FRACTIONATION OF CELLULOSE ACETATE

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ABSTRACT

By means of a series of three successive fractional precipitations, a solution containing 2 kg of commercial cellulose acetate was separated into 15 fractions varying in degree of polymerization from 30 to 380. The procedure involved the fractional precipitation of the acetate from a solution in acetone, using ethyl alcohol as the precipitant.

From the viscometrically estimated chain-lengths of the fractions, the distribution of chain-lengths in the starting material (excepting the first fraction) was obtained. The first fraction was not completely soluble in acetone or Methyl Cellosolve, and therefore no estimate of its degree of polymerization was obtained. It was shown that a large proportion of the ash and haze-producing materials are contained in this first fraction. All of the other fractions have very low ash contents, and with the exception of the fractions of very low degrees of polymerization, the acetyl contents are constant. A phase diagram showing some of the solubility relationships of the starting material and several of the fractions is given.

CONTENTS

I. INTRODUCTION

It is generally recognized that cellulose and its derivatives are composed of long, unbranched, chainlike molecules of varying lengths. The recognition of this fact has led to a number of investigations, reviewed elsewhere [1, 2],[3] concerning the relation of chain-length to certain mechanical properties. In most of these studies, a quantity of cellulosic material was fractionated with respect to chain-length, and the mechanical properties of the fractions were then investigated. It appears, however, that much of this earlier work has been handicapped by the lack of a sufficient quantity of the fractionated materials to allow them to be satisfactorily characterized. In addition, with

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few exceptions, the fractionations have consisted in a division of the materials into a very few portions, without adequate repeated separations. In order to overcome such shortcomings, the fractionation of a large quantity of cellulose acetate was undertaken, and the mechanical properties of the various fractions and their blends were studied. The present report is limited to a description of the separation and a few of the characteristics of the fractions.

II. EXPERIMENTAL PROCEDURE

I. MATERIALS

The starting material was 150 liters of a filtered solution of commercial cellulose acetate of the type used in rayon manufacture.[4] It contained 2.5 percent of cellulose acetate, 95.5 percent of acetone, and 2.0 percent of water by weight. The acetate had an Eastman viscosity of 93 seconds in 4:1 acetone solution [3], a precipitation value of 68.8 percent [3], a melting point of 250° C, and a char point of 301° C. The acetyl and ash contents were 38.6 and 0.06 percent, respectively.

2. METHODS

(a) ESTIMATION OF RELATIVE CHAIN-LENGTH

The relative degrees of polymerization[5] (henceforth referred to as *DP*) of the starting material and the various fractions were estimated viscometrically by the use of Staudinger's relationship $DP = \eta_{sp}/K_m C$ [6], where η_{sp} is the specific viscosity, K_m is Staudinger's constant of proportionality, C is the concentration in grams of solute per liter of solution, and *DP* is the degree of polymerization.

The specific viscosities were measured of solutions containing 2.64 g of cellulose acetate per liter of solution at temperatures of 25.1° C and 60.6° C, with Methyl Cellosolve (ethylene glycol monomethyl ether) as the solvent. Staudinger constants of 9.7×10^{-4} and 7.0×10^{-4} were used for calculating the results at 25.1° C and 60.6° C, respectively. These constants were obtained from Staudinger's value for the constant at 20° C [6], using the assumption that the molecular weight of a given sample is the same at all three temperatures. The *DP* values reported in tables 1 and 2 are the means of the values obtained by measurements at 25.1° and 60.6° C.

(b) ESTIMATION OF ACETYL CONTENT

The acetyl contents of the samples were estimated by the method of Eberstadt, according to the recommendations of Genung and Mallatt [7]. The samples were first ground in a Wiley mill, to promote intimate contact between the sample and the solution.

FRACTIONATION PROCEDURE

The fractional precipitation technique was used in preference to other fractionation procedures, since the method appears to be as

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[4] We are indebted to the Tennessee Eastman Corporation for furnishing us with this material.
[5] By "degree of polymerization" is meant the average number of glucose residues per chain. The calculated molecular sizes have been expressed as *DP* values in this paper as a matter of convenience; *DP* values are directly converted to molecular weights by multiplying by the equivalent weight, in this case, 260. Because of the limitations of the method of determining them [4, 5], the *DP* values should be considered as relative values.

