

DETERMINATION OF HAZE AND INSOLUBLE RESIDUE AFTER ACETYLATION OF WOODPULP

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DETERMINATION OF HAZE AND INSOLUBLE RESIDUE

AFTER ACETYLATION OF WOODPULP¹

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Abstract

A convenient and rapid procedure is described for determining the haze-forming tendency of woodpulp after acetylation and the amount of insoluble residue in the acetate solution.

The method prescribes (1) a pretreatment that involves steeping the sample in water if it is air-dry, followed by steeping it in 85 percent acetic acid at room temperature, (2) displacement of the dilute acetic acid with glacial acetic acid, (3) acetylation with a mixture of glacial acetic acid, acetic anhydride, and sulfuric acid catalyst, and (4) measurement of haze and insoluble residue in the acetate solution before and after centrifuging. Approximately 5 hours are required for acetylation and measurement of haze.

For a commercial softwood sulfite pulp of acetylating grade, the initial haze was 1.6 to 3.0 percent and the insoluble residue was 0.13 to 0.32 percent; after centrifuging, the haze was 1.6 to 2.0 percent.

Introduction

In work at the U. S. Forest Products Laboratory on the purification of woodpulp for chemical conversion, the need arose for a rapid method of measuring the

¹This work was done in association with the late Ralph M. Kingsbury, Forest Products Laboratory chemist.

²Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

haze-forming tendency of pulps and the amount of insoluble residue that forms after acetylation. A low haze content is an important requirement of cellulose acetate to be used in the production of high-luster yarns, plastics, and lacquers. The insoluble residue should be low to facilitate filtration of cellulose acetate solutions. Residues can also cause breaks in the yarns during the spinning operation.

Acetylation procedures found in the literature and by direct inquiry involve rather lengthy treatments that include pretreating the pulp, acetylating it to the primary or triacetate stage, hydrolyzing the triacetate to acetone-soluble secondary acetates and, in some instances, purifying the product. 3, 4, 5

In the present study, various pretreatments, acetylation conditions, and catalysts that are described in the literature were investigated. Conditions for effective activation and acetylation are described in the proposed method and the amounts of haze and insoluble residue are measured directly on the triacetate in glacial acetic acid solution to avoid the time-consuming hydrolysis and purification treatments. The results of this work provide a measure of the quality of an acetate pulp, from the standpoint of haze and insoluble residue, by comparison with the results of the same tests on a standard pulp of acceptable quality.

Exploratory Experiments

The exploratory experiments on the effect of variations in activating treatments and in acetylation conditions were conducted on a viscose grade of cotton linters. Later experiments and tests of the final method were made on a sample of a softwood sulfite pulp of acetylating grade. The results of these experiments (table 1) show that the woodpulp acetylated somewhat more readily than the cotton linters.

For convenience in handling, a sample of 10 grams of pulp, moisture-free basis, was selected for acetylation in all of the experiments. Seventy-five grams of acetic anhydride and 250 grams of glacial acetic acid were used. These amounts gave solutions that were not too viscous for the determination of haze and insoluble residue.

³-Heuser, Emil, Shockley, William, and Van den Akker, J. A. Determination of the Suitability of Wood Pulp for Acetylation. Tappi 32 (6):251-253, 1949.

⁴-Seymour, G. W. The Chemistry of Cellulose Acetate-Colloid Chemistry, 6:887, 1946.

⁵-Unpublished communication with Merle Heath, Institute of Paper Chemistry, April 21, 1950.

In the first acetylation experiment (table 1) a sample of cotton linters was pretreated by steeping for 10 minutes in glacial acetic acid as recommended by Jayme and Schenk.⁶ It was then drained and acetylated at 25° C. using 2 grams of sulfuric acid for the catalyst. The reaction was very slow and had not reached completion in 24 hours, as is shown by the high haze value of 6.5 percent. In the second experiment, the same proportion of catalyst was used, but the temperature was raised from 27° to 43° C. during the addition of the acetic anhydride and held at 43° C. for approximately 2 hours (table 1). The reaction rate was still too slow, however. The rate of acetylation improved somewhat when the amount of catalyst was increased to 8 grams and the starting temperature increased to 30° and 35° C. in the third and fourth experiments. The haze values in these tests were still considerably higher than published values for acetylating pulps even though the amount of catalyst was several times the amount usually recommended. Perchloric acid and a mixture of chlorine and sulfur dioxide were found to be unsatisfactory catalysts.

