Fractionation of Cellulose Acetate and Distribution of Non-Cellulosic Components between the Fractions

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Introduction

As raw materials for the production of cellulose acetate, cotton linters have usually been used, but recently wood pulps purified more than 95% α have been used, mixed with or without cotton linters. Also in Japan, studies of high-grade pulp for cellulose ester are now in progress.

It has generally been observed[1] that acetone solutions of cellulose acetates from wood pulp are hazy, and films and fibers produced are weaker in strength than those from cotton linters. It is important and interesting to make clear the cause of these defects of wood pulp although the haziness of the solution does not prevent their application to fibers.

In this research, secondary cellulose acetates from linters and pulp were fractionated and their chain-length distributions were compared, and viscosities in acetone and cupriethylene diamine solutions, acetic acid contents and pentosan contents of the individual fractions were determined.

Much[2] has been written about fractionation of secondary cellulose acetate but only recent investigations will be referred to here. Sookne et al.[3] fractionated cellulose acetate by precipitation with ethanol from acetone solution and obtained fifteen fractions. The acetic acid content remained constant for all fractions except three of very low chain length which showed slightly higher values. Most of the haze-producing material in the acetate was found to be contained in the higher-molecular fraction. But details of the experiment are not known in Japan. Howlett and Urquhart[4] fractionally dissolved acetate and found that the high-molecular fraction, which was low in acetic acid content, gave a hazy acetone solution. Scherer and Thompson[5] used the acetone-water-heptane system and D. P. of the first fraction was lower than that of the second. The acetic acid content of the fractions increased from 51.1 to 54.9% as the D. P. decreased on account of acetolysis. Wales and Swanson[6] believed the incomplete solubility of the first fraction to be caused by association between calcium ions and sulfuric half-ester groups or carboxyl groups of the polymer. Any further study of the incompletely soluble fraction has not yet been made.

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(2) L. H. Cragg and H. Hammerschlag, *Chem. Rev.*, **39**, 79 (1946).
(3) A. M. Sookne, H. A. Rutherford, H. Mark and M. Harris, *J. Res. Nat. Bur. Standards*, **29**, 123 (1942).
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(5) P. C. Scherer and R. B. Thompson, *Rayon & Synthetic Textiles*, **32**, No, 9, 69; No. 10, 51 (1951).
(6) M. Wales and D. L. Swanson, *J. Phys. & Colloid Chem.* **55**, 203 (1951).

Experimental Procedures and Results

The samples used were cellulose acetates from cotton linters, Rayaceta and a domestic pulp. The samles (each 5 g.) were dissolved in acetone to give 1% solution and fractionally precipitated with ethanol. The precipitant was added to give a slight precipitate in the solution, then the solution was warmed in a water bath to make it clear and kept standing in an incubator for 24 hours. The precipitate formed was separated from the supernatant liquid, washed with water and dried in a vacuum desiccator. The last fraction was obtained by evaporating and concentrating the solution and by filtering the precipitate on a glass filter. The D. P. calculated from the viscosity of acetone solution and the pentosan content of each fraction were tabulated in Tables 1—3. (in acetone $Km=9\times10^{-4}$ at 20°C.). The acetic acid content of each fraction was also determined. Fractions incompletely soluble in acetone showed slightly lower acetic acid content but the result was not clear as the accuracy of the determination was low, on account of the small quantity of the sample (0.1 g.). Then 20 g. of another acetate from Rayaceta was fractionated into five fractions and the D. P. from acetone solution, the D. P. from cupriethylene diamine solution, the acetic acid content and the pentosan content of each fraction were determined. The results are shown in Table 4. In this case, the first fraction was divided into two fractions, by redissolving in acetone, the upper hazy solution (F1S) and the under gel-like precipitate (F1P).

