On the Mechanism of Pulp Bleaching. II[1]. *On the Residual Lignosulfonic Acid Existing Undissolved in Unbleached Sulfite Pulp*

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In order to make clear the mechanism of pulp bleaching, it is most important to know the chemical and physical nature of the residual lignin in unbleached pulp, in so far as it is the main material to be bleached. Knowledge about this residual lignin can be expected also to contribute to better understanding of the cooking mechanism of wood inasmuch as it will give information why some amount of lignin always remain undissolved in the pulp after the cooking.

Although there exist a few investigations into this lignin, not much is known as yet. Kawamura[2] prepared acetylated thiolignin from acetylated beech kraft pulp and showed that the thiolignin is chemically combined with xylose. Kratzl[3] compared the acid lignin obtained from unbleached pulp with that obtained from wood, concluding that they are at least partly identical. By nitrobenzene oxidation Bland[4] showed that there exists not much difference between the nuclear structures of the lignins in wood, in waste liquor and in unbleached pulp. Kullgren[5] extracted lignosulfonic acid from unbleached sulfite pulp by prolonged washing of the pulp and showed that the lignin thus obtained contained one carboxyl group per sulfonic acid group.

As for the reasons for the difficulty of dissolution of the total amount of lignin in the case of the sulfite process, one or several of the following reasons is conceivable.

1) Residual lignin is not sulfonated sufficiently, 2) it is firmly combined to carbohydrate, 3) it goes into solution with difficulty because of the morphological structure of its fiber, and 4) it is condensed to other lignin units during the digestion. As has been reported preliminarily before[6], we have succeeded in dissolving residual lignosulfonic acid from unbleached sulfite pulp by a drastic beating in water, which causes the fibrillation of the fiber. By this treatment any morphological hindrance to the dissolution of the lignin can be expected to be diminished. As is well known, the primary wall and the other layer of the secondary wall are said to be distructed successively by beating, while the fibrillation proceeds gradually into the middle layer of the secondary wall[7], thus enabling the dissolution of the low sulfonated residual lignosulfonic acid.

Residual lignosulfonic acid was isolated from the unbleached sulfite pulp prepared from a mixture of *Picea jezoensis* (spruce) and *Abies mariana* (fir), and the chemical nature of the isolated residual lignosulfonic acid was investigated. The isolable yield of the residual lignosulfonic acid thus obtained from the unbleached pulp is about one fifth of the total amount of lignin present in the pulp.

Experimental

Extraction of the Residual Lignosulfonic Acid. —540 g. of unbleached sulfite pulp from the mixture of *Picea jezoensis* and *Abies mariana* (Sieber Zahl 52, cuproammonium disperse viscosity (Japan Industrial Standard) 18.0 were suspended in water (21 l.) and beaten with a Niagara type 1 to 1/2 pound beater (TAPPI-Standard T200 m-45) for up to 20 hr. During the course of the beating, the SR-value, chlorine absorption[8], permanganate number (TAPPI-Standard T214m-50), specific surface area and degree of polymerization of the beaten pulp were measured and are shown by curves I, II, III, IV and V respectively in Fig. 1. The relative viscosity of the pulp was measured according to the Japan Industrial Standard, the specific outer surface area, by immersing the pulp in a solution of benzo fast scarlet 4BS and measuring the decrease of the absorption at 506 mμ[9], and the degree of polymerization, according to Okada's method[10].

Curve I shows that the SR-value approaches 100 after 10~12 hr., while the chlorine absorption (curve II) and the permanganate number (curve III) decrease monotonously. Although the SR-value reaches its maximum after 10~12 hr., the specific surface area of the fiber (curve IV) continues to increase, showing the progress of fibrillation. The degree of polymerization of the beaten pulp decreases along curve V.