In experiments 5 through 12 (table 1), pretreatments similar to one described in an acetylation process patented by Goff and others⁷ were tried to obtain more effective activation and acetylation of the pulp. In these pretreatments, the pulp was soaked in distilled water, drained, and steeped 30 minutes in 85 percent acetic acid at 25° C., drained again, and steeped 15 minutes in glacial acetic acid at 60° C. The results of experiments 5 and 6 showed that a short soak in hot water or a longer soak in cold water in conjunction with the acid steeps were equally effective activating treatments. The subsequent acetylation of cotton linters using 2 grams of catalyst was complete in 2 hours as was shown by a constant haze value. Under the same conditions the acetylation of a sample of the woodpulp was complete in 30 minutes (experiments 7 and 8). In experiments 9 to 12, it was found that the glacial acetic steep at 60° C. could be omitted from the pretreatment and that the amount of sulfuric acid catalyst could be decreased to 0.3 gram without seriously decreasing either the rate or extent of the acetylation. Viscosity data given in table 2 show that the smaller amount of catalyst caused considerably less degradation of the cellulose than did the larger amount.

Later, tests were made to determine: (1) the effect of soaking dried pulp in glacial acetic acid in place of the pretreatment with hot water and 85 percent acetic acid, and (2) the possibility of using the time of acetylation required

⁶Jayme, G. and Schenk, U. Test for Showing the Suitability of Pulps for Acetylation. Paper Industry and Paper World 31(3):376-377. 1949.

⁷Goff, Lionel E., Sheldon, Lyle M., Herzog, Milton L., and Olsen, F. Wood Cellulose and Method of Making. U. S. Patent 2,187,710 (Jan. 16, 1940).

to reach minimum haze as a measure of pulp reactivity. The time of acetylation and the minimum haze content of the acetate solution from the woodpulp were approximately tripled by this pretreatment. The change in haze content was too gradual to provide an accurate measure of time to minimum haze when applied on high-grade commercial acetate pulp and experimental pulps of varied reactivity.

Procedure for Acetylation and Determination of Haze and Insoluble Residue

The conditions for the activation and acetylation of pulps and the determination of haze and insoluble residue in the acetate solutions are described in the following paragraphs.

Activating Pretreatment

A weight of sample equivalent to 10 grams of pulp on the moisture-free basis is used for acetylation. If the pulp is in the air-dry condition, it is dispersed from either bulk or sheet form, by means of a suitable agitator, in about 500 milliliters of water at a temperature near the boiling point, and steeped 1 hour without additional heating. The steeped pulp is drained with suction and weighed. The steeped and drained pulp containing about 75 to 80 percent water, or pulp without steeping if not previously dried, is mixed at room temperature with an amount of glacial acetic acid that will produce an acid concentration of 85 percent by weight. After 30 minutes, the sample is filtered with suction and washed twice with 50-milliliter portions of glacial acetic acid, also with suction, after which the wet pad is weighed.

Removal of water from dilute suspensions of pulp and also acetic acid from acid-treated samples is done with a Büchner funnel fitted with a 100-mesh stainless steel screen. The filtrate in all instances is refiltered through the pulp mat to recover any fibers that pass through the screen in the initial filtration.

Acetylation

The weighed sample is transferred to a reaction vessel in a constant temperature bath at 30° C. A pint, wide-mouth fruit jar, with the metal disk in the lid replaced with rubber gasket material about 1/8 inch thick, is satisfactory for this purpose. This rubber disk should have one hole in the center for entry of a stainless steel agitator shaft and a second hole, off

center, for the introduction of chemicals and a thermometer. It appears to be unnecessary to seal these holes during the reaction. A variable-speed agitator is desirable.

Glacial acetic acid at room temperature, containing 0.3 gram (0.17 milliliter) of 1.84 specific gravity sulfuric acid, is added to the acid-wet pulp sample in the reaction vessel. The weight of acetic acid to be added is the amount required to bring the total weight of pulp and acids to 260 grams. (The composition of this acetylating mixture and those used by the industry and others 4, 5, 6, 7 are compared in table 3.)