Table 1

Fractionation of Cellulose Acetate from Cotton Linters. AcOH 54.7%, D. P. 200, Pentosan under 0.02%

Fraction	Weight %	D. P.	Solubility in Acetone	Pentosan %
1	0.60	400	81.7	—
2	6.72	352	hazy	0.07
3	8.72	290	100	<0.02
4	9.30	276	100	<0.02
5	9.97	255	100	<0.02
6	8.88	224	100	<0.02
7	11.50	189	100	<0.02
8	3.68	184	100	<0.02
9	4.57	158	100	<0.02
10	4.70	140	100	<0.02
11	4.22	126	100	<0.02
12	6.98	111	100	<0.02
13	5.63	103	100	<0.02
14	15.16	59	hazy	0.04

Table 2

Fractionation of Cellulose Acetate from Rayaceta. AcOH 54.7%, D. P. 210, Pentosan 0.1%

Fraction	Weight %	D. P.	Solubility in Acetone	Pentosan %
1	0.20	—	—	—
2	3.63	260	85.3	0.5
3	4.25	300	26.9	1.0
4	3.58	353	92.4	0.25
5	5.11	396	100	<0.02
6	2.23	340	100	<0.02
7	14.50	308	100	<0.02
8	7.39	267	100	<0.02
9	6.23	233	100	<0.02
10	4.81	205	100	<0.02
11	7.35	189	100	<0.02
12	8.57	162	100	<0.02
13	5.35	131	100	<0.02
14	3.15	118	100	<0.02
15	9.87	101	100	<0.02
16	6.17	63	100	<0.02
17	7.58	35	yellowish hazy	0.1

Table 3

Fractionation of Cellulose Acetate from a Domestic Pulp. AcOH 55.7%, D. P. 261, Pentosan 0.3%

Fraction	Weight %	D. P.	Solubility in Acetone	Pentosan %
1	10.79	260	precipitate, soly. not determined	1.0
2	8.37	429	precipitate, soly. not determined	1.5
3	5.79	440	hazy	0.2
4	5.22	411	100	<0.02
5	8.95	342	100	<0.02
6	10.49	316	100	<0.02
7	5.39	277	100	<0.02
8	4.75	245	100	<0.02
9	8.71	197	100	<0.02
10	4.90	170	100	<0.02
11	5.78	147	100	<0.02
12	5.34	116	100	<0.02
13	4.23	83	100	<0.02
14	6.13	66	100	<0.02
15	5.16	35	82	0.1

Table 4

Fractionation of Cellulose Acetate from Rayaceta

Fraction	Weight %	D. P. in Acetone*	D. P. in $Cu(En)_2$**	Solubility in Acetone	AcOH %	Pentosan %
original	—	165	163	100	54.8	0.1
1S	8.52	217	203	hazy	54.8	0.3
1P	3.25	184	176	58	—	0.7
2	33.79	227	227	100	54.8	<0.02
3	17.36	162	163	100	54.6	<0.02
4	16.22	107	133	100	54.8	<0.02
5	20.86	66	68	100	55.0	0.03

* $Km=9.0\times10^{-4}$ for cellulose acetate at 20°C.
** $Km=8.8\times10^{-4}$ for cellulose at 20°C.

Discussion

From Tables 1—3, it is seen that the acetate from linters gives only 0.60% of the first incompletely soluble fraction and inversion of D. P. is not observed when solubility of the fraction is taken into consideration, whereas, in the case of the acetate from Rayaceta, the fractions from the first to the fourth are incompletely soluble in acetone and considerable inversion of viscosity is observed even when solubility of the fractions is considered. Scherer and Thompson[5] thought that this was due to the migration of the low-molecular portion into the acetone-insoluble fraction. But we believe this is not the case. It seems these fractions may have actually a low D. P..

In Table 4, the D. P.s of both F1S and F1P are lower than that of F2. We could not decide whether this was due to the presence of the haziness which would prevent the accurate determination of the concentration of the solution, or due to associated products in the solution. If the former is true the D. P. determined from the viscosity of the completely dissolved solution of the fraction would be higher. Therefore viscosity in cupriethylene diamine solution was determined.

