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An Investigation of Haze in Cellulose Acetates Made from Wood Pulps

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AN INVESTIGATION OF THE HAZE IN CELLULOSE ACETATES MADE FROM WOOD PULPS

A thesis submitted by

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INTRODUCTION

Cellulose acetate has attained a substantial importance in the production of synthetic fibers, films, and molded products. Until about 15 years ago the cellulosic raw material for this product was exclusively cotton linters. Then in Europe, and later in the United States, the advance of technology and the shortages of war times brought on the use of specially purified wood pulps. Although these pulps are now used extensively, cotton linters must still be used if a high quality product is to be obtained.

In this country the wood pulps which are used for acetylation purposes are chiefly sulfite pulps from spruce or hemlock, whereas in Europe the pulps are also produced from hardwoods by the nitric acid process or by kraft pulping following an acid hydrolysis. Even after extensive purification wood pulps yield acetates whose solutions are turbid; these solutions are said to be hazy or to contain haze. It is desirable for the pulp manufacturer to produce pulps cheaply and in high yield which will not yield excessive amounts of haze and which will acetylate readily. From the standpoint of the finished product the haze is troublesome mainly where clarity is of importance, as in the manufacture of films. During the manufacture the haze causes trouble in the filtration of acetone solutions of the acetate, thus increasing the operating costs through time losses and filter expenses. It can be seen that an understanding of the haze constitution and its formation in acetylation is of primary importance for the commercial utilization of wood pulps for acetylation purposes.

HISTORICAL REVIEW

Experience has shown that the tests which are ordinarily used to characterize celluloses, such as alpha-cellulose, copper number, uronic acids, and cuprammonium solution viscosity, correlate poorly with the suitability of the

celluloses for acetylation purposes. Two qualities are generally said to determine the suitability of celluloses for acetylation, namely, the reactivity and the purity. Reactivity, or activity, denotes the speed and thoroughness of the acetylation reaction. The cellulose must be purified either because the impurities form insoluble acetates, or because they shield the cellulose so as to make it inaccessible to the reagents. The pulp manufacturer faces the dilemma that treatments which are necessary to purify pulps often cause them to become unreactive (1).

In recent years laboratory methods of determining the suitability of celluloses for acetylation have been developed which are based on a sample acetylation and subsequent evaluation of the product. Jayme and Schenk (2) have described a laboratory procedure for acetylating a pulp using a high ratio of reactants to cellulose and a long acetylation time. According to this procedure the triacetate in a solution of the acetylating medium was evaluated by its original turbidity, by the amount of coarse insoluble material removed by centrifuging, and by the turbidity after centrifuging. The effect of the reactivity of the pulp was separated from other effects by acetylating with and without an activation pretreatment with acetic acid (3). A similar procedure was reported by Heuser, Shockley, and Van den Akker (4) who used a modification of the transparency meter for determination of the turbidity, thus eliminating the effect of color in the determination. Frey and Schwalenstöcker (5) have criticized these methods because of the extreme reaction conditions, and because the criteria for suitability of the acetates are not significant for the acetate manufacturer's purposes. They recommended a test acetylation under conditions designed to simulate commercial conditions.

The reaction was carried out until the reaction mixture became clear. The pulp was evaluated by the acetylation time, and by the filterability, viscosity, and clarity of the triacetate solution. A determination of the activity of the pulp was made by a comparative acetylation after activation with water at room temperature.

The Du Pont Company (6) evaluates experimental acetates by measuring viscosity at two concentrations, the amount of undispersed material which settles out of acetone solution, the clarity and filterability of an acetone solution, and the color stability.

Jayme and Schenk (7) believed that the highly dispersed fraction of the haze, as evidenced by the turbidity of the acetic acid solution of the triacetate after centrifuging, was caused by hemicelluloses. On the other hand, the undispersed portion, that which was removed by centrifuging the acetic acid solution of the triacetate, was ascribed to the generally unreactive nature of the pulp. This view was supported by a positive correlation between the pentosan and mannan contents of various pulps and the turbidities of their acetates, and by the fact that the amounts of undispersed residue were decreased by activation pretreatments of the pulps. An analysis of their data shows that the mannan in the pulps also correlated with the amount of undispersed material.

It seems certain that hemicelluloses form haze because their acetylated derivatives are not acetone-soluble but are highly swollen, although Jayme (8) maintains that xylan, mannan, and even holocellulose can be acetylated to form soluble derivatives under the proper conditions. Millet and Stamm (9) acetylated the water-soluble hemicellulose fraction from aspenwood and obtained a chloroform-soluble product. The 1 and 5% sodium hydroxide extracts formed

poorly soluble products when acetylated. Wethern (10) acetylated two hemicellulose fractions from black spruce chlorite holocellulose. Neither product was soluble in organic solvents.

Jayme (11) found that xylan, extracted by hot alkali from straw formed an acetylated product which gave clear solutions in acetic acid. A xylan removed by cold alkaline extraction from straw gave an acetylated product which was turbid in acetic acid solution. Neither of these products was acetone-soluble. Whistler (12), from studies on various xylans, reports that a high grade (high molecular weight) xylan diacetate is insoluble in most solvents. When the diacetate is degraded it becomes soluble first in pyridine, then chloroform, and finally acetic acid. This may explain the findings of Jayme mentioned above. Yundt (13) acetylated a purified barley straw xylan; the diacetate was insoluble in the solvents tried. He attempted a partial de-esterification to improve the solubility without success. Sobue and Fujimura (14) acetylated beech xylan; it acetylated more rapidly than cellulose, but the acetate was only slightly soluble in acetic acid, pyridine, halogen compounds, and acetone. Partial saponification did not increase the acetone-solubility.

Patterson (15) acetylated ivory nut mannan with acetic acid, acetic anhydride, and sulfuryl chloride catalyst. After twenty-four hours at 70°C., about a third of the total starting material had been acetylated and could be dissolved in chloroform. The acetate showed a tendency to gel in chloroform. The mannan from orchid tubers has been isolated and acetylated with pyridine and acetic acid by Pringsheim and Liss (16) to the triacetate; the product was soluble in chloroform, acetic acid, and nitrobenzene. The mannan which was extracted from ivory nut with 10% sodium hydroxide was acetylated by Klages and Niemann (17) to form a chloroform-soluble acetate.

The work on isolated hemicelluloses shows generally that they form acetates which are insoluble in acetone, but which may be soluble in acetic acid. This indicates that the haze in the acetic acid solution of the triacetate may be different than the haze in the acetone solution of the diacetate. The non-cellulosic polysaccharides which are present in purified pulps are resistant to extraction and may differ physically or chemically from the isolated hemicelluloses which have been acetylated.

Other causes of insolubility or poor solubility are found in certain minor functional groups. Roos (18) maintains that oxycellulose interferes with the acetylation. Malm, Smith, and Tanghe (19) found that the salt effect--i.e., the increase in acetone-solution viscosity caused by washing an acetate with aqueous solutions of calcium salts, was correlated with the content of carboxyl groups and sulfuric acid ester groups. This effect was believed to be caused by cross-links through the divalent calcium atom. Magnification of these effects may cause complete insolubility. The effects of very small amounts of cross linkages can be very great as Mark (20) has pointed out. Howlett and Urquhart (21) state that haze can be caused by sulfate groups linked with calcium. However, Caille (22) found that the smallest molecular weight fractions, isolated by ultrafiltration, contained the greatest percentage of sulfate groups. Deripasko (23) was able to solubilize primary cellulose acetates by reprecipitation from acetic acid solution, by means of which the sulfate groups were removed.

The effects of certain inorganic cations, particularly calcium, magnesium, or sodium, are thought to be harmful. A number of patents have as their goal the removal of calcium, magnesium, or sodium salts. Engelmann (24) claims that uronic acids are bound to calcium which is not readily split off; consequently

these groups persist in the acetates and cause insolubility. He found that both uronic acids and calcium were concentrated in the haze-containing fractions of various cellulose acetates.

Some doubt is cast on the effect of divalent ions on haze by an experiment reported by MacClaren (25). Pulps which were carefully washed with distilled water to exclude calcium ions were acetylated and formed "muddy" acetates. Mellor (26) believes this to be due to the high polarity of free carboxyl groups which causes them to be more strongly bonded within the cellulose fiber thus decreasing the reactivity.

The activity of cellulose toward the acetylation reaction is affected adversely by any treatment which decreases its tendency to swell in acetic acid. As measured by the temperature increase during acetylation, (27) the impure celluloses usually show a greater reactivity toward the acetylation mixture than cotton linters. Staudinger, Dohle, and Heick (28) classified celluloses in three groups according to their reactivity toward acetic anhydride and pyridine:

1. Natural celluloses are semiactive despite activation treatments.
2. Mercerized celluloses are inactive but become active when swollen with water if the water is subsequently removed by displacement with organic liquids which do not swell cellulose.
3. Regenerated celluloses are inactive but become highly active when activated as in the above case.

Jayme (27) acetylated an ordinary grade of dissolving pulp and obtained 25% of the pulp as an undispersed residue in which all hydroxyl groups were acetylated. When this pulp was refined with 10% sodium hydroxide and acetylated,

he obtained 67% of the pulp as a residue which was only 6% acetylated. This illustrated the effect which purification treatments often have on the reactivity. The purified pulp could then be activated by heating with acetic acid. The acetate produced from the activated pulp contained a residue of 8% which was 90% acetylated.

Centola and Pancirolli (29) acetylated a cellulose that had been artificially cross-linked with formaldehyde. Its behavior was similar to that of unreactive celluloses, indicating that poor reactivity is caused by cross links.

Malm (1) states that turbidity of cellulose acetate is caused by non-uniform reactivity; consequently, anything which promotes differences in activity should be avoided in the production of pulp for acetylation purposes.

The method of pulping seems to have a decided effect on the suitability of pulps. Sulfate pulps are unreactive and cannot be activated by the usual treatments. If the sulfate cook is preceded by an acid hydrolysis, the pulp can be purified to give an acceptable pulp. MacKinney (30) investigated these differences and found that an acid hydrolysis following sulfate pulping was not effective in producing a suitable pulp. Frey and Schwalenstöcker (5) state that the sulfate process does not free the cellulose molecules sufficiently. In this connection Dolmetsch, Franz, and Correns (31) have investigated the swelling behavior of sulfite and sulfate pulps by various reagents. The outer layer of the secondary wall in sulfate pulps is not affected by acid hydrolysis, whereas the secondary wall of sulfite pulps develops cracks in the cross direction.

Jayme and Köppen (32) found that prehydrolysis of wood followed by sulfate pulping produced a better pulp for acetylation purposes than did sulfite pulping.

They believe that the prehydrolyzed kraft pulp had a more uniform distribution of hemicelluloses than the sulfite pulp, thus allowing a more uniform reaction.

Ritter (33) says that the nature of the haze can be determined by following the acetylation under the microscope. The reaction leaves behind undissolved fiber bits which constitute the haze. Haas (34) using the same method found that insoluble substances were formed from incomplete dispersion of the inner layer of the secondary wall.

There is a possibility that the skin substance is related to the haze in cellulose acetates. The skin substance is the outer layer of the cell wall which is observed as an insoluble "skin" when the cellulose is dissolved in cupramonium hydroxide. Brauns and Lewis (35) isolated this skin substance from western hemlock sulfite pulp by means of its insolubility in cuprammonium solution. It consisted of a polysaccharide containing no apparent mannose and galactose and formed an insoluble acetate.