The vessel is closed, the agitator started, and 75 grams of acetic anhydride are added over a period of 15 minutes. Within this time, the temperature is raised to $43^{\circ} \pm 1^{\circ}$ C. and maintained until two successive values for haze of solution are essentially the same. This time will occur within 1 hour from the start of the addition of the acetic anhydride for a pulp suitable for acetylation.

When the minimum haze value is reached, approximately 90 grams of the solution are withdrawn, weighed, divided into two portions of equal weight, and centrifuged. A centrifuge that is equivalent to a size 2, International Equipment Company centrifuge with head No. 234 and two 50-milliliter tubes rotated at 2,000 revolutions per minute for 30 minutes is satisfactory for this operation. Haze value for the supernatant liquid is then determined and the insoluble residue from both tubes is collected by filtration. Part of the original solution can be retained at $25^{\circ} \pm 1^{\circ}$ C. for 24 hours to determine any change in the amount of haze or residue during this interval.

Measurement of Haze

Haze in the triacetate solution is measured by the light scattering effect of the solution by using a Model 402-E Lumetron instrument or equivalent, a cell of 10 millimeters light path, and a narrow band filter with a transmission peak at 595 millimicrons.

The sample cell containing the test solution is placed adjacent to the photocell, Position 1 of the Lumetron, and the balance photocell is adjusted to give a zero reading on the galvanometer scale when the slide wire dial is set at 100. The sample cell is then moved as close to the light source as possible, Position 2, and the slide wire dial adjusted to bring the galvanometer reading to zero. The haze value, in percent, is the difference between 100 and the slide wire dial reading when the sample cell is in Position 2. These values are essentially independent of the color of the acetate solution.

This procedure corresponds in principle to ASTM Designation D672-45T.⁸ However, the distance between Positions 1 and 2 for the Lumetron instrument is 15 centimeters as compared to 18 inches in the ASTM method.

Determination of Insoluble Residue

The insoluble residues are washed out of the two sample tubes with glacial acetic acid into an RA98 alundum crucible on a suction filter. The residue is washed first with four 20-milliliter portions of glacial acetic acid and then with four 30-milliliter portions of chloroform, after which the crucible and contents are dried to constant weight at about 105° C. The amount of residue is reported in percent based on weight of original pulp.

Instances occur with pulps of low quality for acetylation in which the residue plugs the crucible to an extent that washing is practically impossible.

When this happens, another weighed portion of the original solution must be centrifuged, the supernatant liquid decanted, glacial acetic acid added to the tube and mixed with the residue, followed by centrifuging and decanting the clear liquid. This treatment is repeated twice and is followed by the usual filtration and washing.

Comparisons on Experimental and Commercial Pulps

The amount of haze and insoluble residue of several experimental pulps and a commercial acetate-grade pulp are compared in table 4. These results show that the amount of haze in the triacetate solutions from dried pulps depends on the type of activation treatment before acetylating. Soaking the dried pulps in water (2 hours at near 100° C. or 24 hours at room temperature) lowered haze values to about the same level as those of triacetate solutions from undried pulps. Soaking in glacial acetic acid was much less effective than the water soak and resulted in different relative haze values for the various pulps.

The haze contents of acetate solutions from the experimental pulps were considerably higher than those of the acetate solution from the commercial acetate-grade pulp. In most instances, however, there was very little difference in the amount of insoluble residue in these solutions.

⁸-American Society for Testing and Materials. Tentative Method of Test for Haze in Transparent Plastics by Photoelectric Cell. ASTM Designation: D672-45T.

In the laboratory of a commercial acetate manufacturer, tests showed that some of the aspen pulps, despite their relatively high haze, were superior to the commercial acetate-grade pulp in filterability and viscosity of the acetate solutions. These pulps had bleach numbers 2182, 2195, 2224, and 2232. The higher haze values of the experimental pulps do not appear to be due to differences in the alpha cellulose, pentosan, or ether-soluble material in the pulps since the composition of bleach 2182 was almost the same as that of the commercial pulp, yet its haze value was 5 to 7 times that of commercial pulp. However, the higher haze values correspond with higher pentosan content of the birch pulps, bleaches 1904, 1969, and 2053.

