On the State of Pentosan in Wood Pulps

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1. Introduction

Many discussions[1,2] have been made on the state of pentosan in wood pulps. However, as our previous report[3] showed, it is difficult to determine a small quantity of pentosan by the phloroglucin or bromate method. Accordingly, the conclusions reached do not seem to be correct. In this research, pentosan determinations by paper chromatography and by the colorimetric method with aniline were applied to the acid-hydrolyzed samples as well as to the alkali-extracted samples, and the state of pentosan in wood pulps was discussed.

2. Experimental Procedures and Results

(1) The Pentosan Contents of Acid-hydrolyzed Pulps.—Five g. each of sulfite rayon pulps from red pine (*Pinus densiflora* S. et Z.) and beech (*Fagus crenata* Blume) were hydrolyzed with 300 cc. of boiling 4N hydrochloric acid for 1, 3, 5 and 7 hours. Since recrystallization of split chains was observed during acid-hydrolysis,[4] the acid-hydrolyzed samples were treated with a boiling 1% sodium hydroxide solution for half an hour to eliminate[5] the recrystallized particles. The pentosan contents of the acid- and acid-alkali-treated samples were determined by paper chromatography.[6] The result is tabulated in Table I. The degrees of polymerization were determined from the viscosities of cupri-ethylene diamine solutions[7] of the samples.

TABLE I

THE PENTOSAN CONTENTS AND DEGREES OF POLYMERIZATION OF ACID-HYDROLYZED AND ACID-ALKALI TREATED PULPS

Time of Acid-Hydrolysis	Treatment	Red Pine			Beech		
		yield %	pentosan* %	D.P.**	yield %	pentosan* %	D.P.**
0	original	...	2.0	720	...	3.0	650
	alkali	88.2	1.25	710	92.6	2.0	620
1	acid	70.5	0.45	111	72.4	0.60	113
	acid-alkali	36.0	0.31	121	41.1	0.50	120
3	acid	47.9	0.30	102	49.2	0.30	102
	acid-alkali	23.9	0.22	87	25.0	0.20	98
5	acid	33.3	0.15	87	35.8	0.10	87
	acid-alkali	11.0	0.10	80	12.7	trace	92
7	acid	23.6	0.13	81			
	acid-alkali	7.1	0.05	80			

* % in the residue, determined by paper chromatography

** Cupri-ethylene diamine solution, $Km=8.0\times10^{-4}$

(2) The Pentosan Contents of Cold Alkali-treated Pulps.—Two g. each of red pine and beech pulps were treated with 50 cc. of 4–17.5% sodium hydroxide solutions for half an hour at 20°C, stirring every five minutes. The samples, pressed on a glass filter to make them free from the residual alkaline solution as far as possible, were treated again with 50 cc. of a sodium hydroxide solution of the same concentration and processed as before, washed successively with water, and 1% acetic acid solution and water, and dried. In another series of experiments, the cold alkali-treated samples whose cellulose micelles are more or less disordered were treated with 200 cc. of 2.5N sulfuric acid at 95–100°C for an hour to remove pentosan thoroughly. The pentosan contents of the samples were determined by the colorimetric method[3] and partly by paper chromatography. The results are tabulated in Table II and Table III.

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1) K. H. Meyer, "Hoch polymere Chemie" Vol. 2 (1940) p. 216; H. Maeda, *J. Text. Cell. Ind. Japan*, **1**, 669 (1945); H. Sobue, K. Matsuzaki, A. Hatano and Y. Arisawa, ibid., **8**, 79 (1952).

2) A. Meller, *Paper Trade J.*, **124**, No. 9, 104 (1947).

3) T. Abe, K. Matsuzaki, A. Hatano and H. Sobue, This Bulletin, **26**, 255 (1953).

4) H. G. Ingersoll, *J. Applied Phys.*, **17**, 924 (1946); J. A. Howsmon, *Textile Research J.*, **19**, 152 (1949); O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950); A. Meller, *J. Polymer Sci.*, **4**, 619 (1949); P. H. Hermans and A. Weidinger, ibid., **4**, 317 (1949).

5) H. Maeda, *J. Text. Cell. Ind. Japan.*, **1**, 651 (1945).

6) H. Sobue and A. Hatano, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **54** 460 (1951); **55**, 131 (1952).

7) Tappi Standard T230 Sm-50.

TABLE II

THE PENTOSAN CONTENTS OF COLD ALKALI- AND ALKALI-ACID-TREATED RED PINE PULPS

NaOH, %	Treatment	Yield, %	Pentosan,* %
4	Alk.	97.1	0.93 (0.9)
	Alk.-acid	92.4	0.69
6	Alk.	93.7	0.69 (0.6)
	Alk.-acid	90.4	0.46
8	Alk.	88.9	0.53 (0.5)
	Alk.-acid	85.4	0.35
10	Alk.	85.6	0.42 (0.3)
	Alk.-acid	82.6	0.24
12	Alk.	88.9	0.32
	Alk.-acid	85.4	0.21
14	Alk.	89.0	0.39
	Alk.-acid	86.4	0.19
17.5	Alk.	91.2	0.38
	Alk.-acid	87.5	0.22

* By colorimetric method, except ( ) which was determined by paper chromatography

TABLE III

THE PENTOSAN CONTENTS OF COLD ALKALI- AND ALKALI-ACID-TREATED BEECH PULPS

NaOH, %	Treatment	Yield, %	Pentosan,* %
4	Alk.	95.7	0.73
	Alk.-acid	92.9	0.68
6	Alk.	94.2	0.65
	Alk.-acid	91.4	0.52
8	Alk.	89.8	0.53
	Alk.-acid	86.9	0.38
10	Alk.	88.3	0.48
	Alk.-acid	82.8	0.22

* By colorimetric method

3. Discussion

The foremost interest would be the problem of whether or not the pentosan penetrates into the crystalline region.