The material which imparts the turbidity to acetate solutions--i.e., the haze, has been isolated in a few instances although it was probably not free of soluble cellulose acetate. Sookne, et al. (36) fractionated a commercial acetone-soluble acetate by fractional precipitation with water from acetone solution. The fraction which precipitated first contained the hazy material. This fraction contained a large amount of ash and could be fractionated into a chloroform-soluble fraction, an acetone-soluble fraction, and an insoluble fraction. Engelman (24) investigated acetates prepared from purified celluloses from various sources including linters, hardwoods, softwoods, and annual plants (reeds). The least soluble fractions of the acetates, as isolated by fractional precipitation, contained the haze and most of the uronic acids, pentosans, and

ash, and had a higher percentage of calcium in the ash. These fractions showed a greatly increased tendency to associate in solution, as shown by a decrease in viscosity with increased rate of shear.

PRESENTATION OF THE PROBLEM

The object of the thesis was to isolate the haze from a typical acetate made from coniferous wood pulp. This haze was to be characterized physically and chemically to ascertain what differences were responsible for its insolubility. An attempt was to be made to determine what substances in the pulp gave rise to the haze. The ultimate goal of this thesis was to clarify the present knowledge as to the causes of haze in wood pulps.

It has been mentioned above that the haze causes difficulty by the plugging of filters. However, the methods of haze isolation used in this thesis did not include filtration; consequently, the material which is most troublesome from the filtration standpoint may not have been isolated and studied. Filtration was omitted because of the difficulty of recovering haze from the filter and because a filter retains successively smaller particles as the filter becomes plugged and the pore size decreases.

For the purposes of this thesis, the haze in cellulose acetates has been defined in a dual manner--i.e., as any material which can be removed by centrifuging from acetone solution, and as any material which imparts a high turbidity to an acetone solution. Neither of these classifications includes material which is not molecularly dispersed. They may, however, exclude some material which is not molecularly dispersed but whose refractive index is so near to that of acetone that it does not cause the solution to be turbid.

RAW MATERIALS

Four acetate samples were obtained as starting materials for the isolation of haze. Two of these were commercially suitable acetates, one prepared from cotton linters and the other from wood pulp. The wood pulp was prepared from softwoods by the sulfite process by Rayonier, Incorporated, and had the designation Rayaceta (37). These "commercial acetates," which contained very little haze, are designated throughout the thesis as "linter acetate" and "pulp acetate," respectively.

The other two acetates were prepared in the laboratory; they were obtained through Dr. Blume of the Du Pont Company research department. Both of these acetates were prepared from a viscose grade of wood pulp made by Rayonier, Incorporated, from softwoods and designated Rayacord. These acetates were very hazy. Both were prepared by conventional procedures--i.e., activation with acetic acid followed by acetylation with acetic acid, acetic anhydride, and sulfuric acid catalyst. The acetates do not differ greatly except that one was degraded more in preparation. These acetates were designated by the Du Pont Company as SW-51-385 and SW-51-539. They are designated throughout the thesis as "experimental acetate I" and "experimental acetate II." The results of tests made by the Du Pont Company to evaluate these acetates are given in Table I.

TABLE I

COMPARATIVE SPECIFICATIONS OF EXPERIMENTAL ACETATE SAMPLES

	Exp. Acetate I	Exp. Acetate II
Combined acetyl, %	39.3	39.7
Viscosity of a 24% soln. in acetone, empirical units	615	300
Specific viscosity of a 0.091% soln. of the acetate in 92% acetic acid	0.180	0.164
Deposit -- the amount of material which settles out of a 1.5% acetone soln. in 24 hours on an arbitrary scale	25	20
Clarity -- the depth in mm. at which a black spot just appears in 7% acetone soln.	55	65
Filterability -- the lb. of 15% acetone soln. which can be filtered (at 75 p.s.i.) per sq. ft. of a standard filter paper	22	40
Color stability -- the color referred to an arbitrary scale after accelerated aging	7	10

A sample of the viscose pulp used to prepare the experimental acetates was obtained. The alpha-cellulose content of the pulp, as determined by Institute Method 421 (38), was 93.6%. The pulp was also hydrolyzed and the hydrolyzate was analyzed by paper partition chromatography as will be described below. The percentages of total sugars in the hydrolyzate were 95% glucose, 3% mannose, and 2% xylose.

The present investigation was concerned primarily with the experimental acetate II of which a large sample was obtained. The other acetates were investigated largely for comparison purposes.

GLOSSARY

The original acetates and the fractions obtained from them are given designations in the sections on raw materials and isolation of haze. These designations will be used throughout the thesis and consequently are summarized here for reference purposes. If further clarification is desired, Figure 1, page 19, and the sections in which the designations are presented should be consulted.

Centrifuged acetate -- the acetate which remained after centrifuging to remove coarse haze.

Centrifuged hazy fraction -- the portion of the total hazy fraction which remained after centrifuging to remove coarse haze.

Coarse haze -- the coarse material removed by centrifuging an acetone solution of cellulose acetate.

Commercial acetates -- the cellulose acetates which were prepared on a commercial scale and were acceptable for use in the trade.

Dispersed hazy fraction -- the haze-containing fraction which was removed by fractional precipitation of the supercentrifuged acetate.

Experimental acetates -- the very hazy acetates which were prepared in the Du Pont Company laboratories from a viscose-grade wood pulp.

Experimental acetate I -- the first experimental acetate sample.

Experimental acetate II -- the second experimental acetate sample.

Fine haze A -- the fine material removed by supercentrifuging an acetone solution of cellulose acetate.

Fine haze A + B -- the fine material removed by supercentrifuging the centrifuged hazy fraction.

Fine haze B -- the fine material removed by supercentrifuging the dispersed hazy fraction.

Linter acetate -- the commercial acetate which was prepared from cotton linters.

Pulp acetate -- the commercial acetate which was prepared from wood pulp.

Supercentrifuged acetate -- the acetate which remained after supercentrifuging the centrifuged acetate to remove fine haze A.

Supercentrifuged hazy fraction -- the remainder of the total hazy fraction after removal of coarse haze, fine haze A, and fine haze B.

Total hazy fraction -- the haze-containing fraction removed by fractional precipitation of the original acetate.

EXPERIMENTAL PROCEDURES AND RESULTS

TURBIDITY MEASUREMENT

One of the criteria established for the presence or absence of haze was based on the turbidity of the acetates in acetone solution. The turbidity was measured with the transparency meter as described by Heuser, Shockley, and Van den Akker (4). The apparatus consisted essentially of a light source, a photocell, and a galvanometer for measuring the photocell current. The acetate solution in a transmission cell of 1 cm. thickness was placed between the light source and the photocell and adjacent to the light source; the galvanometer reading at this position measured the parallel transmission. A reading with the cell adjacent to the photocell measured the total transmission. The turbidity was the percentage of the total transmitted light which was scattered and was calculated according to the equation: percentage turbidity = 100 (1 - parallel transmission/total transmission). The cells used in this work had turbidity values of 0.5 to 1.3% when filled with acetone; no correction was made for the blank. Six measurements were usually made giving results which were precise to 0.5% turbidity.

Solution concentrations were determined by pipetting a known volume of solution into a tared beaker and weighing the solids after drying in an oven at 105°C. The concentration was then adjusted to that at which the measurement was to be made, either at 1, 2, or 4%.* The concentration measurements were least accurate at high concentrations because of inaccuracies in pipetting

* All concentrations of cellulose acetate solutions are given as percentages where 1% = 1 gram / 100 ml.

viscous solutions, but turbidity measurements were most precise at high turbidities or high concentrations. Consequently, the concentrations used were based on a compromise between these factors.

ISOLATION OF HAZE

The acetate sample was dissolved in acetone at 4% concentration and centrifuged for 15 minutes in the International Equipment Company, centrifuged (size 1, type C) at 2000 r.p.m., at which speed the average acceleration was 5.7×10^5 cm./sec.^{2}. The supernatant solution was then decanted from the sediment, which was washed in the centrifuge bottle three times with acetone; the washings were combined with the original supernatant solution. The combined solutions were designated the "centrifuged acetate." The sediment was washed into a beaker with acetone and allowed to dry in the hood at room temperature; this fraction was designated "coarse haze." Formation of tough, horny films of the hazy materials was prevented by adding benzene to the suspension; the dried precipitate then had a powdery form. The centrifuged acetate was diluted to 2.5% concentration in acetone and centrifuged in the Sharples supercentrifuge at 23,000 r.p.m.; at this speed the acceleration at the rotor wall was 1.3×10^7 cm./sec.^{2}. The solution was injected into the supercentrifuge rotor through a fine nozzle, having an orifice diameter of 1 mm., under a head of one meter of solution. After passing the acetate solution through the supercentrifuge, 300 ml. of acetone were passed into the rotor to displace the acetate solution which remained, and the supercentrifuge was stopped. The solution which remained within the rotor drained into a pan and was combined with the solution which had passed through the supercentrifuge. The sediment was washed from the wall of the rotor with acetone, and the suspension was then poured into a beaker. The precipitate was suspended in

acetone and washed by passing through the supercentrifuge once more. The washings were combined with the solution which had passed through the rotor supercentrifuge; this composite solution was designated "supercentrifuged acetate." The sediment was washed out as before and allowed to dry at room temperature; it was designated "fine haze A."

This treatment did not suffice to remove all of the hazy material from the acetates. A number of unsuccessful attempts were made to remove substantially all of the haze. Among these were filtration through sintered glass, supercentrifuging at high dilutions, supercentrifuging of solutions containing small amounts of water and alcohol, batch supercentrifugation, fractional precipitation from acetone solution with water and alcohol, and filtration through magnesol.

The only successful method found was to fractionally precipitate the supercentrifuged acetate in acetone solution with benzene. This precipitant had the advantage that the fractions could be dried or the benzene could be removed by evaporation without increasing the turbidity through hornification. In carrying out a fractional precipitation it was found necessary to precipitate a large fraction in order to separate all of the hazy material; this large fraction was subsequently reprecipitated several times to remove soluble cellulose acetate.

The supercentrifuged acetate solution was evaporated to 5% concentration. To 900 ml. of solution in a 2-liter flask, a total of 950 ml. of benzene was added with stirring, causing a high turbidity in the suspension. The suspension was heated to 50°C. to dissolve the precipitate. The solution was allowed to stand overnight at room temperature, and the supernatant clear

solution was then decanted from the precipitate. The precipitate without drying was redissolved in acetone at about 4% concentration, and benzene was added slowly with stirring until precipitation began. The mixture was heated to 50°C. and allowed to stand for two days to precipitate. If the supernatant liquid was turbid the mixture was stirred and heated with a small additional amount of benzene and precipitated once again. The supernatant liquid was decanted and added to the clear acetate removed in this manner until the clear acetate which could be removed by a single refractionation step was less than 0.5% of the original acetate. This required six or more refractionation steps. In each case the criterion for complete precipitation was the clarity of the supernatant solution, which was judged visually in actual operation. The combined supernatant clear solutions were designated the "clear fraction"; the final precipitated fraction was designated the "dispersed hazy fraction."