1) Presented briefly in this Bulletin, **31**, 660 (1958).
2) I. Kawamura and T. Higuchi, *J. Soc. Textile Cellulose Ind. (Japan)*, **9**, 454 (1953).
3) K. Kratzl and A. Graf, *Holzforsch. u. Holzverwert*, **9**, No. 4, 60 (1957); *Chem. Abstr.*, **52**, 1604i (1958).
4) D. E. Bland and C. Stamp, *The World's Paper Trade Review*, **21**, April, 1293 (1955).
5) C. Kullgren, *Svensk Papperstidn.*, **55**, 1 (1952).
6) K. Sato, K. Ebisawa and H. Mikawa, This Bulletin, **31**, 660 (1958).
7) H. W. Emerton, *Tappi*, **40**, No. 7, 542 (1957).
8) H. Okada and E. Hayakawa, *Cellulose Chem.*, **13**, 33 (1933).
9) E. F. Thode, J. W. Bedmesderfer and A. J. Chase, *Tappi*, **35**, No. 8, 379 (1952).
10) H. Okada, *Rayon World (Japan)*, **3**, 194 (1935).

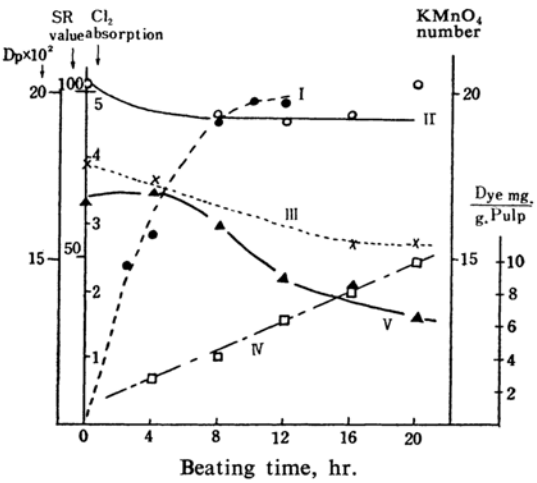

Fig. 1. Properties of the beaten unbleached sulfite pulp versus beating time. I, SR-value; II, Chlorine absorption; III, Permanganate number, IV, Specific surface; V, Degree of polymerization

The dissolution of the residual lignosulfonic acid was measured by the ultraviolet absorption spectra of the filtrate of the beaten pulp, which was diluted three times with water. Curve II in Fig. 2 shows the optical density at 280 mμ thus obtained, and curve III, the total amount of the dissolved lignosulfonic acid calculated from the optical density, assuming the molar extinction and methoxyl content of the lignosulfonic acid as 3000 and 11% respectively. As shown by curve II, the dissolved amount of lignosulfonic acid reaches its maximum at about 10~12 hr., although as stated previously the fibrillation continues to proceed even after this period of time. Curve I here is the same curve as curve I in Fig. 1.

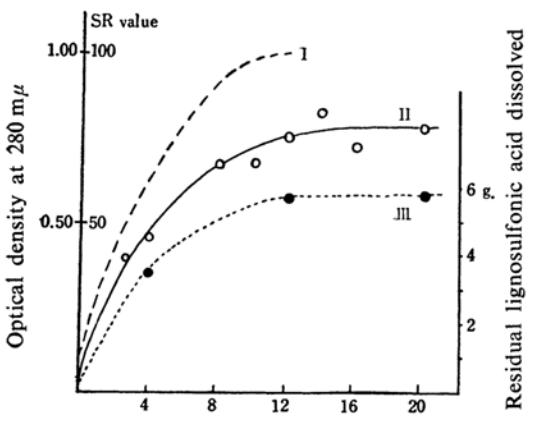

Fig. 2. Properties of beating water versus beating time. I, SR-value; II, Optical density of the beating water after being diluted three times with water; III, Calculated amount of the dissolved residual lignosulfonic acid.

After having been beaten for 20 hr., the pulp was separated by a centrifuge and washed with water, and the combined mother liquor and the washings (ca. 40 l.) were concentrated to 2 l. under 40°C in vacuo, centrifuged again in order to remove fine flocculating pulp fibers, and passed through ion exchange resin IR-120 in hydrogen form, after which the lignosulfonic acid was precipitated by adding 1-(*N*-piperidinoacetylamino)-naphthalene sulphate[11]. The precipitate was washed well with water, to which was added dilute sodium hydroxide solution until pH 8~9. After about one hour the separated free base was filtered and the filtrate passed through ion exchange resin IR-120 in hydrogen form, neutralized with barium carbonate until pH 6, centrifuged and poured into alcohol. The precipitated barium lignosulfonate was separated by centrifuge and then washed twice with alcohol, ether and petroleum ether successively. The yield was 5.5 g., which is not much less than the dissolved amount estimated from the optical density of the beating water (curve II, Fig. 2). As the total amount of the residual lignosulfonic acid contained in the pulp used is estimated as about 27.5 g., the isolated amount corresponds to about 20% of the total. The existence of no carbohydrate components in the sample was confirmed by paper chromatography after hydrolyzing the sample with 2% sulfuric acid at 100°C for 5 hr.[12] Anal. C, 45.36; H, 5.09; S, 3.73; Ba, 12.80; CH_3O, 11.12%.