No attempt was made to correlate the amount of haze or the insoluble residue in triacetate solutions with those of acetone solutions of secondary acetates from the same pulps.

Conclusions

After a suitable pretreatment, pulps ranging in quality from experimental textile-grade viscose pulps to commercial acetate-grade pulps can be acetylated in 1 to 3 hours with a mixture composed of 25 parts glacial acetic acid, 7.5 parts of acetic anhydride, and 0.03 parts of sulfuric acid (97 percent) to 1 part pulp.

Dried pulps can be activated by soaking 1 hour in hot water or 24 hours in cold water, followed by a 30-minute steep in 85 percent acetic acid.

The reproducibility of the method is satisfactory, and the difference in haze content of triacetate solutions is sufficient to differentiate the haze-forming tendency of different pulps. However, the amounts of haze did not correlate with other important characteristics of cellulose acetate solutions, such as filterability and viscosity.

Variations in the amount of insoluble residue in the triacetate solutions of different pulps were small, 0.13 to 1.41 percent. Although this residue did not correlate with the amount of haze, it may provide an indication of the filterability of cellulose acetates made from the various pulps.

The time required to reach minimum haze value is not a reliable measure of the reactivity of the pulps toward acetylation.

Table 1.--Effect of activation treatments and acetylation conditions on the acetylation of commercial cotton linters and softwood sulfite acetate-grade pulp

Pulp	Experiment No.	Pretreatment	Acetylation ¹		Haze	Percentage of residue ²			
			Sul-furic acid ³	Temperature			Initial	After 24 hours	
			Start:Final	Centri-fuged	Total	Centri-fuged			
			Initial:Final	Initial:Final	Initial:Final	Initial:Final			
			Centri-fuged	Centri-fuged	Centri-fuged	Centri-fuged			
			24 hours	24 hours	24 hours	24 hours			
			Percent	Percent	Percent	Percent			
			Per-cent	Per-cent	Per-cent	Per-cent			
			Min.	°C.	°C.	cent			
Cotton linters:	1	(4)	2.0	75	28	25	6.5	2.8	0.18
Do.....	2	(4)	2.0	130	27	43	70.7		
Do.....	3	(4)	8.0	150	30	43	21.7	.8	
Do.....	4	(4)	8.0	150	35	43	5.3		
Do.....	5	(5)	2.0	90	30	43	3.2	1.3	0.09
Do.....	6	(6)	2.0	30	32	43	3.2	1.7	.08
Woodpulp	7	(5)	2.0	30	30	43	1.6	1.6	.19
Do.....	8	(6)	2.0	30	30	43	1.8	1.5	.13
Do.....	9	(6)	.3	60	30	43	2.1	1.8	.18
Do.....	10	(7)	.3	60	30	43	2.3	1.8	
Do.....	11	(7)	.3	60	30	43	2.2	1.7	
Do.....	12	(7)	.3	45	30	43	2.1	1.7	.32

¹Sample of 10 grams (moisture-free basis), 250 grams glacial acetic acid, and 75 grams acetic anhydride.

²Based on cellulose.

³Specific gravity 1.84.

⁴Steeped 10 minutes in glacial acetic acid.

⁵Dispersed in distilled water at 100° C., allowed to cool 2 hours, then steeped 30 minutes in 85 percent acetic acid at 25° C., and 15 minutes in glacial acetic acid at 60° C.

⁶Soaked 24 hours in distilled water, steeped 30 minutes in 85 percent acetic acid at 25° C., and 15 minutes in glacial acetic acid at 60° C.

⁷Soaked 24 hours in distilled water and steeped 30 minutes in 85 percent acetic acid, then washed twice with glacial acetic acid.

Table 2.--Viscosity of cellulose triacetate solution made from commercial softwood sulfite acetate-grade pulp

Acetylation ¹		Viscosity	
Catalyst	Time	1 hour ²	2 hours ²
G.	Min.	C.p.s.	C.p.s.
2.0	30	125	112
.3	45	415	405

¹Ten grams pulp; 250 grams glacial acetic acid, and 75 grams acetic anhydride.

²After start of the acetylation.