The dispersed hazy fraction was diluted to 0.5% with acetone and supercentrifuged using the procedure given above. This solution contained small amounts of benzene, approximately 5%, from the fractionation step. The material removed in this step was designated "fine haze B"; the fraction which remained was designated the "supercentrifuged hazy fraction."

A simpler scheme for isolating the haze was evolved from the above procedure. The "total hazy fraction" was first fractionally precipitated with benzene from a 4% solution of the original acetate and refractionated several times in the manner described above. The "coarse haze" was removed from the total hazy fraction by centrifuging in the manner described above; the supernatant liquid was designated the "centrifuged hazy fraction." A fraction designated as "fine haze A + B" was removed by supercentrifuging the centrifuged hazy fraction at 0.5% concentration in the manner described above. The

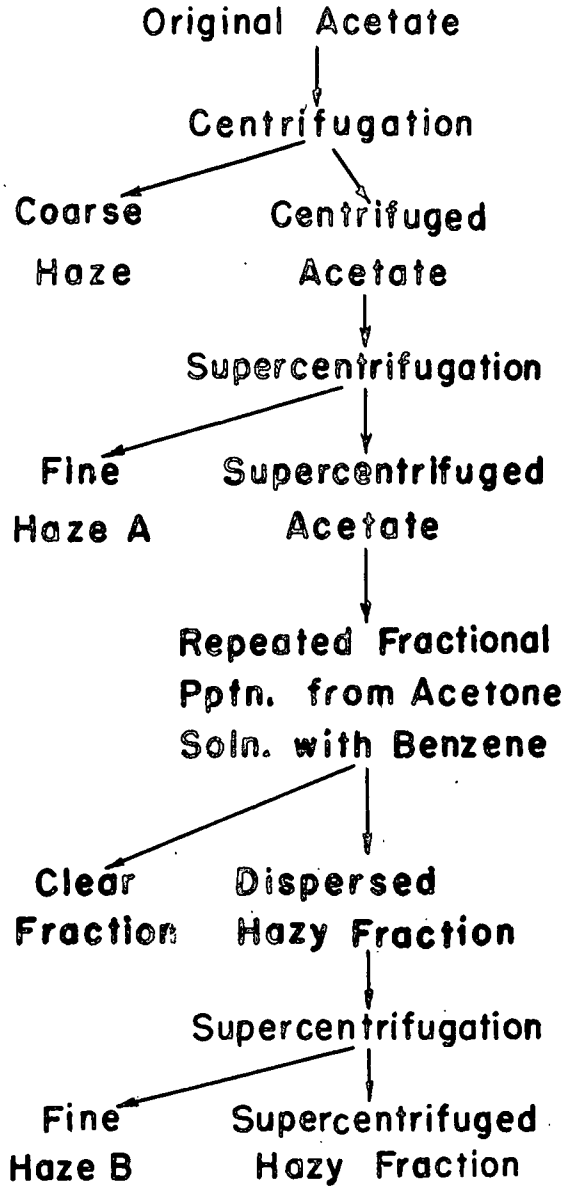
material which passed through the supercentrifuge was desigrated "supercentrifuged hazy fraction." The flow diagrams for these schemes are shown in Figure 1.

The reproducibility of the fractionation procedure was indicated by the results of three separations made according to the second scheme of haze isolation. Three 400-gram batches of experimental acetate II were fractionated with total hazy fraction yields of 18.0, 20.0, and 19.3%.

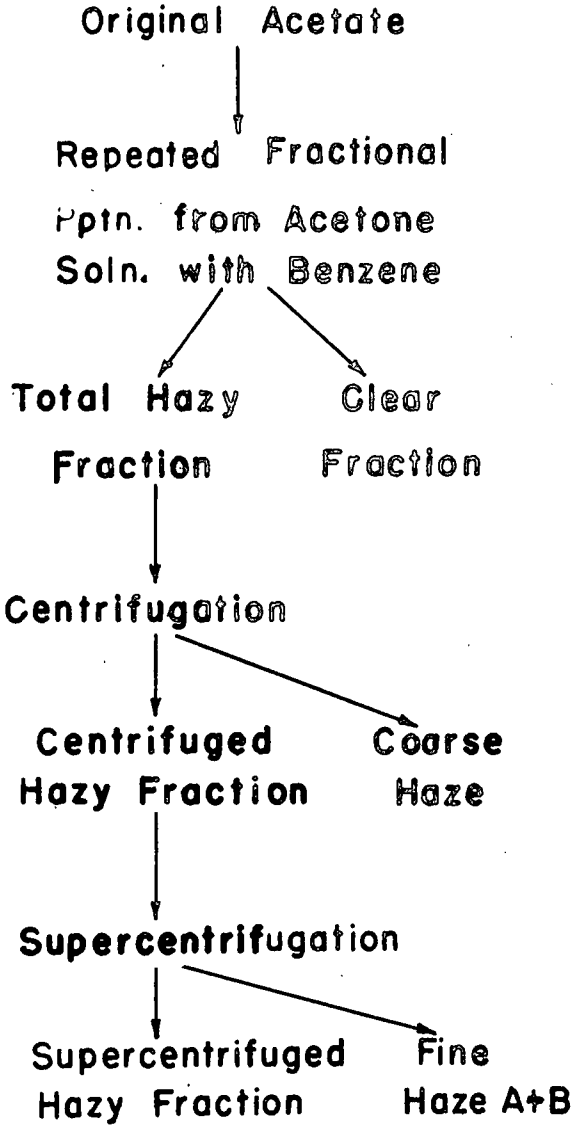
A further removal of haze could also be accomplished by supercentrifuging an acetone solution of the supercentrifuged hazy fraction to which 20% benzene had been added. The isolation by supercentrifuging from mixed solvents was not pursued any further.

FILTERABILITY OF HAZE FRACTIONS

Qualitative tests of the filterability were made on the experimental acetate II, the clear fraction, and the total hazy fraction isolated therefrom. One hundred milliliters of each sample at 2% concentration were filtered through a medium porosity fritted glass funnel. One hundred milliliters of acetone filtered through the filter under a vacuum of 560 mm. of mercury in 1 minute and 22 seconds. Under the same conditions, 100 ml. of clear acetate solution filtered in 67 minutes. The original acetate seemed to plug the filter so that only one fourth of the solution had filtered after 12 hours. The hazy fraction plugged the filter in much the same way.



Scheme I.



Scheme II.

Figure I. Schemes for the Isolation of Haze from Cellulose Acetate Solutions.

COMPARISON OF ISOLATION METHODS

The two schemes of isolation of haze from experimental acetate II were compared, primarily because both methods had been used during the course of the work, and it was desirable to know if the two separation schemes gave similar results. For this purpose the turbidities and yields of the supercentrifuged hazy fractions were compared, and the yields of the coarse haze and fine haze were compared as shown in Table II.

This comparison showed that there was little difference between the two schemes of isolation. Consequently the coarse hazes and the supercentrifuged hazy fractions, isolated by either scheme, were considered to be equivalent. The fine haze A combined with fine haze B, both isolated by scheme I, were considered to be the equivalent of fine haze A + B, isolated by scheme II.

COMPARISON OF THE ACETATE SAMPLES

The acetate samples were compared by the isolation of coarse haze

TABLE II

COMPARISON OF ISOLATION METHODS

	Scheme I	Scheme II
Turbidity at 1% conc. of supercentrifuged hazy fractions, %	17.7	18.8
Yield, %, based on original acetate		
Coarse haze	0.3	0.2
Fine haze A	1.9	- -
Fine haze B	0.7	- -
Fine haze A + B	2.6	2.4
Supercentrifuged hazy fraction	16.7	16.5
Total hazy fraction	19.6	19.1

and fine haze A according to scheme I. The turbidities of the solutions of the acetates were measured after centrifuging and after supercentrifuging. The yields of haze were determined in each case. In addition the yield of dispersed hazy fraction from the pulp acetate was compared with that from experimental acetate II, These values are compared in Table III.

TABLE III

COMPARISON OF ACETATE SAMPLES

Sample	Linter Acetate	Pulp Acetate	Experimental Acetates I	Experimental Acetates II
Turbidity, %, at 2% conc.				
Centrifuged acetate	2.9	4.3	24.2	25.3
Supercentrifuged acetate	2.3	3.1	9.2	13.8
Yields of haze, %, based on the original acet.				
Coarse haze	0.1*	0.15*	0.5	0.3**
Fine haze A	0.3	0.3*	1.4	1.9**
Dispersed hazy fraction	- -	13.5	- -	17.4

*Average of two determinations.

**Average of five determinations.

Even the commercial acetates contained material which could be removed by centrifuging and supercentrifuging, although the amounts were much less than in the case of the experimental acetates. After supercentrifuging the turbidities of the experimental acetates were much greater than those of the commercial acetates. The dispersed hazy fraction from the pulp acetate was almost as large as that from the experimental acetate II.

The turbidity of the clear fraction from the experimental acetate II was compared with that of the linter acetate after centrifuging. The turbidities at 4% concentration were 3.2 and 5.0% respectively.

PHYSICAL EXAMINATION

LIGHT MICROSCOPE

The coarse haze and fine haze A from the experimental acetate II in acetone suspension were examined under the light microscope. They appeared as small, irregularly shaped masses. The saponified coarse haze was also examined in a water suspension, which was more easily prepared. This fraction contained some whole fibers and fiber fragments. There was no indication that the haze particles were derived from some particular layer of the cell wall or that they had any morphological significance.

Examination of the coarse haze fractions from the linter acetate, pulp acetate, and experimental acetate I showed the presence of fibers and fiber fragments in these fractions also.

ELECTRON MICROSCOPE

Attempts were made to form films from the fine haze A from experimental acetate II for examination with the electron microscope. These attempts were not successful because the films were weak; they disintegrated when heated by the electron beam. Films were formed, at thicknesses of approximately 0.15 mu, of both the clear fraction and the centrifuged hazy fraction from experimental acetate II. The films were formed by dipping a microscope slide into a 0.5 to 1% acetone solution. The acetate dried on the glass and was removed by floating onto water. Electron

micrographs of these films are shown in Figures 2 and 3 at a magnification of 36,000 diameters. The films show slight differences; in contrast to the film from the clear fraction, the hazy fraction contains a large number of indistinct particles which appear as thick spots in the film, as though highly swollen particles were present at these points before drying. A thinner film of the hazy fraction, formed at 0.3% concentration, as shown in Figure 4 has a large number of discrete holes; evidently the thin areas of the film broke up in drying and the film was held together by a network of thick regions.

SOLUBILITY

The haze from experimental acetate II was generally insoluble. The dispersed hazy fraction could be redispersed in acetone. The fine haze A could be partially redispersed in acetone or acetic acid; it was dispersed by chloroform and methanol (9:2) to form a slightly turbid sol. It appeared to dissolve in pyridine but could be removed by centrifuging the clear pyridine solution. This indicated that the appearance of solution was caused by a close match between the refractive index of the haze and the solvent. Formic acid dissolved the fine haze A + B. The solution was still slightly turbid, and a small amount of material, about 0.1%, was not soluble and could be removed with a coarse filter.