effective as others and much more convenient. On the basis of the results of preliminary experiments, 95 percent ethyl alcohol was chosen as the precipitant. The general procedure was to add a quantity of ethyl alcohol insufficient to cause a permanent precipitate to a solution of cellulose acetate at room temperature (20° to 25° C) contained in a 5- or 10-gallon bottle. The concentration of acetate after the addition of alcohol was 1.2 percent or less throughout the first fractionation. The precipitate initially formed by high local concentrations of alcohol was dissolved by stirring until a homogeneous solution was obtained. The vessel was then slowly cooled to a temperature of 10° C. A gelatinous precipitate slowly formed in the bottom of the vessel, the quality of the precipitate being such that the supernatant solution could be easily removed by decantation. The attainment of equilibrium was hastened by occasional stirring and by scratching the bottles. That the process is a reversible one was shown by the fact that the precipitate could readily be redissolved and a homogeneous solution obtained by warming the system to room temperature. The supernatant solution was separated from the precipitate by decantation, and an additional quantity of alcohol was added to the solution. The process described above was then repeated until the desired number of fractions was obtained. The quantity of alcohol to be added was determined in each case by a preliminary test-tube experiment, after which the test sample was returned to the solution.

With the possible exception of the precipitate obtained by the first addition of alcohol, for which no estimate of the *DP* could be obtained (see section III), materials of high molecular weight were precipitated first by this procedure, and successive additions of alcohol precipitated materials of lower molecular weight in a progressive manner.

The acetate solution was divided into 3 portions of about 50 liters each, and each of these was then treated so as to obtain 7 fractions of roughly equal weights. In each case the first fraction was not completely soluble in acetone. These first fractions, which will be described later, were combined and set aside. Fractions of approximately equal *DP*'s among the remaining fractions were combined to give 7 mixtures, which were then refractionated to yield a total of 29 fractions. The concentration of acetate after the addition of alcohol was 5 percent or less in this and the subsequent fractionation. Fractions of similar *DP* were again combined to 7 mixtures, which were again split into a total of 28 fractions. The fractions of approximately equal *DP* were finally combined into 14 fractions, which will be described later.

III. RESULTS AND DISCUSSION

The results of the complete fractionations, with the exception of the first fractions, are shown in table 1. The third column for each fractionation gives the value of the integral distribution function, $I(P)$,[8] corresponding to each *DP* value given in the first columns. The values of $I(P)$ were obtained as follows: To one-half of the weight percentage of each fraction was added the sum of the weight percentages of all of the fractions appearing above it in the table. The values of $I(P)$ so obtained represent the total percentage of the entire material with *DP* values between unity and the *DP* under consideration.[6]

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[6] This procedure for obtaining $I(P)$ involves the assumption that the chain-lengths in any fraction are symmetrically distributed about the average chain-length of the fraction [8].

TABLE 1.—*Results of three successive fractionations of a cellulose acetate sample*

First fractionation			Second fractionation			Third fractionation		
DP	Weight	I(P)	DP	Weight	I(P)	DP	Weight	I(P)
	Percent			*Percent*			*Percent*	
81	9.9	5.0	52	5.6	2.8	24	1.8	0.9
88	7.5	13.7	56	6.2	8.7	37	0.9	2.3
95	4.5	19.7	94	6.1	14.9	67	6.6	6.0
110	8.8	26.3	95	2.4	19.1	78	8.4	13.5
137	7.0	34.2	105	1.8	21.2	80	2.1	18.8
143	3.2	39.3	107	7.0	25.6	111	8.5	24.1
145	10.7	46.3	136 }	6.4	32.3	131	4.3	30.5
146	6.9	55.1	136 }			140	2.7	34.0
149	2.9	60.0	139	4.4	37.7	149	3.5	37.1
184	3.3	63.1	140	5.7	42.8	151	4.7	41.2
228	6.0	67.7	157	2.6	46.9	162	3.9	45.5
229	5.2	73.3	158	2.4	49.4	166	5.5	50.2
245 a }	7.7	79.8	172	1.2	51.2	185	1.7	53.8
245 }			175	2.4	53.0	189	1.2	55.2
277	7.0	87.1	187	4.5	56.5	193	4.9	58.3
284	6.6	93.9	192	5.7	61.6	213	4.3	62.8
290	3.0	98.7	203	2.2	65.5	214	3.3	66.7
			211	2.2	67.7	238	2.4	69.5
			215	3.6	70.6	241	2.9	72.2
			216	0.6	72.7	263	3.4	75.3
			223	3.9	75.0	273	1.4	77.7
			234	2.7	78.3	291	4.9	80.9
			248	2.2	80.7	292	1.8	84.2
			253 }	4.1	83.9	298	4.4	87.3
			253 }			351	3.3	91.2
			270	3.9	87.9	361	2.9	94.3
			290	1.8	90.7	370	2.3	96.9
			332	4.9	94.1	397	1.9	99.0
			337	3.9	98.5			

a In a number of cases, 2 fractions of identical DP were obtained. The values for these fractions are combined in columns 2 and 3.

