On the Mechanism of Pulp Bleaching. V. Further Investigations on the Residual Lignosulfonic Acid in Unbleached Sulfite Pulp*

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The residual lignosulfonic acid in unbleached spruce (*Picea jezoensis*) sulfite pulp has previously been partly dissolved out by intensive beating of the fiber in water¹⁾. Nearly 20% of the total amount of the residual lignosulfonic acid was thus isolated as barium salt in a pure state and analyzed. The material was isolated from the beating water obtained after beating the fiber until no lignin dissolved. In the present communication the beating of the fiber is described step by step. The paper also tells how the residual lignosulfonic acids dissolved during each step were isolated separately and analyzed to see if any differences exist between these fractions.

As has been reported previously¹⁾, the residual lignosulfonic acid remaining undissolved in the beaten pulp was extracted further by dimethyl sulfoxide together with carbohydrate. It was confirmed that no chemical linkages exist between the two components. This residual lignosulfonic acid was prepared in a pure state and analyzed. Nitrobenzene oxidation of the residual lignosulfonic acids obtained by beating and by dimethyl sulfoxide extraction is described in the present communication, and the yields of vanillin obtained both from these residual lignosulfonic acids and from ordinary α-lignosulfonic acid separated from waste liquor are compared.

The authors also attempt to compare the amount of lignin extracted by beating and by dimethylsulfoxide with the amount of lignin remaining in the pulp undissolved by these processes.

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* Presented in part at the Third Lignin Symposium of Japan, November, 1958.

1) K. Sato and H. Mikawa, This Bulletin, 35, 477 (1962); ibid., 31, 660 (1958); K. Sato, A. Kobayashi and H. Mikawa, ibid., 35, 483 (1962).

Step by Step Dissolution of Residual Lignin from Soft Wood Unbleached Sulfite Pulp

Emerton reported[2] that the fibrillation of the fiber begins at the so-called P and S_1 layers when the pulp is beaten by an ordinary beater, and proceeds gradually to the inner layer of the fiber. The fiber is fibrillated first to fibrils and then to microfibrils. It is therefore expected that the residual lignosulfonic acid dissolved in the early stage of the beating comes more or less from the outer layer of the fiber cell wall, perhaps from the P and S_1 layers, and from the rather coarse fibrils; on the other hand, that dissolved in the later stage of the beating is from the S_2 and S_3 layers or from fine fibrils.

Unbleached sulfite pulp prepared from *Picea jezoensis* and *Abies mariana* (3 : 1, 1500 g.) was beaten, just as has been reported previously, changing the beating water at appropriate intervals, and six fractions of the residual lignosulfonic acid were prepared (Table I). The first four fractions thus obtained were analyzed for sulfur, sulfonic acid sulfur, and methoxyl. The total amount of the phenolic hydroxyl group was estimated by the so-called $\Delta\varepsilon$-method[3]. Types I and II phenolic hydroxyl groups and carboxyl group were estimated as usual by a combination of conductometric titration and the ultraviolet absorption spectra[4]; the results of the analyses are shown in Table II. Here, the values of the functional groups are shown on a methoxyl basis, as it is already clear from the previous communication[1] that the number of methoxyl groups per C_9-unit is approximately one. Not much variation was observed throughout these fractions. The average of the analytical values shown in the lower part of the table is calculated from the analytical values and the yield of the fractions.

TABLE I. YIELDS OF THE FRACTIONS OF THE RESIDUAL LIGNOSULFONIC ACID PREPARED BY STEP BY STEP BEATING OF THE UNBLEACHED SULFITE PULP FROM SPRUCE AND FIR

Fract. No.	SR values of beaten pulp and beating time.	Optical density of beating water at 280 mμ*	Yield of barium lignosulfonate g.
1	50	1.10	2.8
2	70	—	3.5
3	92	1.30	4.5
4	5 hr. more	0.80	3.2
5	5 hr. more	0.34	—**

* Without any dilution.

** Lignin was not separated.

Nitrobenzene Oxidation of the Residual Lignosulfonic Acid Isolated from Unbleached Sulfite Pulp

Among the many reactions of lignin which are used to discover differences in the structure of lignins, ethanolysis and nitrobenzene oxidation are very well studied and are very often used. As has been already reported[1], the amount of the type I phenolic hydroxyl group of the residual lignosulfonic acid is lower than that of ordinary α-lignosulfonic acid separated from the waste liquor, suggesting the existence of some difference in nuclear structure between these two lignosulfonic acid preparations.