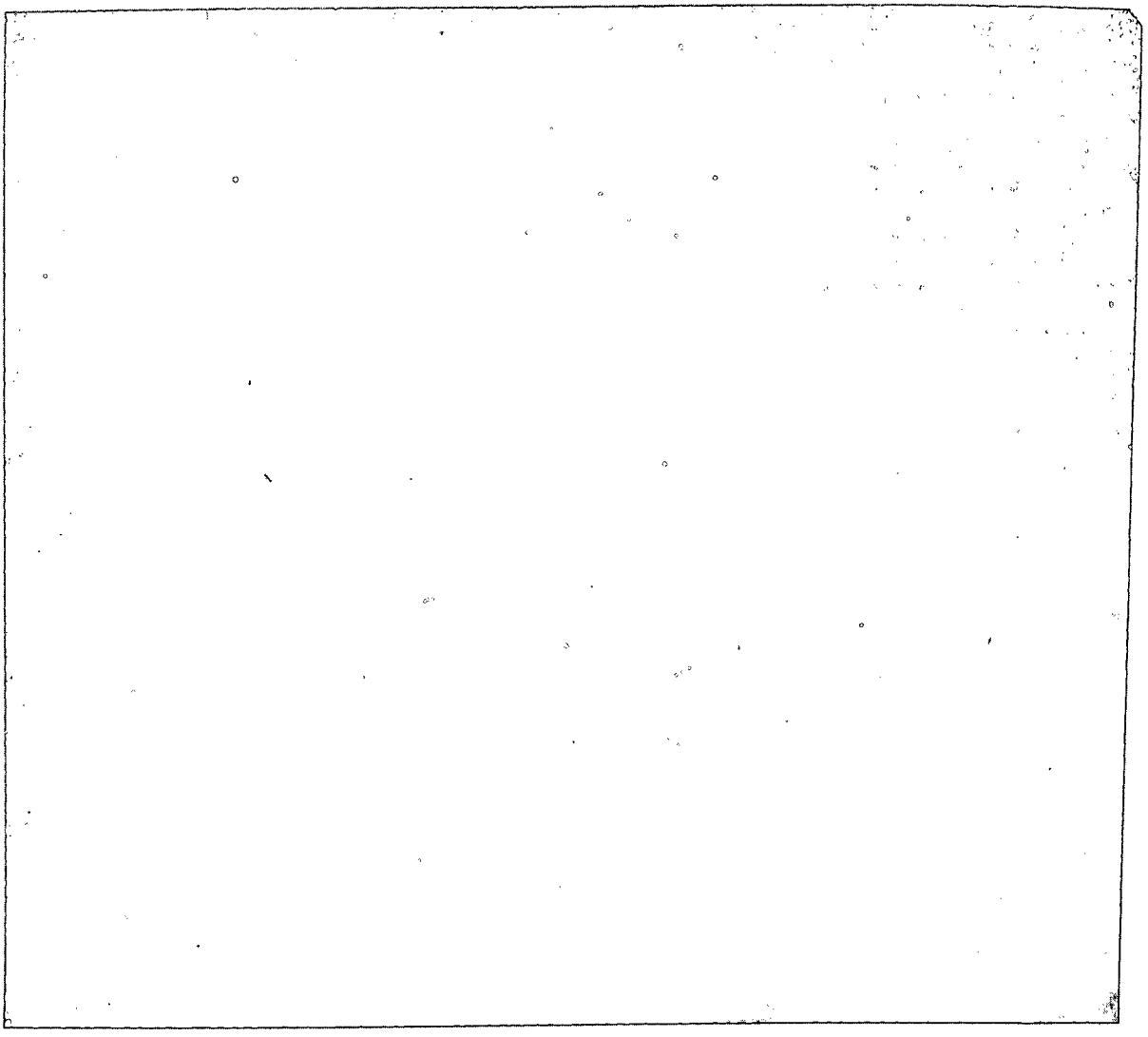


Figure 2. Electron Micrograph of the Centrifuged Hazy Fraction of Experimental Acetate II, 35,000 X. (This is a positive, i.e., thick spots appear dark).

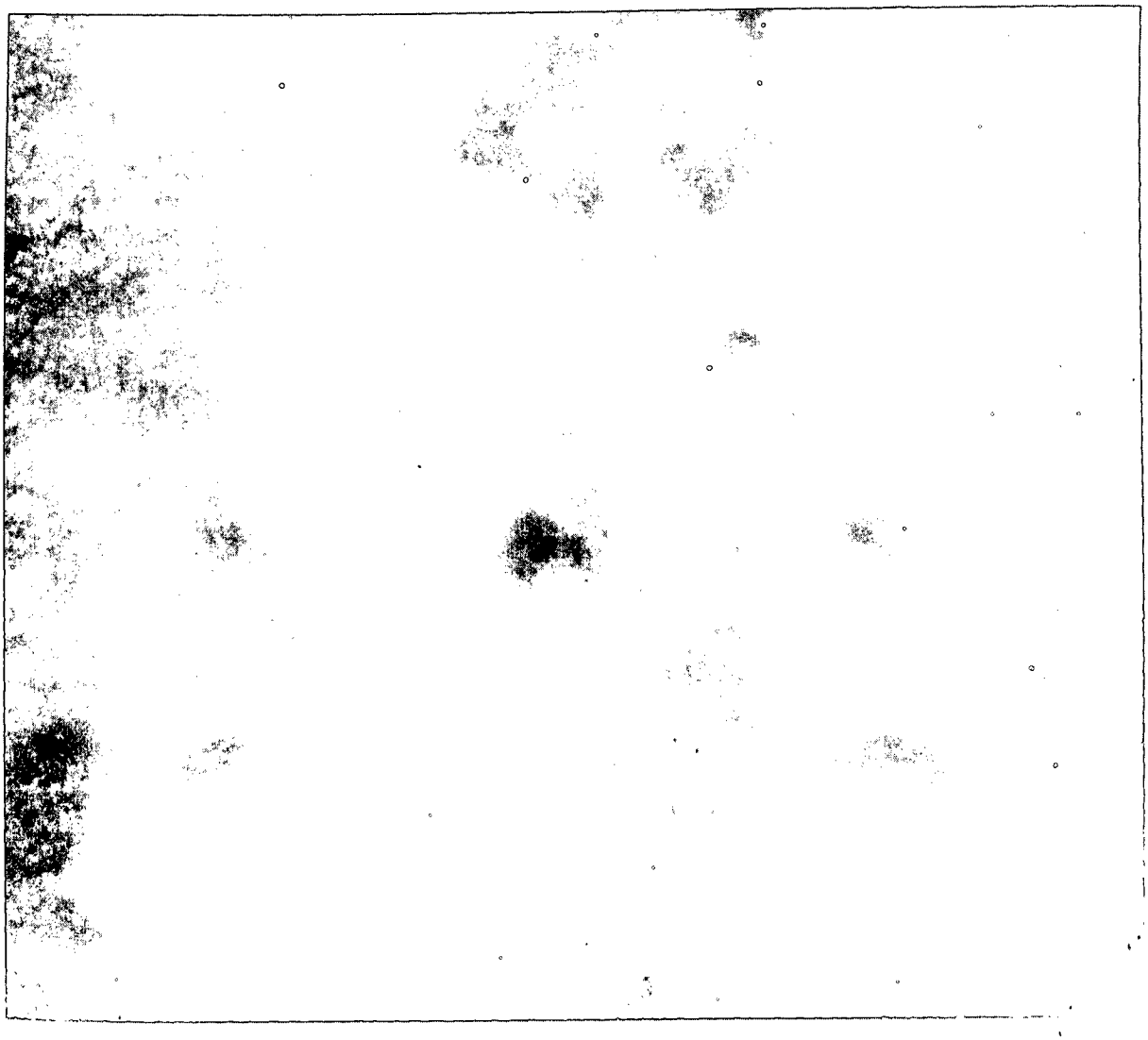


Figure 3. Electron Micrograph of the Clear Fraction of Experimental Acetate II, 35,000 X. (This is a positive, i.e., thick spots appear dark).

Figure 4. Electron Micrograph of the Thin Film of the Centrifuged Hazy Fraction of Experimental Acetate II, 35,000 X. (This is a positive, i.e., thick spots appear dark).

REFRACTIVE INDEX

The refractive indexes of several haze fractions were measured with the Abbé refractometer according to the method given by Bauer (39). The method requires that the film be translucent and have one plane face. The plane side of the film was pressed against the prism of the refractometer which had been wet with bromobenzene. This resulted in a film of the bromobenzene between the prism and the film surface. Measurements were made with ordinary white light at 25°C.

The refractive indexes of the experimental acetate II, its dispersed hazy fraction, and fine haze A + B were measured. To form the films a layer of solution was spread over a glass plate, air dried, and the film was removed by soaking in water. Films of the original acetate and the dispersed hazy fraction were cast from acetone solution. In the case of the fine haze A + B the films were cast from formic acid solution and from a chloroform-methanol suspension. A small amount (3%) of dimethylphthalate was incorporated into the films of the fine haze A + B as a plasticizer. This increased the refractive index slightly, but the increase was smaller than the expected accuracy. The results of the determinations are shown in Table IV.

TABLE IV

REFRACTIVE INDEXES OF FILMS OF FRACTIONS
FROM EXPERIMENTAL ACETATE II

	Refractive Index				
	1	2	3	4	Average
Original acetate	1.495	1.495	1.485	1.495	1.493
Dispersed hazy fraction	1.495	1.501	1.497	1.495	1.497
Fine haze A + B					
Cast from formic acid	1.496	1.496	1.495	1.493	1.495
Cast from $CHCl_3$ and MeOH suspension	1.495	1.498	1.496	1.501	1.498

The refractive indexes of the fine haze and the dispersed hazy fraction A + B approximated that of the original acetate.

CHEMICAL ANALYSES OF HAZE

ACETYL CONTENT

Acetyl determinations were made by a modification of the Eberstadt method as described by Genung and Mallatt (40). The samples were either dried in vacuo at 50°C., or a separate moisture determination was made. A 0.1 gram sample was swollen 30 minutes at 55°C. with 10 ml. of 75% ethyl alcohol. Ten milliliters of 0.5 N sodium hydroxide were added, the sample was heated 15 minutes at 55°C., and the saponification was completed at room temperature. After 24 hours the solution was acidified with 10 ml. of 0.5 N hydrochloric acid. After standing one hour to allow

the alkali to diffuse out of the pulp, the sample was back-titrated with 0.1 N sodium hydroxide solution. This procedure gave acetyl values for the experimental acetates which checked well with the values determined by the Du Pont Company. The acetyl contents of haze fractions from the various acetates are given in Table V.

In the case of the experimental acetates, all of the haze fractions had acetyl contents which were in the range necessary for acetone solubility. [Cellulose acetates having acetyl contents from 36 to 42% may be acetone soluble (41)]. This was not true of the haze fractions isolated from the commercial acetates, all of which had acetyl contents below this range.