Functional Groups of the Residual Lignosulfonic Acid.—As is well known, the conductometric titration curve of the lignosulfonic acid has two "breaks", the first being the completion of the neutralization of the sulfonic acid group. Richtzenhain proved[13] that lignin contains at least two types of phenolic hydroxyl groups; one is the phenolic hydroxyl group of the simple guaiacyl type (type I), and the other is that having a C-C side chain at the ortho position to the phenolic hydroxyl group of the guaiacyl type (type II). As was found by some of the present authors[14], the type I phenolic hydroxyl group was conductometrically titratable, while type II was untitratable; the second break represents the complete neutralization of the carboxyl group plus the type I phenolic hydroxyl group. It is possible to estimate the amount of both the types I and II phenolic hydroxyl groups separately by measuring the change in the $\Delta\varepsilon$-value[15] of the solution during the conductometric titration.

Barium salt of the residual lignosulfonic acid (500 mg.) was passed through ion exchange resin IR-120 in hydrogen form. The eluate was made up to 50 ml. and was titrated conductometrically with sodium hydroxide as usual (curve I, Fig. 3). The amount of sodium hydroxide consumed until the first break gives the amount of the sulfonic acid group, and that consumed between the first and the second break the amount of the carboxyl group

11) B. Leopold, *Acta Chem. Scand.*, 6, 64 (1952).
12) H. Toda and C. Hamada, *J. Jap. TAPPI*, 12, No. 5, 324 (1958).
13) H. Richtzenhain, *Ber.*, 83, 488 (1950).
14) H. Mikawa, K. Sato, C. Takasaki and K. Ebisawa, This Bulletin, 29, 245 (1956).
15) G. A. Erdtman, *Svensk Papperstidn*, 55, 745 (1952).

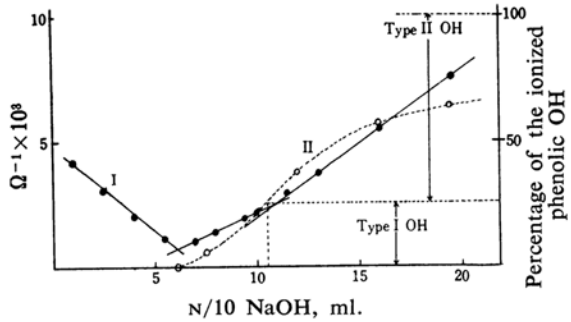

Fig. 3. Conductometric titration of the residual lignosulfonic acid. I, Conductivity; II, Ionization of phenolic hydroxyl group

plus the type I phenolic hydroxyl group. During the course of the titration the ultraviolet absorption spectra of the solution were measured by using a quartz cell 0.07 mm. thick. Curve II of Fig. 3 represents the percentage of the ionized phenolic hydroxyl group thus obtained. About 25% of the total phenolic hydroxyl group is ionized at the second break.

The amount of the type I phenolic hydroxyl group and the amount of the type II phenolic hydroxyl group were calculated separately, as was stated in a previous report[14]. Because, according to the $\Delta\varepsilon$-method of Erdtman[15], the amount of the total phenolic hydroxyl group is estimated as 0.23～0.19/CH_3O, the amount of the type I phenolic hydroxyl group is 0.06～0.05/CH_3O, that of type II, 0.17～0.14/CH_3O, and that of carboxyl group, 0.21/CH_3O. The amount of the sulfonic acid group is 0.32/CH_3O. The molecular formula of the residual lignosulfonic acid is thus expressed as follows:

$$C_9H_{10.55}O_{3.57}(CH_3O)_{0.95}(SO_3Ba/2)_{0.30}S^{neut}_{0.00}Ba^{excess}_{0.09}$$

in which $S^{neut}_{0.00}$ means non-acidic sulfur and $Ba^{excess}_{0.09}$, the amount of barium which is not combined with the sulfonic acid group.