Cellulose acetates are saponified and dissolved in cupriethylene diamine solution. Unesterified cellulose and esterified pentosan would be also dissolved and associated products would dissociate into molecular dispersion. The determination in diamine solution shows the same results as in acetone. D. P. of F1S is higher than that of F1P. This indicates that a part of F1S is a normal fraction which should have a higher D. P. than that of F2, if separately precipitated from the abnormal fraction in F1S, and have normal molecular shape. Then Scherer's opinion might be wrong. Abnormal materials included mainly in F1P and partly in F1S, having actually a low D. P., are responsible for the inversion of the D. P.

A comparison between chain-length distributions of the acetates from cotton linters and Rayaceta shows that the latter has a rather heterogeneous distribution, although their average D. P.s are almost the same. Our previous investigation,[7] as those of others,[8] showed that the chain-length distribution of a wood pulp is more heterogeneous than that of purified cotton and the heterogeneity does not disappear even if acid-hydrolysis takes place. Both the difference in the heterogeneity of the chain-length distribution of the acetates, which Malm could not prove experimentally, and the heterogeneity in chemical composition e. g. acetone-insoluble fractions, may account for the weakness in their mechanical properties and for their viscometric behavios.

Next, the pentosan content of each fraction was determined. The determination by phloroglucin gives about 1% of pentosan content even to pentosan-free materials such as glucose or linters, on account of oxymethyl furfural produced from hexose. The error due to oxymethyl furfural increases as the pentosan content decreases. A part of the error can be corrected by treating the wet precipitate of the phloroglucide with ethanol,[9] but a trace of pentosan (under 0.1% of the sample) would not be detected and determined. Therefore, determination of pentosan by paperchromatography[10] was adopted.

Tables 1—3 indicate that all fractions which give a hazy acetone solution or show incomplete solubility in acetone, include pentosan. The last fractions obtained by evaporating the solvent also include pentosan, but its quantity is small.

It is noticed that even the acetate from linters include pentosan, though it can not be detected from the acetate itself. It is concentrated in the first, second and the last fraction. The acetate from Rayaceta contains 0.1—1.0% pentosan in its initial fractions and the last fraction. The behavior of the acetate from a domestic pulp was almost the same.

These indicate that there is a clear relationship between pentosan content and the haziness of acetone solution of acetates as Jayme and Schenck[11] proved. It is observed that the greater the pentosan content of a fraction, the greater the haziness of its acetone solution or its acetone-insolubility. The acetates from wood pulp invariably include a higher content of the portions which show incomplete solubility in acetone and a higher content of pentosan. Table 4 shows that F1P contains more pentosan than F1S. The acetic acid content of each fraction remained almost constant. Since the acetic acid content of F1P could not be determined, it is still uncertain that the acetone-insoluble fractions are low-esterified cellulose.

Thus, it can not be decided whether the

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(8) L. Jörgensen, Dissertation, Oslo 1950; N. Glarén, Dissertation, Uppsala 1944.

(9) H. Sobue, K. Matsuzaki and T. Abe, unpublished work.

(10) H. Sobue, K. Matsuzaki, A. Hatano and U. Arisawa, *J. Soc. Tex. Cell. Ind. Japan*, **8**, 79 (1952); H. Sobue and A. Hatano, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **55**, 131 (1952).