TABLE V

ACETYL CONTENT OF VARIOUS ACETATE FRACTIONS

Sample	Acetyl Content, %				Average
	1	2	3	4	
Linter acetate					
Original acetate	39.4	40.1	40.1	40.6	40.1
Coarse haze	31.0	25.0	----	----	28
Fine haze A	32.0	----	----	----	32
Pulp acetate					
Original acetate	40.5	40.5	39.7	39.0	39.9
Coarse haze	26.0	33.0	----	----	29.5
Fine haze A	36.0	35.8	----	----	35.9
Experimental acetate I					
Original acetate	40.4	39.3	----	----	39.9
Coarse haze	40.9	40.6	39.2	----	40.2
Fine haze A	45.0	37.0	----	----	41
Experimental acetate II					
Original acetate	40.5	39.6	40.7	39.3	40.0
Coarse haze	39.1	37.0	36.1	----	37.4
Fine haze A	38.6	40.2	39.1	----	39.3
Dispersed hazy fraction	39.5	38.7	----	----	39.1
Fine haze A + B	39.9	40.0	40.8	----	40.2

CARBOHYDRATE COMPOSITION

The proportions of simple sugars in polysaccharides were determined by hydrolysis of either the acetylated material or the saponified substance followed by quantitative paper partition chromatography. The quantitative analysis was based on the method given by Hirst and Jones (42) which uses periodate oxidation of the sugars and titration of the resultant formic acid. Sodium periodate quantitatively oxidizes the hexose sugars to five moles of formic acid per mole of sugar, and

pentose sugars and rhamnose to four moles of formic acid per mole of sugar.

The hydrolysis procedure was essentially the same as that used for the determination of mannan according to Institute Method 22 (43), but the sample size was reduced. About 0.1 gram of the sample was dissolved in the cold with 1 ml. of 72% sulfuric acid. The solution was diluted to 35 ml. and boiled for 4 hours. After neutralization with barium carbonate and filtration of barium sulfate the solution was concentrated on a steam bath to about 0.5 ml.

Application of paper partition chromatography to the analysis of pulp hydrolyzates has been adequately described by Wise, Green, and Rittenhouse (44). The development of chromatograms was carried out in an insulated stainless steel tank equipped with 4-inch wide glass troughs for holding the developing solvent and the paper chromatogram. The solutions were first analyzed in a qualitative manner by chromatographing on Whatman No. 1 paper for 36 to 48 hours with a butanol, pyridine, and water (10:3:3) solvent mixture. The positions of sugar spots were determined by spraying the sheet with a 0.1 M butanol solution of aniline hydrogen phthalate. After heating in the oven at 105°C. for five minutes the sugars formed reddish-brown spots with the reagent. The spots were identified by comparing their positions on the chromatogram with those of known sugars.

Quantitative chromatograms were then prepared by drawing a line of the sugar solution by means of a capillary tube across the upper part

of a 4 by 24 inch strip of Whatman No. 1 filter paper. The chromatograms were developed 60 to 72 hours for adequate separation of the sugars. The sugar bands were located by spraying a 1-cm. wide guide strip which was cut from the middle of the paper. The zones of paper containing the sugars were cut out to be eluted. Skewing or tilting of the bands of sugars or channeling at the edges of the paper interfered with the method since sugar would thereby be lost or gained by a particular zone. This could be detected by spraying the strip of paper which was cut from between adjacent sugar zones. Appropriate corrections could then be made.

The sugar was eluted by extracting four times with 1.5 to 2 ml. of water. The band containing the sugar was rolled into a cylinder and inserted in a 6 by 1-cm. glass cylinder with a stopcock attached. The paper was covered with water and allowed to stand for 20 to 30 minutes. The water extract was drained into an oxidation tube and the paper covered with water again. Four extractions in this manner were sufficient to remove the sugar from the paper.

The sugar was oxidized in a 15 to 20-cm. long glass tube with a 29/42 ground glass stopper and a small bulb blown at the end. One milliliter of 0.25 M sodium periodate was added to the tube, and the stopper was inserted. The tube was heated on the steam bath for 10 minutes and then cooled under the tap. The excess periodate was reduced with 10 drops of ethylene glycol. The formic acid was titrated with 0.003 N sodium hydroxide solution until yellow to methyl red

indicator. The exact end point was obtained by matching with a blank determination. In titrating a weak acid such as this, the indicator changes slowly from the red to the yellow. The end point chosen occurred at a pH of about 6.3. A potentiometric titration showed that the inflection point occurred at a pH of 7.6 to 7.8. The ratio between the two sugars, found by using the inflection point, was 9.97 compared to a ratio of 9.65, found by using the methyl red end point.

A blank was determined on a section of the paper which did not contain any sugars. The acidity of the blank arose chiefly from the methyl red indicator.

The blank value was subtracted from the volume of sodium hydroxide solution used in titrating each sugar. The corrected volume in the case of xylose was adjusted by dividing by 0.96, which is the ratio between the equivalent weights of pentoses and hexoses. The adjusted volumes were proportional to the percentage of each sugar.

The method was first tried on two known mixtures. The first contained 78% glucose, 12% mannose, and 10% xylose. Three determinations averaged 75% glucose, 14% mannose, and 11% xylose. A second known contained 82% glucose, 7% mannose, and 11% xylose; five determinations averaged 83% glucose, 8% mannose, and 9% xylose.

The effect of hydrolysis on free sugars was determined by dissolving a known mixture of glucose, mannose, and xylose in 72% sulfuric acid and "hydrolyzing" the mixture by the usual procedure. The starting

mixture contained 72% glucose, 18% mannose, and 10% xylose. The "hydrolyzed" mixture analyzed 76% glucose, 16% mannose, and 8% xylose. The "hydrolysis" caused no significant change in the mixture of sugars.

Certain hydrolyzates appeared to contain only glucose, that is to say, only a spot for glucose could be observed on the chromatogram. However, it was difficult to detect very small amounts of other sugars, i.e., less than 1% of the amount of glucose present. For these hydrolyzates several chromatograms were prepared as for quantitative analysis, and developed for 24 hours with the butanol, pyridine, and water solvent mixture. The glucose zones were located and the regions outside those zones were cut off so as to include a small portion of those zones. These regions were eluted and the eluate was chromatographed. If no sugars, other than glucose, were then found, it was concluded that they were absent.

The fractions of haze isolated from the commercial acetates were analyzed, after saponification, qualitatively and in a few instances quantitatively for their constituent sugars. These analyses are summarized in Table VI.

An especially significant feature of these results was the high proportion of glucose units which were present in the hazy materials in every case. The hazes from the pulp acetate contained significant amounts of mannose and xylose units. The linter coarse haze contained large amounts of xylose.

The fractions of experimental acetate I were analyzed qualitatively. The original acetate contained glucose with very small amounts of mannose and xylose, the coarse haze and fine haze A contained slightly larger amounts of mannose and xylose.

The fractions from experimental acetate II were analyzed quantitatively for their constituent sugars. These analyses are shown in Table VII.

The method of analysis was inaccurate when applied to mixtures containing very small amounts of some sugars. This is especially evident if the analyses of the original acetate and the acetate after being supercentrifuged are compared.

TABLE VI

CARBOHYDRATE ANALYSES OF COMMERCIAL ACETATE FRACTIONS

Sample	Percentage of Total Sugars in the Hydrolyzate		
	Glucose	Mannose	Xylose
Linter acetate			
Coarse haze	93	0	7
	92	0	8
	92	0	8
	92	0	8
	93	0	7
Average	92	0	8
Fine haze A	Glucose was the only sugar which was detected		
Pulp acetate			
Coarse haze	Large	Trace	Trace
Fine haze A	Large	Trace	Trace
*Dispersed hazy fraction	94	3	3
	94	3	3
	92	5	3
	91	6	3
	93	5	2
Average	93	4	3

*This fraction was not saponified before hydrolysis.

These results showed that the complete removal of the hazy fraction also effected the complete removal of mannan and xylan from the acetate.

TABLE VII

CARBOHYDRATE ANALYSES OF EXPERIMENTAL ACETATE II FRACTIONS

Sample	Percentage of Total Sugars in the Hydrolyzate		
	Glucose	Mannose	Xylose
Original Acetate*	95	3	2
	96	2	2
	96	1	3
	97	1	2
Average	96	2	2
Coarse haze	93	5	2
	95	4	1
	94	4	2
	93	5	2
Average	94	4	2
Fine haze A	83	10	7
	85	10	5
	83	10	7
	86	8	6
Average	84	10	6
Supercentrifuged acetate*	94	3	3
	95	3	2
	95	3	2
	96	3	1
	96	2	2
Average	95	3	2
Dispersed hazy fraction	86	6	8
	89	5	6
	89	5	6
	88	5	7
	89	5	6
Average	88	5	7

*These analyses were made on saponified materials.

(TABLE VII CONTINUED)

CARBOHYDRATE ANALYSES OF EXPERIMENTAL ACETATE II FRACTIONS

Sample	Percentage of Total Sugars in the Hydrolyzate		
	Glucose	Mannose	Xylose
Clear fraction	100.0	0.0	0.0
Total hazy fraction	88	6	6
	88	6	6
	86	7	7
Average	88	6	6
Fine haze B	50	8	42
	53	11	36
	47	9	44
Average	50	9	41

A noticeable trend was observed in the ratios of mannose to glucose and xylose to glucose. These ratios increased greatly with the degree of dispersion of the haze fractions. The haze isolated by supercentrifuging the supercentrifuged hazy fraction in 20% benzene solution (page 16) also was rich in xylan and mannan, indicating that this trend was continued.

By this method only the proportions of simple sugar units present in polysaccharides could be calculated. To determine the actual percentage of sugars in a sample a weighed amount of a reference sugar was added to a weighed sample and the ratios of the sugars to the reference sugar were determined. The actual sugar unit analyses were determined on the saponified coarse haze and fine haze A from experimental acetate II. The saponified samples were weighed, hydrolyzed, and a known amount of rhamnose was added to the sample before neutralization with barium carbonate. The proportions of the sugars as analyzed and the calculated percentages of anhydro-sugars in the original samples are shown in Table VIII.

TABLE VIII

ACTUAL CARBOHYDRATE PERCENTAGES IN HAZE
FROM EXPERIMENTAL ACETATE II

Sample	Grams Rhamnose Per Gram Sample	Percentage of Total Sugars in the Hydrolyzate			
		Glucose	Mannose	Xylose	Rhamnose
Coarse haze	0.0961	85	6	1	8
		82	6	2	10
		88	5	1	6
		85	6	2	7
	Average	85	6	1	8
		Anhydro-sugar in sample, %			
		94	6	1	
Fine haze A	0.0634	81	9	3	7
		83	8	3	6
		80	9	4	7
		83	7	3	7
	Average	82	8	3	7
		Anhydro-sugar in sample, %			
		67	6	2	

The saponification caused a loss of some sugars as shown by the change in the ratios of glucose to mannose, and glucose to xylose by comparison with Table VII. These determinations indicated that these haze fractions after saponification were composed predominantly of polysaccharides.

IDENTIFICATION OF SUGARS

Mannose and xylose were tentatively identified by their positions of chromatograms. They were identified chemically by chromatographic separation and preparation of derivatives. A sample of the total haze fraction from experimental acetate II was hydrolyzed and the hydrolyzate was streaked along the top of a number of Whatman filer paper sheets. They were chromatographed for 48 hours; the zones were located by spraying a guide strip, and the mannose and xylose zones were cut out. The sugars were eluted with methanol and water and the sugar solutions were concentrated on the steam bath. About 10 to 15 mg. of each sugar were isolated in this manner.