TABLE II. ANALYSES OF THE FRACTIONS OF THE RESIDUAL LIGNOSULFONIC ACID PREPARED BY STEP BY STEP BEATING OF THE UNBLEACHED SULFITE PULP FROM SPRUCE AND FIR

Fract. No.	Total S %	SO_3H S %	CH_3O %	$\frac{SO_3H}{CH_3O}$	$\frac{\text{weak acid}}{CH_3O}$	$\frac{OH^*}{CH_3O}$	$\frac{\text{Type I OH}^*}{CH_3O}$	$\frac{\text{Type II OH}^*}{CH_3O}$	$\frac{COOH}{CH_3O}$	$\frac{\text{Type I OH}^*}{\text{Type II OH}^*}$
1	4.37	3.7	11.4	0.32	0.17	0.21 −0.17	0.04 −0.03	0.17 −0.14	0.14 −0.13	1/4
2	3.54	3.8	11.3	0.32	0.21	0.24 −0.19	0.07 −0.05	0.17 −0.14	0.16 −0.14	1/2.5
3	3.67	3.4	11.8	0.29	0.14	0.22 −0.16	0.04 −0.03	0.18 −0.13	0.11 −0.10	1/4
4	3.78	3.6	11.7	0.31	0.12	0.21 −0.17	0.04 −0.03	0.17 −0.14	0.09 −0.08	1/4
Aver.			11.5	0.31		0.22 −0.17	0.05 −0.04	0.18 −0.12	0.12 −0.11	1/3

Percentage is for barium salt.

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[2] H. W. Emerton, *TAPPI*, **40**, 542 (1957).

[3] G. A. Erdtman, *Svensk Papperstidn.*, **55**, 745 (1952).

[4] H. Mikawa, K. Sato, T. Takasaki and K. Ebisawa, This Bulletin, **28**, 653 (1955).

The authors have therefore attempted to see if any difference can be observed in vanillin yields when nitrobenzene oxidation is applied to ordinary α-lignosulfonic acid (from sulfite waste liquor), to residual lignosulfonic acid separated from the unbleached sulfite pulp (by beating), and to that separated by dimethyl sulfoxide extraction of the beaten sulfite unbleached pulp. The nitrobenzene oxidation of the lignin was performed according to Stone's micro method[5]; the results are shown in Table III.

TABLE III. YIELDS OF VANILLIN OBTAINED BY NITROBENZENE OXIDATION OF ORDINARY α-LIGNOSULFONIC ACID, OF RESIDUAL LIGNOSULFONIC ACIDS EXTRACTED BY BEATING AND OF THAT EXTRACTED WITH DIMETHYL SULFOXIDE

	CH_3O% (Ba-salt)	Yield of vanillin % (methoxyl basis)	Aver.
α-Lignosulfonic acid	11.4	26.4 25.8	26.1
Residual lignosulfonic acid (beating)	10.8	28.6 24.0	26.3
Residual lignosulfonic acid (dimethyl sulfoxide)	11.8	26.2 24.8	25.5

As can be seen from Table III, there is not much difference in the yields of vanillin from these lignin preparations. It is well known that ether linkages in lignin at position 4 are cleaved by nitrobenzene oxidation. Leopold[6] reports that acetoguaiacyl-dihydrodehydro-diisoeugenol and octahydro-tri-(acetoguaiacyl)-acetoguaiacon methyl ether give vanillin by nitrobenzene oxidation in a yield of 60~80% of the theoretical. Purves[7] and Pew[8] recognized the formation of a considerable amount of vanillin from a veratryl type structure.

Probably not such a large difference exists between the etherified structural units of the lignosulfonic acids separated from the waste liquor and from unbleached sulfite pulp to give different vanillin yields, although the amount of the type I phenolic hydroxyl group in the former acid is a little higher than that in the latter acid, as has been stated previously.

On the Lignin Balance in the Beating and Extraction with Dimethyl Sulfoxide of Unbleached Sulfite Pulp

The lignin balance in the beating of unbleached sulfite pulp in water and its extraction with dimethyl sulfoxide was determined by measuring the amount of the residual lignosulfonic acid remaining unextracted in the pulp. Twenty-seven grams of unbleached sulfite pulp (*Picea jezoensis* + *Abies mariana* 3 : 1) were beaten in a Lampen mill for about 40 hr. with 800 ml. of water. A small amount of beaten pulp was, with a little water, taken out from the mill six times during the beating. The pulp was filtered, and the water was diluted twelvefold and measured for ultraviolet absorption at 280 mμ, from which the amount of the dissolved lignosulfonic acid was calculated (Fig. 1). The pulp was suspended in alcohol and filtered with a fine glass filter to make an extremely thin paper. Ten milligrams of the thin paper thus prepared were shaken with 25 ml. of 85% phosphoric acid (free from ultraviolet absorption near 280 mμ) for 12 hr. in a 50 ml. glass tube[9], and the ultraviolet absorption of the solution thus obtained was measured at 280 mμ (Fig. 2). As can be seen in Figs. 1 and 2, the absorption curves are typical for lignosulfonic acid, having a maximum and minimum at 280 and 260 mμ respectively. The values of the maximum optical density at 280 mμ of Figs. 1 and 2 are plotted in Fig. 3 against the duration