Table 3.--Composition of typical acetylating mixtures

Materials	Composition, in parts, of acetylation mixtures proposed or used by				
	FPL	Industry as reported by Seymour	Goff patent	Jayne and Schenck	Heath
Cellulose	1	1	1	1	1
Acetic acid	25.0	5.6-16.5	7.0	24.8	5.7
Acetic anhydride	7.5	1.8-3.1	2.2	7.5	2.6
Sulfuric acid	.03	.006-.15	.026	.2	.028

Table 4.--Chemical composition and the properties of the triacetate solution of commercial and experimental acetylating pulps

Bleach No.	Pulp			Triacetate solution ¹					
	Wood	Type	Alpha cellulose	Pentosan	Condition and treatment before acetylation	Haze	Residue		
			Percent	Percent		Initial	Initial		
1368	Coigue	Sulfite ²	92.5	4.5	Dried, Resoaked in water	19.0	17.7	17.8	0.28
1368	do	do ²	92.5	4.5	do	19.0	15.9	20.0	.27
1504	Southern pine	Prehydrolysis-kraft ³	91.7	3.9	do	14.4	17.8	26.2	1.41
2061	do	do ³	92.4	2.5	Wet	9.3	14.0	18.0
2070	do	do ³	do	9.5	13.6	21.2	.40
1904	Paper birch	Sulfate	95.5	11.1	Dried, Resoaked in water	58.5	54.1	48.2
1969	do	Prehydrolysis-kraft ³	91.8	8.8	do	20.6	18.8	20.4	.23
1969	do	do ³	91.8	8.8	do	27.6	18.2	28.0	.57
2053	do	Prehydrolysis-kraft ⁴	91.8	5.6	Wet	12.3	11.0	13.0	.13
2053	do	do ⁴	91.8	5.6	do	12.4	11.0	11.0	.38
2143	Aspen	Sulfite ²	96.6	do	7.713
2140	do	do ²	96.9	do	7.019
2182	do	do ²	96.3	.3	do	14.0	12.5	13.5	.30
2182	do	do ²	96.3	.3	Dried, Resoaked in water	9.7
2182	do	do ²	96.3	.3	Dried, Resoaked in water ⁵	11.024
2195	do	do ²	94.4	1.5	Wet	10.013
2195	do	do ²	94.4	1.5	Dried, Soaked in acetic acid ⁶	14.9
2224	Aspen	Prehydrolysis-kraft ⁷	97.3	2.0	Wet	10.0	9.530
2224	do	do ⁷	97.3	2.0	Dried, Resoaked in water	11.5	9.7
2224	do	do ⁷	97.3	2.0	Dried, Soaked in acetic acid ⁶	21.0	16.0
2232	do	do ⁷	95.6	2.5	Wet	13.3	12.543
2232	do	do ⁷	95.6	2.5	Dried, Resoaked in water	11.5
2232	do	do ⁷	95.6	2.5	Dried, Soaked in acetic acid ⁶	23.5	21.5
.....	Softwood	Sulfite ⁸	96.5	.8	Dried, Resoaked in water	1.6	1.6	2.2	.19
.....	do	do ⁸	96.5	.8	do	1.8	1.5	2.0	.13
.....	do	do ⁸	96.5	.8	do	2.1	1.818
.....	do	do ⁸	96.5	.8	do	3.0	2.022
.....	do	do ⁸	96.5	.8	Dried, Soaked in acetic acid ⁶	8.2
.....	do	do ⁸	96.5	.8	do	7.0	6.3

¹Acetylation conditions: wet pulp soaked 30 minutes in 85 percent acetic acid, washed with glacial acetic acid and acetylated at 30° to 45° C. with 25 parts glacial acetic acid, 7.5 parts acetic anhydride and 0.03 to 0.2 parts sulfuric acid.

²Ammonia base.

³Prehydrolysis in water, heating period 90 minutes to 170° C., zero minutes at 170° C.

⁴Prehydrolysis in water, heating period 90 minutes to 170° C., 15 minutes at 170° C.

⁵Dried pulp extracted with ether before the water soak.

⁶Glacial, 3 to 4 hours at 38° to 40° C. The soak in 85 percent acetic acid before acetylation was omitted.

⁷Prehydrolysis in water, heating period 90 minutes to 170° C., 30 minutes at 170° C.

⁸Commercial acetate grade.