The mannose solution was evaporated to dryness. One ml. of phenylhydrazine reagent, prepared by mixing two volumes of phenylhydrazine, one volume of acetic acid, and three volumes of water, was added to the sugar in a conical weighing flask, together with a small crystal of sodium acetate. The preparation was allowed to stand 48 hours in the refrigerator. The mannose phenylhydrazone precipitate was washed with water, ethyl alcohol, and ether, and dried. The melting points on the Fisher block were 188°C. and 195°C. for two separate prepartions. In addition mannose phenylhydrazone was prepared from the hydrolyzate and recrystallized from ethyl alcohol and water; the melting point was 195°C. After a second recrystallization the melting point was 194°C. The melting point given in the literature for D-mannose phenylhydrazone is 199 to 200°C.

The xylose solution was evaporated to dryness, the sugar was taken up in methanol, and some methanol-insoluble material was removed by centrifuging. The methanol solution was evaporated to dryness on the steam bath, and dried in a vacuum oven at 50°C. One ml. of the reagent of Breddy and Jones (45), consisting of benzaldehyde dissolved in dilute methanolic hydrogen chloride, was added. The sparingly soluble dimethyl acetal of dibenzylidene D-xylose crystallized out after standing in the refrigerator for two days. The derivative was washed with water and methanol and recrystallized from chloroform and methanol. The melting point was 210°C.; the melting point according to Breddy and Jones is 211°C. A mixed melting point with a known gave no depression.

COMBINED SULFATE

The combined sulfate content of cellulose acetate was determined according to the procedure given by Malm and Tanghe (46). The method consisted of washing the acetate with dilute acid to remove uncombined sulfate and oxidizing the acetate with concentrated nitric acid. The sample was fused with potassium nitrate and the nitric acid was displaced by hydrochloric acid. The salt mixture was taken up with water and the sulfate precipitated and weighed as barium sulfate.

Combined sulfate determinations were made on the original experimental acetate II, the total hazy fraction and the clear fraction isolated therefrom. The results are shown in Table IX.

TABLE IX

COMBINED SULFATE CONTENT OF FRACTIONS FROM EXPERIMENTAL ACETATE II

Fraction	Sulfate, %			
	Sample			
	1	2	3	Average
Original acetate	0.033	0.033	----	0.033
Total hazy fraction	0.10	0.07	0.06	0.08
Clear fraction	0.03	0.03	----	0.03

The combined sulfate content was significantly higher in the hazy fraction.

URONIC ACIDS

Uronic acid determinations were made by the Institute Analytical Department and by Mrs. Ruth Rollinson of the Institute staff. The procedure used was that given by Institute Method 25 (47) consisting of decarboxylation with 12% hydrochloric acid and weighing of the evolved carbon dioxide.

Determinations were made on the experimental acetate II and the dispersed hazy fraction, total hazy fraction, and clear fraction from that acetate. The results are shown in Table X reported as per cent uronic anhydride.

The results showed a significantly higher amount of uronic acids in the total hazy fraction. The value for the clear fraction is

similar to that obtained from pure cellulose or free sugars.

TABLE X

URONIC ANHYDRIDE ANALYSES OF EXPERIMENTAL ACETATE II FRACTIONS

Sample	Uronic Anhydride, %			
				Average
Original acetate	1.39 1.33	1.39 1.34	1.29	1.35
Dispersed hazy fraction	1.2	1.5		1.4
Total hazy fraction	1.9	1.9		1.9
Clear fraction	1.2	1.2		1.2

Naphthoresorcinal tests for uronic acids on the fine haze A and the total hazy fraction from experimental acetate II were negative. No indications of uronic acids were observed in the chromatograms of the hazy fraction hydrolyzates. This casts some doubt on the presence of uronic acids as indicated by the quantitative analysis, but neither of these tests were sufficiently sensitive to show the absence of uronic acids.

The difference between the uronic acid content of the total hazy fraction and the dispersed hazy fraction indicated a high uronic acid content in either the coarse haze or the fine haze A.

ASH CONTENT

Ash determinations were made according to Institute Method 422 (48). The samples were ashed in a muffle furnace at 900°C. Certain

micro-ash determinations were made by the Analytical Department of the Institute. A number of fractions of experimental acetate II were ashed; their ash contents are listed in Table XI.

Two material balances were calculated from the data and are given in Table XII. This was done by comparing the ash from the original acetate with the sum of the individual ash fractions. The fraction yields are taken from Table II, page 21.

TABLE XI

ASH CONTENT OF FRACTIONS OF EXPERIMENTAL ACETATE II

Fraction	Ash, %			
				Average
Original acetate	0.07	0.06	0.06	0.06
Coarse haze	1.1	1.0	----	1.1
Fine haze A	0.8	0.7	----	0.8
Supercentrifuged acetate	0.07	0.05	----	0.06
Total hazy fraction	0.31	0.32	0.35	0.33
Clear fraction	0.04	0.06	----	0.05

TABLE XII

MATERIAL BALANCE ON THE ASH OF EXPERIMENTAL ACETATE II

Basis: One hundred grams of the original acetate.

	Fraction Yield, %	Ash, %	Ash, g.
Ash of the original acetate	100	0.06	0.06
Ash of coarse haze	0.3	1.1	0.003
Ash of fine haze A	1.9	0.8	0.015
Ash of the supercentrifuged acetate	97.8	0.06	0.06
			0.078
Ash of total hazy fraction	19.1	0.33	0.063
Ash of clear fraction	80.9	0.05	0.04
			0.103

The differences between the total ash and the sums of the ashes of fractions show that some ash was added during the fractionation procedures. The ash content was much greater in the coarse haze, fine haze A, and total hazy fraction than in the clear fraction.

It was found that the high percentage of ash which was present in the fine haze A + B could be decreased if the haze was dissolved in formic acid and regenerated by precipitation into water. By this procedure the ash content was decreased from 0.6% to 0.2%. This did not change the insolubility of the haze in acetone.

The ash samples were analyzed spectrographically by Leonard Dearth of the Physics Department. Estimates of the relative line intensities were made which gave a rough indication of the amounts of the elements present.

The spectrographic analyses of the ashes of the fractions listed in Table XI gave no indication of any major differences between the metallic constituents of the various ash fractions. The ashes of all fractions gave lines of strong intensity for calcium and magnesium.

The metallic constituents which gave medium line intensities varied from fraction to fraction. The ashes of the original acetate, the coarse haze, and the fine haze A gave lines of medium intensity for copper and silicon, whereas the ashes of the supercentrifuged acetate, the hazy fraction, and the clear acetate gave lines of medium intensity for silicon, aluminum, and zinc. Certain elements (zinc, boron, sodium, lead, tin, nickel, molybdenum, and silver) were present in trace and small amounts in the ashes of some fractions but were not found in the ash of the original acetate. These elements had been added to the ash during the isolation of the fractions.

REACETYLATION

The acetyl determinations on the haze fractions of experimental acetate II (Table V) indicated that they had an acetyl content in the range necessary for acetone solubility. These fractions might have consisted of incompletely acetylated material mixed with a triacetate. Portions of the haze might have been present in the least soluble fractions because, due to poor mixing, they were not exposed to the acetylating mixture or the hydrolyzing mixture. The haze should therefore be solubilized, at least in part, by reacetylation of the haze.

The total hazy fraction was reacetylated using the porportions of reactants given by Frey and Schwalenstöcker (5) for determination of the suitability of pulps for acetylation. Thirty grams of the hazy fraction were suspended in 180 ml. of acetic acid and allowed to stand overnight. Ninety ml. of acetic acid containing 0.54 ml. of 95% sulfuric acid were added and the reaction mixture was stirred for 1 3/4 hours at 15°C. Ninety ml. of acetic anhydride were added dropwise and the mixture was heated to 35°C. over a half-hour period. After 40 minutes at this temperature the acetylation was stopped by the addition of 135 ml. of 60% acetic acid containing 1.1 ml. of 95% sulfuric acid. The acetate was hydrolyzed at room temperature for 27 hours and was then precipitated into water. It was washed by boiling with water until the wash water was neutral to brom-thymol blue. The acetate was then washed once with two liters of water containing 0.5 gram of sodium bicarbonate, twice more with distilled water, and air dried. The reacetylated material had an acetyl content of 42%.

The coarse haze and fine haze A + B were isolated from the reacetylated total hazy fraction. The turbidities and haze yields of the original fraction are compared with those of the reacetylated fraction in Table XIII.

TABLE XIII

EFFECT OF REACETYLATION ON THE CHARACTERISTICS OF THE TOTAL HAZY FRACTION

	Original Hazy Fraction	Reacetylated Hazy Fraction
Turbidity, %, at 1% conc.		
Centrifuged hazy fraction	52.9	46.9
Supercentrifuged hazy fraction	18.8	24.9
Yield of hazy materials in percentage of the original fraction		
Coarse haze	1.2	0.3
Fine haze A + B	12.7	7.6

The viscosity of the fraction was decreased noticeably from qualitative observations. The effect of reacetylating the total hazy fraction was to disperse the haze. This was shown by the fact that the reacetylated material had a lower turbidity than the original fraction, but after removal of the fine haze A + B by supercentrifuging, the turbidity of the reacetylated material was greater. The amount of coarse haze was reduced.

The coarse haze from the reacetylated fraction had an acetyl content of 30%. The percentage of total carbohydrates in the fine haze A + B from the reacetylated fraction was 70% glucose, 11% mannose and 19% xylose. The fine haze A + B from the original fraction contained 75% glucose, 9% mannose and 16% xylose. There was a slight increase in the mannose to glucose, and xylose to glucose ratios.

EXTRACTION OF THE HAZE WITH SODIUM HYDROXIDE

An attempt was made to separate the mannan and xylan from the cellulosic portion of the haze. Forty grams of the air-dried hazy fraction were deacetylated by soaking overnight in one liter of N alcoholic sodium hydroxide. The regenerated cellulose was filtered off and washed with acetic acid and ethyl alcohol, then with ethanol and ether, and air dried. The air-dried, regenerated substance, 25 grams, was extracted with 575 ml. of 17.5% sodium hydroxide solution at 20°C. After standing 40 minutes, the mixture was diluted with 500 ml. of water and the residue was separated by centrifuging. The residue was washed in the centrifuge bottle with water, dilute acetic acid, and finally with acetic acid. The residue was not dried; instead, a sample was removed to determine the dry content. The ovendry weight of the residue was 4.2 grams. Because most of the material had been removed by the extraction, the extract was precipitated and then extracted with 5% sodium hydroxide. The residue from this extraction was washed as above, and the water was replaced by acetic acid. The two residues combined weighed 15.6 grams (ovendry); a large amount of cellulose must have been removed by the extraction.

The residue was analyzed and found to contain 97% glucose, 2% mannose, and 1% xylose. The alkaline extraction had decreased the mannan and xylan content considerably.

Fifteen grams of the residue was acetylated by first treating with 150 ml. of acetic acid containing 0.45 ml. of concentrated sul-

furic acid. After 1 3/4 hours, 75 ml. of acetic anhydride were added, and the reaction mixture was heated to 35°C. After one hour at this temperature, the material had not dissolved to any extent. An additional 0.45 ml. of sulfuric acid was added whereupon solution occurred readily. The reaction was stopped by adding 112 ml. of 60% acetic acid containing 0.6 ml. of concentrated sulfuric acid. The acetate was hydrolyzed for 24 hours at room temperature and precipitated into water.