(11) G. Jayme and U. Schenck, *Melliand Textilberichte*, **31**, 153, 230 (1950).

insoluble fractions are due to association by the salt bridge effect of calcium ions between carboxyl or sulfuric half-ester groups as Wales and Swanson[6] suggested, or due to the remaining structure (e. g. incompletely digested fragments) of the wood tissues which could be considerably acetylated but would not yield a mono-molecularly dispersed solutiou. In our opinion, both are responsible but the latter more so, because the hazy portions are always accompanied by pentosan, and the determination of the protein content of each fraction by paper chromatography revealed that the acetone insoluble fractions include it more than acetone soluble fractions. But it does not seem that all pentosan is combined with cellulose, a part of it is molecularly dispersed, and acetylated, saponified and precipitated, though most of it is removed in the saponification stage. (e. g. Rayaceta contained 0.5% pentosan, the acetate 0.15% based on cellulose)

Now we may say the following as to the acetylation and refining of wood pulp.

1. Pentosan in pulp must be removed as far as possible although most of it is removed during the ripening stage as above mentioned. Pentosan itself or pentosan-cellulose complex cause haziness of the acetone solution and result in heterogeneity of the acetate. Pentosan remained as an important index for the degree of the refinement of pulp.

2. Carboxyl and sulfuric acid groups must be removed as far as possible. Sulfuric acid groups can be removed in the stabilization process. Carboxyl groups are mainly formed during bleaching stages. In this respect, bleaching which does not accompany modification and degradation of cellulose, such as by sodium chlorite, is prefered.

3. Jayme classified acetylation characteristics of pulp into those inherent to pulp and those produced by pretreatments etc. All the above mentioned are referred to the characteristics inherent to pulp. Of course, pretreatments and drying conditions etc. (e. g. boiling after cold alkali refinement and the drying temperature must not be raised over 60°C. and the drying must not be continued until they become bone-dry) should be controlled strictly.

Experimental

Pentosan content was determined as follows. 0.2—0.3 g. of a sample was dissolved and degraded in 70% sulfuric acid, diluted to 2—3% and boiled under reflux for 8 hours. Saccharide solution refined by the usual method was developed by butanol-water-acetic acid mixture (4:1:1). Quantitative estimation was made by determination of the area of the spot or of the intensity of the light transmitted through the spot colored by aniline hydrogen phthalate. As the spots of glucose and xylose were overlapped slightly, the area method was generally adopted. Amino acid was colored by ninhydrine, and approximate estimation was made by its color intensity.

Cupriethylene diamine solution was prepared after T230 Sm—50.[12] The acetates were dissolved in this solution and kept under nitrogen atmosphere for 24 hours.

Acetic acid content was determined as follows. About 0.5 g. of a sample was dissolved in 50 cc. of acetone, saponified with 50 cc. of 0.2 N potassium hydroxide solution. After three hours, 50 cc. of 0.2 N hydrochloric acid solution was added and back titrated with the alkali.

As the D. P.s were determined in 0.6% solution, the solubilities were also determined in this solution. D. P.s of the incompletely soluble fractions were corrected for the solubilities when they were known. It was observed that the insoluble fractions became gradually dispersed as the concentration of the solutions was lowered. This is seen from the fact that F1P which was at first a gel-like precipitate showed 58% solubility by redissolving in acetone.

Summary

1. Three cellulose acetates from cotton linters, Rayaceta and a domestic pulp were fractionally precipitated from acetone solution with ethanol, and viscosity measurements in acetone solution and pentosan determinations by paper chromatography of the individual fractions were made.

2. Another acetate from Rayaceta was again fractionated into five fractions and viscosities in acetone and cupriethylene diamine solution and pentosan contents of the individual fractions were determined.

3. The results showed a close relationship between the initial acetone-insoluble fractions or in acetone haze-producing fractions and their pentosan content. These fractions include abnormal materials which show low viscosity (probably low D. P.) in cupriethylene diamine solution as well as in acetone. They are included much in the acetates from wood pulps.

4. It could not be decided whether these acetone-insoluble fractions were due to association by salt bridge effect of calcium ions between carboxyl or sulfuric half-ester groups, or due to the remaining structure of wood tissues.

5. The chain-length distributions of the cellulose acetates from wood pulp seem to be more heterogeneous than those from cotton linters.

(12) Tappi Standard.

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