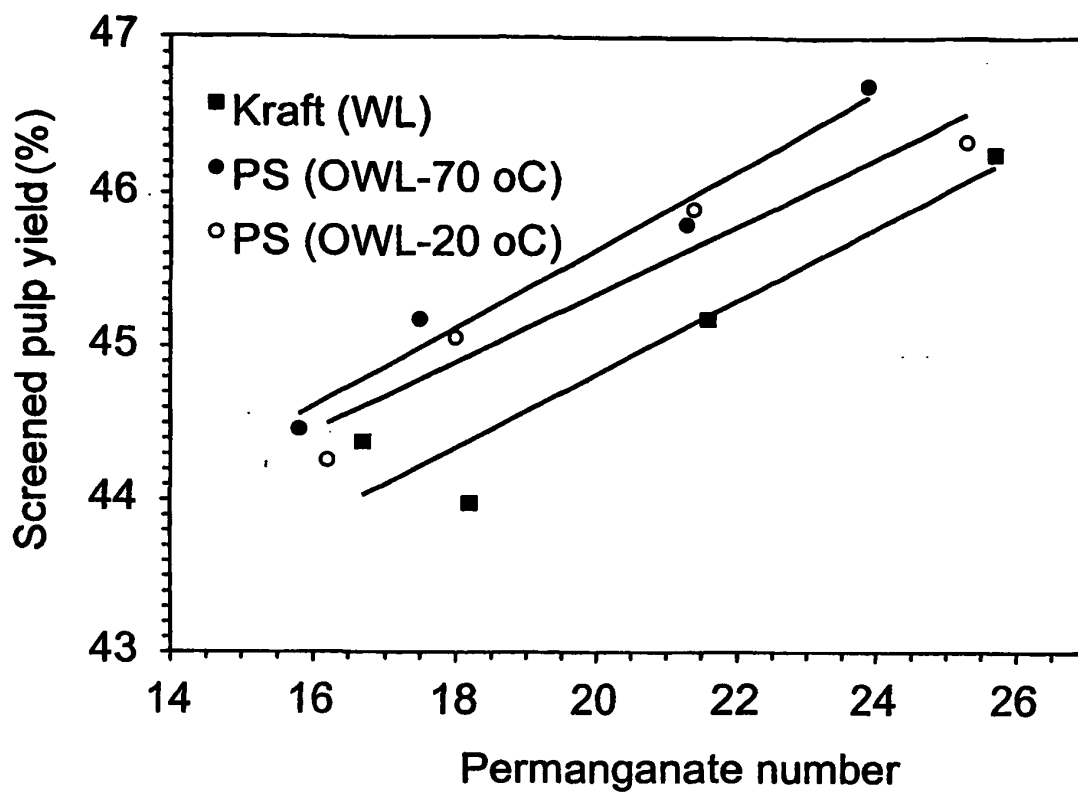


Fig. 3

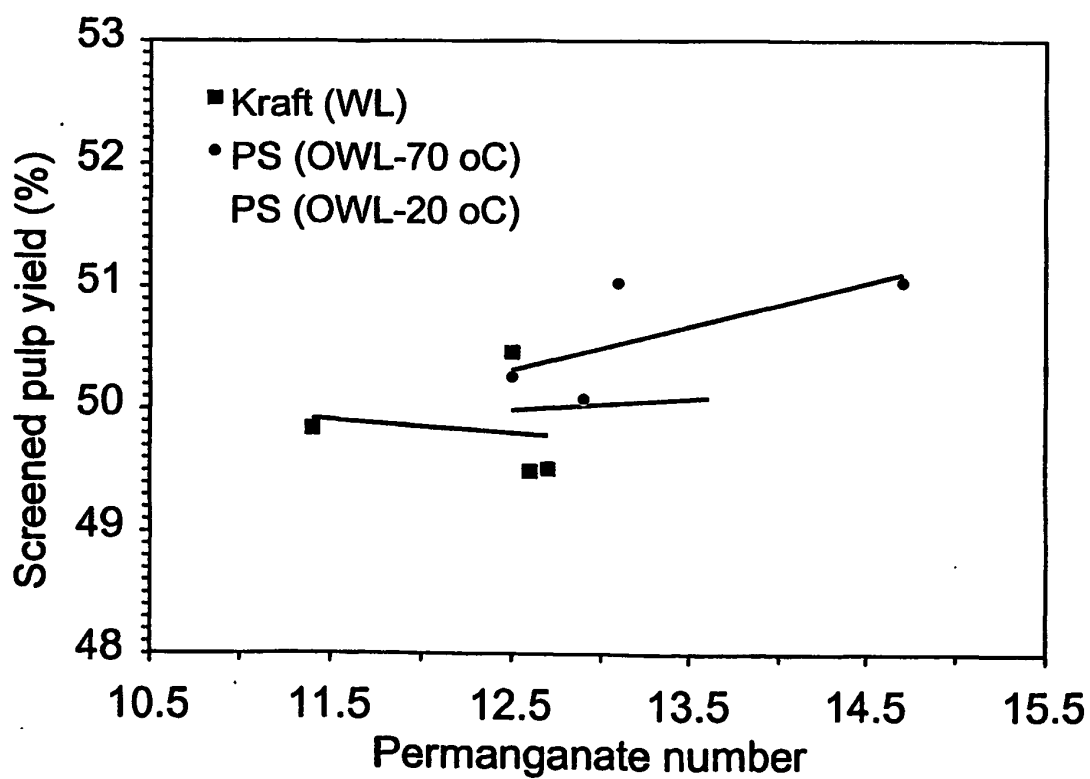


Fig. 4