This acetate was excessively degraded and formed a sol with water in the process of washing. A portion was neutralized with sodium bicarbonate; thereby precipitating the acetate, which was washed with water and dissolved in acetone. The turbidity at 1% concentration was 21.5%, as compared to the turbidity of 46.9% for the reacetylated total hazy fraction.

ACETOLYSIS

The carbohydrate analyses of the various hazy materials indicated that a large amount of cellulose was present in the haze as evidenced by large amounts of glucose in the hydrolyzate. The fine haze A + B from experimental acetate II was acetolyzed as a possible means of identifying this material as cellulose and to gain some information as to possible linkages between the non cellulosic constituents and the cellulose. The procedure was taken from the thesis of John Leech (49).

Twenty-eight and one-half ml. of acetic acid were mixed with an equal volume of acetic anhydride in a 200-ml. round bottom flask and cooled to 10°C. Then 2.85 ml. of 95% sulfuric acid were added slowly with stirring. Five grams of the fine haze were added slowly. The reaction mixture was cooled in an ice bath and stirred for one hour. The haze became well dispersed at the end of this time; the stirring was stopped and the mixture was allowed to stand at room temperature. After a day, the turbidity of the solution had increased greatly and a flocculent material separated. After 70 hours, the acetolysis reaction was stopped by pouring the mixture into three volumes of ice water containing 8.5 grams of sodium acetate to neutralize the sulfuric acid present. A small amount of chloroform was added and the reaction mixture was neutralized with sodium bicarbonate. After standing overnight, the mixture was extracted with about one liter of chloroform The very turbid chloroform solution was evaporated to 500 ml. on the steam bath and the material causing the turbidity was precipitated by adding 300 ml. of 95% ethyl alcohol. The precipitate was removed by centrifuging, washed with alcohol and ether, and dried. Its weight was 0.99 grams. The chloroform-ethanol solution was evaporated to a syrup, dried in a vacuum oven at 50°C., and then in a vacuum desiccator. The total weight of the soluble fraction was 4.97 grams.

The chloroform-soluble material and the precipitate were hydrolyzed with sulfuric acid and analyzed by paper partition chromatography. The precipitate contained 54% glucose, 46% mannose, and no xylose. The soluble fraction contained 78% glucose, 4% mannose, and 18% xylose.

Most of the mannose units were relatively undegraded by the acetolysis reaction.

One gram of the soluble material was deacetylated by the original technique of Zemplén (50). The material was dissolved in 5 ml. of chloroform and cooled in a freezing mixture. Five milliliters of cold methanol containing 0.1 gram of sodium were added with agitation; the solution rapidly became cloudy. After 10 minutes 5 ml. of ice water were added with agitation. Enough acetic acid was added to neutralize the mixture; and the water phase was decanted, passed through a cation exchange column to remove sodium ions, and concentrated on a steam bath. This solution was then chromatographed for 48 hours with an ethyl acetate, acetic acid, and water solution (9:2:2).

The chromatogram indicated a large amount of xylose, only a trace of mannose, a large amount of glucose, a spot which corresponds in position to cellobiose, and a spot which may be cellotriose.

An attempt was made to acetolyze part of the residue by first dissolving 0.14 gram in 1 ml. of 72% sulfuric acid at 0°C. After one hour the material was well dispersed and a mixture of 8.8 ml. of acetic anhydride and 4.2 ml. of acetic acid was added slowly so that high temperatures were not encountered. After half the acid-anhydride mixture had been added the solution became cloudy and a white flocculent material separated. This seemed to disperse again when the addition was completed. After 24 hours, the solution became

very turbid and flocculent material separated. After 70 hours the acetolyzate was isolated by the procedure given above except that the chloroform extract was filtered through magnesol to remove undissolved material. The magnesol was washed with acetone. The acetone-chloroform solution was concentrated to a syrup and dried *in vacuo*. The yield of recovered product was 0.1 gram.

This acetolyzate was deacetylated as described above and chromatographed. The chromatogram contained glucose and mannose spots of approximately equal size, and four spots in the disaccaride region. The second of these corresponded in position to cellobiose, and the fourth to glucosido-mannose. Quantitative chromatograms were prepared of this sugar mixture and developed for five days. The disaccharide regions were eluted, the eluates were hydrolyzed on the steam bath with 5% sulfuric acid, neutralized with an anion exchange resin, and chromatographed again. The hydrolyzate of the first disaccaride was not clear, the second gave a spot for glucose only, the third a spot for mannose only, and the fourth spots for mannose and glucose. The second, third, and fourth dissacharides were thus tentatively identified as cellobiose, a dissacharide of mannose, and a glucosido-mannose, respectively.

DISCUSSION OF RESULTS

Haze has been defined as any material in an acetone solution of cellulose acetate which can be removed by centrifugal means or which imparts a high turbidity to an acetone solution. By these definitions all of the cellulose acetates investigated in this work contained haze (see Table III, page 22). Coarse haze was removed by centrifuging an acetone solution of the acetates; fine haze A was removed by supercentrifuging. The removal of these substances caused a drop in the turbidity of the acetate solutions (see Table III, page 22); therefore, these fractions satisfied both definitions of haze. The amounts of haze present in the commercial acetates were small. On the other hand the experimental acetates contained large amounts of both haze fractions, the removal of which left the experimental acetate solutions much more turbid than the centrifuged commercial acetates.

The remainder of the haze was isolated by fractional precipitation of the supercentrifuged acetate. This was done only on experimental acetate II and the pulp acetate. This dispersed hazy fraction was very turbid, and the clear acetate solution was clear; therefore, this separation removed material which contained haze by the second definition. It was felt that the turbidity of the highest molecular weight fractions of cellulose acetates, prepared by solution procedures, was not as great as the turbidities of the commercial acetates. The criterion for whether or not an acetate fraction had a high turbidity was that its turbidity should

be comparable to, or lower than, that of the commercial acetates. The clear fraction from experimental acetate II had a turbidity of 3.2% as compared to 5.0% for the centrifuged linter acetate (at 4% concentration). This showed that substantially all of the haze had been removed and was concentrated in the hazy fraction.

The total hazy fraction from experimental acetate II caused plugging in filtration whereas the clear fraction did not; this difference indicated that the clear fraction was free from the haze which caused filtration difficulties. The total hazy fraction represented a considerable proportion, 19%, of the experimental acetate II. Under the conditions used for fractionation, any attempt to precipitate a smaller fraction resulted in an incomplete removal of the haze. It is probable that the total hazy fraction contained cellulose acetate of high molecular weight which precipitated along with the haze. Even in the case of the pulp acetate, which had a low turbidity, the total hazy fraction amounted to 14% of the acetate.

Fine haze B was removed by supercentrifuging the dispersed hazy fraction from experimental acetate II, or was removed together with the fine haze A by supercentrifuging the total hazy fraction. Even more haze could be separated from the supercentrifuged hazy fraction if an acetone solution to which 20% benzene had been added was supercentrifuged. The benzene may also have caused some clear cellulose acetate to be removed with the hazy material.

The sequence used in the isolation of certain fractions was shown to have an insignificant effect on the yields of the haze fractions and the turbidities of comparable fractions (see Table II, page 21). This served as the basis for considering that certain fractions were equivalent despite the method of isolation used.

Fractional precipitation was the only method of removing the haze completely, but it was not certain what amount of clear cellulose acetate accompanied it. Supercentrifuging removed haze which was free of soluble cellulose acetate, but it was not certain what proportion of the original haze was removed in this manner. It can be said only that a large part of the turbidity of the acetate had been removed by supercentrifuging; this was shown by the drop in turbidity of the total hazy fraction from 53% to 19% (See Table XIII, page 50). A more complete removal of the haze from the total hazy fraction should be attainable by using a supercentrifuge which produces a greater acceleration. A study of this haze should yield further information as to the mechanism of haze formation.

Microscopic examination of the coarse haze from experimental acetate II showed that the material consisted predominantly of amorphous masses. There was no indication of cell wall structures as Haas (34) has suggested, but the evidences of this may have been destroyed during the processing of the acetate. All of the coarse hazes contained some fibers and fiber fragments. They were probably unacetylated because of poor mixing or non-uniform reactivity.

According to Blume (51) they cause little trouble in filtration. No attempt was made to separate the fibers and fiber fragments from the nonfibrous portions of the haze.

The centrifuged hazy fraction from experimental acetate II was examined with the electron microscope. The film from this fraction presented a mottled appearance (see Figure 2, page 25). This was expected of a film formed from an acetate which contained small, highly swollen, insoluble particles. These particles were of the order of 0.1 mu in diameter. A thinner film formed from this fraction broke up into a continuous network with a large number of holes at the thin spots in the film (see Figure 4, page 27). The mottled appearance of the film of Figure 2 might also have been caused by poor drying conditions. The "lumpy" quality of the film would have resulted if the polymer precipitated during drying. However, a film formed from the clear fraction (see Figure 3, page 26) did not show these variations in thickness.

The fine haze fractions from experimental acetate II were insoluble in cellulose acetate solvents. Formic acid dissolved the fine haze A + B. The fact that the haze was generally insoluble was an indication that the haze was a mixture of polysaccarides of varying degrees of acetylation.

The fine haze A + B from experimental acetate II had a refractive index not significantly different from that of the original acetate. This raises a question as to the cause of the turbidity

of films made from hazy acetates. The film turbidity is probably caused by irregularities in thickness caused by the haze particles or by a tendency for hazy acetates to dry poorly.

The coarse hazes and fine hazes A from the two commercial acetates had acetyl contents below the range (36 to 42%) necessary for acetone solubility (see Table V, page 31). This alone was a sufficient reason for their insolubility. These fractions undoubtedly resulted from unreactive portions of the pulp. This showed that Jayme's and Schenk's (7) evaluation of pulps as to reactivity and purity was incorrect. They ascribed the coarse haze to poor reactivity of pulps and the dispersed haze (as evidenced by turbidity of the acetate solutions) to the impurities. The low degree of acetylation of the fine hazes A from both of these acetates indicated that poorly reactive material may appear in the dispersed portions of the haze.

The various fractions of haze from the experimental acetates were acetylated to the extent which is usually associated with acetone solubility (see Table V, page 31). Acetylation of the haze to this extent should have caused it to become acetone soluble. Although there are several possible ways in which the haze could have reached this acetyl content without being acetone soluble, one mechanism of the haze formation is postulated here:

The substances which preceded the haze existed in the pulp as particles, the outer layers of which were insoluble when fully acetylated. As a consequence of this, they reacted more slowly because the outer layers of the particles were not dissolved away. When the principal portion of the acetate had reached the triacetate stage, these particles were fully acetylated in the outer layers but incompletely acetylated within. They hydrolyzing medium also failed to penetrate these layers and deesterification occurred only at the surface.

This mechanism presents an explanation of how the average acetyl content could be much the same for the haze as for the remainder of the cellulose acetate, as the end product consisted of a mixture of acetates at varying degrees of acetylation.

The coarse haze isolated from the linter acetate contained a fairly large amount of xylan (8%). The fine haze A from this acetate contained only glucose units.

The fractions of haze from the pulp acetate contained small amounts of xylose and mannose units. The mannose and xylose units were concentrated in the total hazy fraction of this acetate, and were not present in the clear fraction.