Further Sulfonation of the Residual Lignosulfonic Acid.—As has been stated above, the degree of sulfonation of the residual lignosulfonic acid was only 0.32/CH_3O, much lower than the 0.6 of the ordinary lignosulfonic acid separated from the waste liquor. In order to know whether the residual lignosulfonic acid no longer has any sulfonatable group or if it has but remained unsulfonated during the sulfite cooking by, say, morphological reasons, further sulfonation of the residual lignosulfonic acid was attempted in a homogeneous solution.

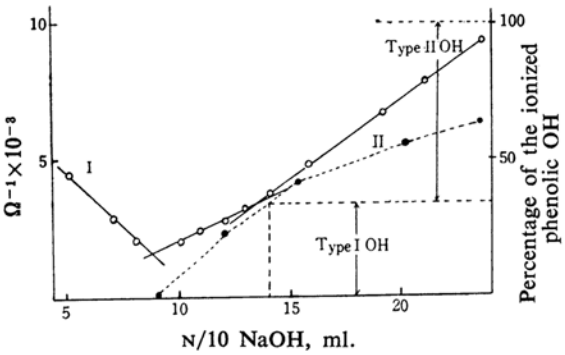

Fig. 4. Conductometric titration of the further sulfonated residual lignosulfonic acid. I, Conductivity; II, Ionization of phenolic OH

Residual lignosulfonic acid (2 g.) was dissolved in a cooking liquor of pH 1.8 (60 ml.) prepared from 5% sodium hydroxide solution and sulfur dioxide and heated at 135°C for 9 hr. The sulfonic acid was separated with 1-(*N*-piperidinoacetylamino)-naphthalene as usual and was obtained as barium salt. Anal. C, 39.92; H, 4.80; S, 5.28; Ba, 15.14; CH_3O, 10.30%. Total phenolic hydroxyl group, 0.24～0.19/CH_3O; type I phenolic hydroxyl group, 0.08～0.07/CH_3O; type II phenolic hydroxyl group, 0.16～0.12/CH_3O; carboxyl group, 0.26～0.25/CH_3O; SO_3H, 0.49/CH_3O. The molecular formula is as follows:

$$C_9H_{11.4}O_{4.08}(CH_3O)_{1.00}(SO_3Ba/2)_{0.49}S^{neut}_{0.01}Ba^{excess}_{0.05}$$

Discussion

The fact that the residual lignosulfonic acid in the unbleached sulfite pulp was at least partly dissolved out by drastic beating of the fiber in water seems to support strongly the thesis that this part of residual lignosulfonic acid remained undissolved in the fiber during the cooking because of morphological reasons. It is said that the residual lignin in the unbleached sulfite pulp is distributed across the whole section of the fiber, but the amount is larger near the outer surface[16] and near the inner surface around the lumen. As has been made evident in the present report, the dissolution of the residual lignosulfonic acid reaches its maximum when the SR-value of the beaten pulp reaches its maximum value of 100. Even though the outer specific surface of the fiber estimated by dye absorption continues to increase by prolonged beating, dissolution of any significant amount of the residual lignosulfonic acid was not observed any more. This fact will be well understood from the fact that during the beating process fibrillation proceeds from the surface of the fiber and that the amount of the residual lignin is comparatively larger near the outer surface of the fiber. As is shown in Table I, the residual lignosulfonic acid prepared carefully in the present paper contained no carbohydrates, although that prepared previously contained some. It seems, therefore, to be certain that there exists no chemical linkage between carbohydrates and the residual lignosulfonic acid obtained by beating.

16) G. Jayme and A. V. Köppen, *Das Papier*, **4**, 455 (1950).