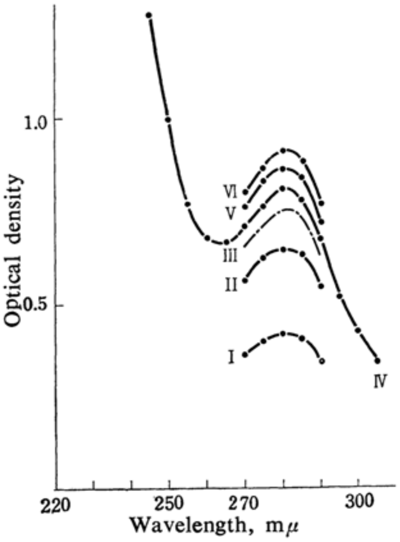

Fig. 1. Ultraviolet absorption curves of beating water obtained at various stages of beating. Curve I, absorption after beating 6 5/6 hr.; II, 20 1/3 hr; III, 25 2/3 hr.; IV, 30 2/3 hr.; V, 35 55/60 hr.; VI, 40 55/60 hr.

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[5] J. E. Stone and M. J. Blundell, *Anal. Chem.*, **23**, 771 (1951).

[6] B. Leopold, *Acta Chem. Scand.*, **4**, 1523 (1950).

[7] W. J. Brickman and C. B. Purves, *J. Am. Chem. Soc.*, **75**, 4336 (1953).

[8] J. C. Pew, ibid., **77**, 2831 (1952).

[9] P. Q. Bethge, G. Gran and K. E. Ohlsson, *Svensk Papperstidn.*, **55**, 44 (1952).

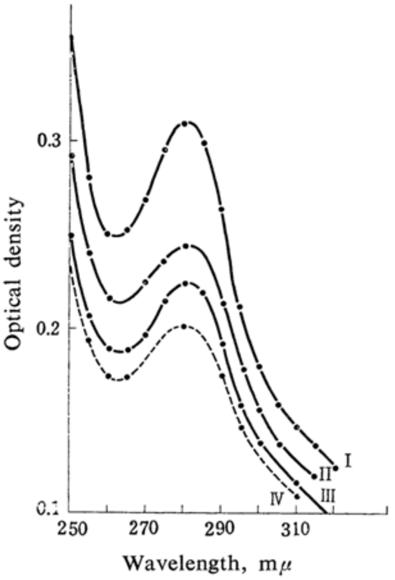

Fig. 2. Ultraviolet absorption curves of phosphoric acid solutions of beaten pulps. Curve I, original pulp; II, pulp beaten for 20 1/3 hr.; III, pulp beaten for 30 55/60 hr.; IV, pulp beaten for 30 55/60 hr. and extracted with dimethyl sulfoxide.

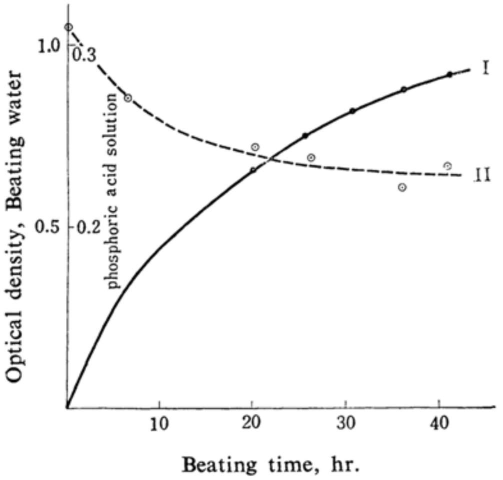

Fig. 3. Optical density at 280 mμ of beating water and phosphoric acid solution of beaten pulp at various stages of beating. Curve I; Beating water, measured after twelvefold dilution. Curve II; Phosphoric acid solution of beaten pulp. (10 mg. of the pulp in 25 ml. of 85% H_3PO_4)

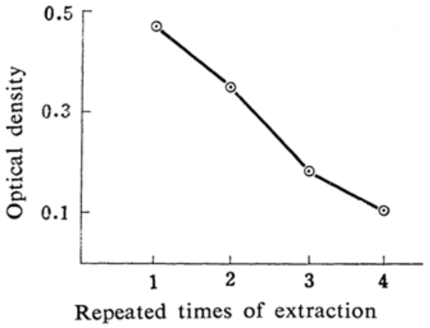

Fig. 4. Decrease of optical density at 280 mμ of dimethyl sulfoxide solutions from the first to fourth extractions of beaten pulp.