The experimental acetate I was not investigated thoroughly for its carbohydrate composition; the coarse haze and fine haze A from this acetate contained a large amount of glucose with smaller amounts of xylose and mannose.

The non-glucosidic units, mannose and xylose, were concentrated in the total hazy fraction of experimental acetate II, and were absent from the clear fraction of this acetate. In other words these non-cellulosic polysaccharides were associated entirely with the haze. It may be concluded that xylans and mannans caused haze because their derivatives were insoluble. These substances might have shielded the cellulose which was associated with them from reaction, in accordance with the postulated mechanism of haze formation. The accompanying cellulose might also have existed in the haze for other reasons, e.g., cross linking.

The amounts of xylose and mannose were greater in the better dispersed fractions of the haze. This trend was continued in a fraction removed by supercentrifuging a benzene and acetone solution of the supercentrifuged hazy fraction; this fraction was also rich in mannan and xylan. The reason for this trend may only be conjectured. The fact that the composition changed with the degree of dispersion indicated that the fine haze A + B was probably not chemically representative of the entire haze.

The saponified coarse haze and fine haze A from experimental acetate II were shown to consist primarily of polysaccharides. The saponified coarse haze analyzed as 99% carbohydrate material, and the saponified fine haze A as 75% carbohydrate material by quantitative paper partition chromatography. The low value for the fine haze A may have been caused by incomplete hydrolysis or a high per-

centage of noncarbohydrate substances. A repeat of this determination was not considered sufficiently important in view of other considerations.

The total hazy fraction from experimental acetate II was significantly higher in combined sulfate than the original acetate or the clear fraction (see Table IX, page 44). Malm, Smith, and Tanghe (19) showed that the combined sulfate content of cellulose acetates was correlated with the salt effect (the salt effect is the increase in acetone-solution viscosity caused by washing the acetate with aqueous solutions of calcium salts).

These authors believe that the salt effect is caused by cross linking, and it is logical that haze may be formed in a similar manner. However, if the postulated mechanism of haze formation is correct, the combined sulfate content would have been higher in the hazy fraction as an incidental occurrence. Combined sulfate groups are known to be removed during the de-esterification reaction (52). The haze particles were not so accessible to the hydrolyzing medium, consequently the removal of sulfate groups was not as efficient. The combined sulfate content of the total hazy fraction, 0.08%, was no higher than the combined sulfate of satisfactory acetates which were analyzed by Malm and Tanghe (46). The combined sulfate was not a major cause of haze in this acetate.

Qualitative tests for uronic acids were negative on experimental acetate II. The qualitative tests were not sensitive enough to show that uronic acids were absent. The quantitative analyses (see Table

X, page 45) do not prove the presence of uronic acids; according to Browning (53), amounts of carbon dioxide below 0.4% (1.6% uronic anhydride) cannot be considered as definite evidence of uronic acids. The only fraction which could be said to contain uronic acids was the total hazy fraction, which analyzed as 1.9% uronic anhydride. The true uronic anhydride content of this fraction was probably of the order of 1%. With a degree of polymerization of 250 a cellulose acetate containing this amount of uronic anhydride would have a possibility of cross linking indefinitely to form a large particle. The chances are small that all uronic acid groups would approach and cross link with other uronic acid groups, so that the amount of cross linking would actually be much less. No work was undertaken to show that such cross linking occurred.

The haze fractions of experimental acetate II contained much greater amounts of ash than the original acetate or the clear fraction (see Table XI, page 46). The coarse haze fraction was highest in ash, and the ash content decreased in the better dispersed fractions. The haze did not consist primarily of inorganic compounds. The method of fractionation would cause the ash to accumulate in the haze fractions, an insoluble inorganic material should be removed by centrifugation and fractional precipitation.

The ashes of all fractions of this acetate were shown to be qualitatively similar by spectrographic analyses. The major constituents were calcium and magnesium. The ash may have caused haze

by cross linking with acid groups through calcium or magnesium ions. These results did not warrant such a conclusion. An attempt was made to remove ash from the fine haze A + B by reprecipitation. The ash was decreased to one third the original value but the acetone solubility was not improved. Experiments should be tried which aim at replacing divalent ions by exchange with monovalent ions as a means of proving or disproving the cross linking theory.

If the postulated haze formation mechanism is correct, solubilization of the haze should be accomplished by acetylating the haze completely and deacetylating once again. The total hazy fraction was reacetylated and then deacetylated to an acetyl content of 42%. This decreased the turbidity of the fraction from 53 to 47% and decreased the haze which could be removed by centrifuging from 12.7 to 7.6%. The reacetylated fraction after supercentrifuging had a higher turbidity than the supercentrifuged original fraction (see Table XIII, page 50). The effect of the reacetylation was to disperse the haze more thoroughly.

The effect of an increased dispersion of the haze by means of a more severe acetylation was also shown by the differences in the experimental acetates (see Table I, page 11 and Table III, page 22). The more degradative treatment of experimental acetate II decreased the amount of coarse material, increased the clarity and filterability, and increased the turbidity of the supercentrifuged acetate.

The fine haze A + B from the reacetylated fraction contained 11% mannose and 19% xylose as compared with 9% mannose and 16% xylose in the original fine haze A + B. This showed that there was a slight decrease in the cellulose content of the fine haze A + B. It was concluded that since the reacetylation caused no large changes in the amount of haze, but only in the dispersion of the haze, the haze was not caused by incomplete reaction during the original acetylation. In other words, the haze did not occur because the operator stopped the reaction too soon.

It may be true that even by this repeated acetylation, the hazy fraction was not acetylated completely before deesterification. Solubilization might be accomplished by acetylating the haze with a better catalyst, followed by de-esterification from solution.

It was thought that the cellulose present in the haze could be acetylated to form a soluble acetate if the mannan and xylan were removed. An extraction with sodium hydroxide of the deacetylated total hazy fraction from experimental acetate II was attempted as a means of removing the mannan and xylan. The removal of mannan and xylan from a degraded material such as this was difficult because a large percentage of the degraded material was soluble in the sodium hydroxide. The removal of approximately 40% of the total material left a residue with approximately the same mannan and xylan content as that of the original cellulose. This residue yielded an acetate with a turbidity of 21% in 1% solution as compared to 46% for the

reacetylated total hazy fraction. The decrease in turbidity was much less than was expected by the removal of most of the mannans and xylans.

The isolation of cellobiose was used as a test for cellulose. A sample of the fine haze A + B from the experimental acetate II was acetolyzed. This fraction was chosen because it was not contaminated with soluble cellulose acetate and did not contain unacetylated fibers or fiber fragments. The amount of cellobiose octaacetate in the acetolyzate was approximately equal to the amount of glucose penta-acetate. The chromatographic identification of cellobiose indicated that cellulose was present in considerable amounts in the fine haze A + B and was the source of the glucose found in the hydrolyzate of that fraction.

It is interesting to note that the xylan present in the haze was readily degraded by the acetolysis, whereas the mannan was extremely resistant to acetolysis. This may have been caused by the extreme insolubility of the undegraded mannan acetate, or the degradation products of mannan may be very insoluble. A similar resistance of mannan to degradation during acetolysis was observed by Wise and Ratliff (54) in the acetolysis of an alpha-cellulose prepared from slash pine holocellulose. However, Leech (49) in the course of studies on the acetolysis of a slash pine alpha-cellulose found an equal distribution of mannose units between the monosaccharide fractions and the cellodextrin acetates. The extreme resistance to acetolysis

found here may be related to the cause of haze formation from mannan in pulps. The commercial acetylation reaction is itself a mild acetolysis reaction which is carried only so far as to bring the acetate into solution.

The chromatogram of the reacetolyzed residue indicated spots which corresponded in position to glucosido-mannose, as found by Leech (49), and cellobiose. It was not proved that this was glucosido-mannose. If it was truly present, it would indicate that mannose was linked to cellulose in the pulp, which may explain its persistance through purification treatments. Also two unidentified spots were found.

SUMMARY OF RESULTS AND CONCLUSIONS

For the purposes of the investigation, haze was defined as any substance which imparted a high turbidity to acetone solutions of cellulose acetates or any substance which was removed by centrifugal means from acetone solution. The general results of this investigation of the haze in cellulose acetates are summarized as follows:

1. Methods were found for the removal of haze from cellulose acetates utilizing repeated fractional precipitation, centrifuging, and supercentrifuging treatments (see Figure 1, page 19). The order in which these operations were used was shown to have little effect on the results of the fractionation.

2. A complete removal of haze from the pulp acetate and experimental acetate II was accomplished by fractional precipitation.

3. All of the cellulose acetates investigated contained some coarse haze and fine haze A.

4. The coarse haze contained fibers and fiber fragments but consisted for the most part of amorphous particles.

5. All of the haze fractions which were isolated were found to have a considerable acetyl content, but in some instances the acetyl content was lower than that necessary for acetone solubility (acetone soluble acetates may have acetyl contents from 36 to 42%).

6. All haze fractions from wood pulp acetates yielded glucose, mannose, and xylose upon hydrolysis.

The results of the investigation of the experimental acetate II are summarized as follows:

1. Microscopic examination showed fibers present in the coarse haze but there was no other indication of cell wall structures. Electron microscopic examination of a film of the total hazy fraction revealed thick spots about 0.1 mu in diameter.

2. The fine haze A + B could not be redispersed in acetone and was insoluble in cellulose acetate solvents, except for formic acid.

3. The fine haze A + B had a refractive index of 1.496 using white light at 25°C. There was no significant difference between the refractive indexes of the haze and the remainder of the acetate.

4. The haze fractions all had acetyl contents in the range necessary for acetone solubility. Despite this they were insoluble in acetone and other solvents. When the total hazy fraction was reacetylated, the haze was dispersed more thoroughly but was not solubilized.

5. The coarse haze and fine haze A consisted predominantly of cellulose with smaller amounts of xylan and mannan. The

presence of cellulose in the fine haze A + B was shown by the production of cellobiose octaacetate by acetolysis.

6. All of the mannan and xylan in the acetate were removed by isolation of the total hazy fraction.

7. The cellulose present with the total hazy fraction could be acetylated to form a much less turbid acetate after removal of most of the mannan and xylan.

8. The total hazy fraction contained a larger percentage of combined sulfate than the clear fraction or the original acetate; the amount was too low for this to be a major cause of haze.

9. Quantitative tests for uronic acids showed that the total hazy fraction yielded a significantly higher percentage of carbon dioxide than the clear fraction or the original acetate.

10. The haze fractions contained much greater amounts of ash than the clear fraction. The ashes of all fractions contained mostly calcium and magnesium and differed only in their minor components.

11. An acetolysis of fine haze A + B yielded a mannan-rich insoluble fraction. Acetolysis of this fraction yielded an oligosaccharide which contained glucose and mannose and occupied the same position on a paper chromatogram as glucosido-mannose.

The conclusions which may be drawn from this investigation are summarized as follows:

1. The haze in cellulose acetates may be acetylated to an acetyl content in the range generally associated with acetone solubility without being soluble.

2. Mannans and xylans in wood pulps cause haze because of the insolubility of their acetylated products.

3. Poorly reactive regions of a pulp may give rise to either coarse haze or dispersed haze. This was shown by the fact that both the coarse haze and fine haze A from the commercial acetates had low acetyl contents.

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