TABLE I. FUNCTIONAL GROUPS OF THE RESIDUAL LIGNOSULFONIC ACID AND THE FURTHER SULFONATED PRODUCTS OBTAINED THEREFROM

C_9 basis	Sample			
	Residual lignosulfonic acid		Further sulfonated residual lignosulfonic acid	
	A	B	Prepared from A	Prepared from B
Total S	0.31	0.31	0.68	0.50
$SO_3Ba/2$	0.28	0.30	0.66	0.49
Neutral S	0.03	0.00	0.02	0.01
CH_3O	0.91	0.95	0.96	1.00
Ba excess	0.02	0.09	0.04	0.08
Total OH*	0.20～0.16	0.22～0.18	0.23～0.19	0.24～0.19
Type I OH*	0.05～0.04	0.06～0.05	0.09～0.07	0.08～0.07
Type II OH*	0.16～0.12	0.17～0.14	0.15～0.12	0.16～0.12
COOH	0.12～0.11	0.16～0.15	0.23～0.21	0.26～0.25
Type I/Type II	1/3	1/3	1/2	1/2
Molecular formula	**	***	****	*****

* Means phenolic hydroxyl group.

A Residual lignosulfonic acid prepared previously[6]. Values are corrected for the contamination of carbohydrate, which was estimated chromatographically. The amount of xylan, mannan and glucan was 1.23, 0.79 and 0.59% respectively.

B The same prepared in the present communication. Carbohydrate was not detected.

** $C_9H_{9.15}O_{3.74}(CH_3O)_{0.91}(SO_3Ba/2)_{0.28}S^{neut}_{0.03}Ba^{excess}_{0.02}$

*** $C_9H_{10.55}O_{3.57}(CH_3O)_{0.95}(SO_3Ba/2)_{0.30}S^{neut}_{0.00}Ba^{excess}_{0.09}$

**** $C_9H_{10.5}O_{3.31}(CH_3O)_{0.96}(SO_3Ba/2)_{0.66}S^{neut}_{0.02}Ba^{excess}_{0.04}$

***** $C_9H_{11.4}O_{4.08}(CH_3O)_{1.00}(SO_3Ba/2)_{0.49}S^{neut}_{0.01}Ba^{excess}_{0.08}$

Functional groups of the residual lignosulfonic acid and of the further sulfonated products obtained therefrom are summarized in Table I. The amount of the sulfonic acid group of the residual lignosulfonic acid, ca. 0.3 per C_9-unit, is low, of the same order of magnitude with that of the so-called low sulfonated lignosulfonic acid prepared from sulfonated wood by the Kullgren procedure, and also approximately half the amount of the sulfonic acid group of the ordinary lignosulfonic acid separated from waste liquor. 0.3 sulfonic acid groups per C_9-unit will be the lower limit of the degree of sulfonation which renders the lignin soluble. The degree of sulfonation could doubled by sulfonating further in the homogenous phase. Nearly half of the sulfonatable groups in lignin seems, therefore, to remain intact in the residual lignosulfonic acid.

The amount of the carboxyl group, 0.11～0.16, of the residual lignosulfonic acid is higher than that of low sulfonated lignosulfonic acid (0.08～0.1) and somewhat lower than that of ordinary lignosulfonic acid (0.16～0.17). The comparatively low degree of sulfonation and the low content of the carboxyl group in residual lignosulfonic acid seem to suggest that the action of the cooking acid is somewhat milder on the lignin in the fiber. The fact that the rather drastic condition of 135°C, for 9 hr., which nearly doubles the content of the carbonyl group in lignin, was required to elevate the degree of sulfonation to 0.5～0.6 seems to suggest that the sulfonatable group remaining in residual lignosulfonic acid is rather difficult to sulfonate in nature.

The ratio of the type I phenolic hydroxyl group to type II is about 1/3, being approximately the same as gymnosperm[17] α-lignosulfonic acid. The value is distinctly lower than that of low sulfonated lignosulfonic acid and of birch α-lignosulfonic acid. The total amount of the phenolic hydroxyl group is about the same as that of the ordinary α-lignosulfonic acid. Although the ratio of the type I phenolic hydroxyl group to type II, I/II, decreases somewhat with the further sulfonation of the low sulfonated lignosulfonic acid, the ratio increases from 1/3 to 1/2 with the further sulfonation of the residual lignosulfonic acid.

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17) H. Mikawa, K. Sato, C. Takasaki and K. Ebisawa, This Bulletin, **28**, 653 (1955).

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