TABLE IV. LIGNIN BALANCE IN THE EXTRACTION OF UNBLEACHED SULFITE PULP BY BEATING AND BY DIMETHYL SULFOXIDE

	mmol. of CH_3O estimated by UV-absorption		%
	Remaining in pulp[*1]	Dissolved in solution[*2]	
Unbleached sulfite pulp used	6.52	—	100
Beating water[*3]	—	2.73	42
Beaten pulp	4.17	—	64
Dimethyl sulfoxide[*4] solution	—	1.13	17
Extracted pulp[*5]	3.13	—	48

[*1] Estimated from the ultraviolet absorption of the phosphoric acid solution of the pulp at 280 mμ.

[*2] Estimated from the ultraviolet absorption of the solutions at 280 mμ.

[*3] The yield of the residual lignosulfonic acid in this solution is 416 mg. when 27 g. of unbleached pulp are used.

[*4] The yield of the dimethyl sulfoxide extract (residual lignosulfonic acid + carbohydrate) in this solution is 353 mg. when 27 g. of unbleached pulp are used.

[*5] The mechanical loss of the pulp is about 8%.

of the beating. Curve I, the optical density of the beating water, continues to increase even after 40 hr., showing that the lignosulfonic acid continues to dissolve even after this time, although the rate of dissolution is small at this time. Curve II, showing the decrease of the ultraviolet absorption of the phosphoric acid solution, demonstrates that the rate of decrease of the residual lignosulfonic acid in the beaten pulp is very small after about 40 hr. Assuming the molar absorption coefficient of lignosulfonic acid per methoxyl group as 3200, the amounts of the residual lignosulfonic acid both dissolved and remaining undissolved in the pulp are calculated and listed in Table IV.

The pulp residue remaining after having been beaten for 40 hr. was separated by a centrifuge, washed successively with alcohol, ether and petroleum ether, and dried. The bone dry pulp thus obtained was defibrated by a Bauer disk refiner and extracted with dimethyl sulfoxide (700 ml.) for 48 hr. with occasional shaking, centrifuged and extracted with the same amount of fresh dimethyl sulfoxide three times more. The ultraviolet absorption spectrum of the dimethyl sulfoxide solution thus obtained is characteristic of lignosulfonic acid, having a maximum and minimum at 280 and 265 mμ respectively; the values of maximum absorption at 280 mμ decrease as shown in Fig. 4 from the first extract to the fourth extract. The amount of the residual lignosulfonic acid in the combined dimethyl sulfoxide extract was estimated from the ultraviolet absorption, assuming the molar absorption coefficient of the lignin at 280 mμ as 3200 per methoxyl, and the residual lignosulfonic acid remaining in the pulp after dimethyl sulfoxide extraction was estimated from the ultraviolet absorption of the phosphoric acid solution of the pulp in just the same manner as has been described above. The results are summarized in Table IV, where the amounts of lignosulfonic acid are expressed in methoxyl group units.

As can be seen from the table, the amount of the residual lignosulfonic acid dissolved by beating is 42%, and the residual lignosulfonic acid remaining in the beaten pulp is 64% of the total amount of residual lignosulfonic acid which existed in the pulp. The amount dissolved by beating, calculated from the lignin remaining in pulp, $100-64=36\%$, is in good agreement with 42%. The total amount of residual lignosulfonic acid dissolved by beating and by dimethyl sulfoxide extraction is $42+17=59\%$ of the total lignin which existed in the pulp, which is in good agreement with the dissolved amount calculated from the amount remaining undissolved in the extracted pulp, $100-48=52\%$.

Summary

1) By beating unbleached sulfite pulp step by step and changing the beating water, four fractions of residual lignosulfonic acids were obtained. Analytically not very distinct differences were observed between these fractions.

2) The residual lignosulfonic acids isolated by beating and by dimethyl sulfoxide were oxidized with nitrobenzene, and the yields of vanillin obtained from these lignin preparations were comparad with that from ordinary lignosulfonic acid separated from waste liquor. Almost no difference was observed.

3) The amounts of residual lignosulfonic acid dissolved by beating and by dimethyl sulfoxide extraction were in good agreement with those calculated from the amount of the residual lignosulfonic acid remaining in the pulp, thus proving the accuracy of the estimation. Approximately 40 and 20% of the total lignin in unbleached sulfite pulp were dissolved by beating and by dimethyl sulfoxide extraction respectively.

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