From Table I, it is seen that the pentosan contents of the acid-treated pulps and acid-alkali-treated pulps decrease with the time of hydrolysis. The relationship between the yield of residue and the quantity of pentosan removed is shown in Fig. 1. Both the acid- and acid-alkali-treated pulps show a similar tendency, and it is seen that the pentosan content depends mainly on the yields of the residues. If the alkali-treatment helps to remove[5] the particles produced by recrystallization of split molecules in the amorphous region containing most of the pentosan, it would be expected that almost all of the pentosan could be removed. This, however, is not the case as can be seen from Table I and Fig. 1. In Fig. 1, the pentosan contents of the acid-alkali-treated pulps are somewhat higher than those of the acid-treated pulps, when the comparison is made between the samples whose yields of the residues are the same.

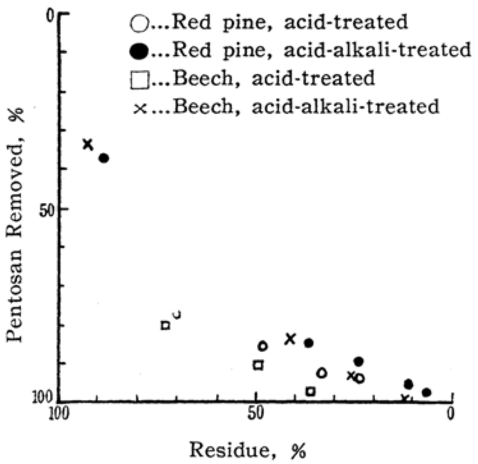

Fig. 1.—Relationship between residue and pentosan removed.

Pentosan removed is expressed as $(1-r)\times 100\%$, where r is the ratio of pentosan content in the treated pulp to that of the original pulps.

It has been asserted that the crystalline region of wood cellulose is 65% by X-ray method[8], and 60–70% by acid hydrolysis followed by dilute alkaline treatment.[5] In Fig. 1, even at 60–70% residue which is thought to consist almost entirely of the crystalline region, 0.5% of pentosan remains in the pulp.

The degrees of polymerization of the acid-alkali-treated pulps were expected to increase for the removal of the recrystallized particles (perhaps of very low D.P.). In Table I, the D.P.'s of the acid-alkali-treated pulps are not apparently different from those of the samples before alkaline treatment. This would be due to the degradation of the high molecular portion.

By using cold caustic solutions of concentrations over 10%, which are believed to be able to penetrate into the crystalline region of cellulose, the pentosan content was reduced to under 0.5%. The after-treatment by the acid of the residues thus treated gave a good effect for pentosan removal. Both pentosan and cellulose molecules in the crystalline region would have been disordered by the conc. alkalies to such an extent that they were readily attacked by the acid solution. Thus wood pulps containing 0.2% of pentosan

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[8] P. H. Hermans, "Physics and Chemistry of Cellulose Fibers", (1949), p. 517.

were obtained with 82–87% yield, although they are unsuitable for practical use.

These results suggest that the resistant pentosan chains share in building the crystalline region with cellulose chains, although larger portion of pentosan is found in the amorphous region. There remain as yet questions, whether or not the xylose units participate in mixed chain formation.

No great difference was observed between the behavior of pentosan in red pine and beech pulps.

It seems reasonable to deduce the following conclusion from the above discussion.

By intermicellar reactions such as hot alkaline treatment, the pentosan content in the purified pulp would not be reduced to under 0.5%, whereas by intramicellar reactions, such as cold alkaline refinement, the pentosan content could easily be reduced to under 0.5%. This will contribute to the purification processes of wood pulps, since the presence of pentosan is thought to be a cause of poorness in the reactivity of pulps to acetylation and xanthation.[9]

Summary

1. The pulps from the red pine and beech were hydrolyzed with boiling 4N hydrochloric acid solution for 1–7 hours and a part of the hydrolyzed pulps was treated with boiling 1% sodium hydroxide solution for half an hour to eliminate recrystallized particles. The pentosan content decreased as a function of the pulp yield. The degrees of polymerization of these samples were determined.

2. The pulps from the red pine and beech were treated with 4–17.5% sodium hydroxide solution for half an hour at 20° and this procedure was repeated. A part of the samples treated with the alkali was hydrolyzed with 2.5N sulfuric acid solution for one hour at 95–100°. The pentosan contents of these samples were determined.

3. The results show that it is difficult to reduce the pentosan content of wood pulp to under 0.5% by intermicellar reactions such as acid-hydrolysis or dilute hot alkaline refinement, whereas by intramicellar reactions such as cold concentrated alkaline refinement, it is easy to reduce the pentosan content to under 0.5%. The resistant pentosan seemed to be built in the crystalline region of wood cellulose.

4. It has no good effect for pentosan removal to eliminate the recrystallized particles produced by acid hydrolysis with dilute alkali, while acid treatment after cold alkaline refinement gave good result for pentosan removal.

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9) W. Klauditz, *Holz Roh-u. Werkstoff*, **4**, 314(1941); G. Jayme, *Sevensk Papperstidn.*, **50**, Hägglund Issue 117(1947); R. E. Dörr, *Angew. Chem.*, **53**, 292(1940).