In figure 1, the values of $I(P)$ are plotted as ordinates against the corresponding DP values as abscissas, for each of the three fractionations. The integral weight-distribution curves shown in this figure appear to show a slight displacement toward the higher DP values in the second and third fractionations as compared with the first. This is particularly noticeable at the upper ends of the curves. It therefore appears that a precise estimation of the distribution of chain-lengths in the starting material can be obtained only by the use of a relatively thorough fractionation procedure. The improvement of the homogeneity of the individual fractions as the fractionation was continued was indicated by the fact that separation became increasingly difficult, because the size of the precipitate was increasingly more sensitive to the quantity of alcohol added.

It must be pointed out that after the procedure described above, the fractions are not homogeneous; their homogeneity has, however, been greatly improved. Since relatively little further improvement is to be expected on continued fractionation beyond this point [8], the present experiments were limited to three fractionations.

The differential distribution curve shown in figure 2 was obtained from the smooth integral weight-distribution curve for the second and third fractionations (solid line, fig. 1). The tangents to this smooth curve (estimated graphically) are plotted as the ordinates in figure 2, against the corresponding DP values as the abscissas. Since the material in the first fraction is not included for reasons discussed later, the distribution of chain-lengths in the starting material is not precisely represented. The inclusion of this fraction would raise the curve slightly in the region of higher DP's.

In marked contrast with the other fractions, the first fraction precipitated in a fibrillar form, which after centrifuging or long standing acquired gel-like properties. The precipitate was not completely soluble in acetone or Methyl Cellosolve, and for this reason, an esti-
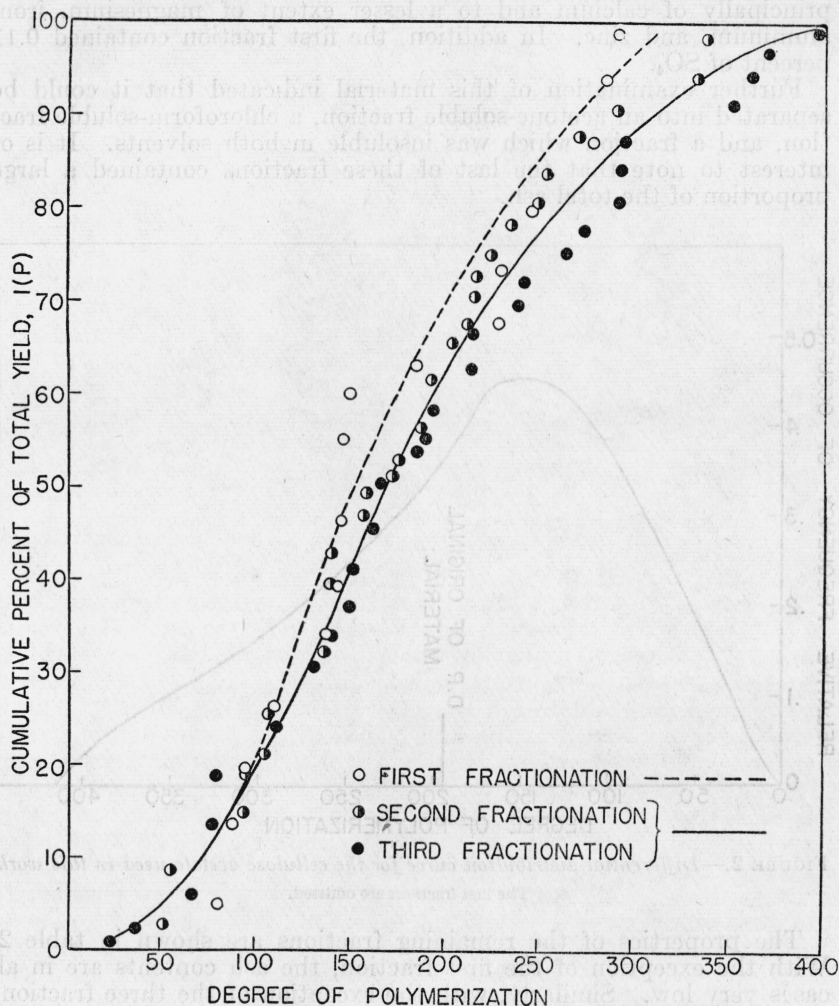

FIGURE 1.—*Integral weight-distribution diagrams, representing the results of the three fractionations of a cellulose acetate.*

The first fractions are omitted. The ordinates represent the cumulative percentages of the total yield included at a given *DP*. For complete explanation, see the text.

mate of its *DP* was not obtained. This fraction contained a large proportion of the ash (see table 1) and the haze-producing materials of the entire starting material, which is in agreement with the results of other investigators [1, 9, 10]. Films and solutions prepared from

this fraction were characterized by their very bad haziness in contrast with those prepared from the other fractions. These results suggest that an improvement in the clarity of films might be effected by a rough fractionation to remove a small percentage of the starting material. Spectroscopic analysis indicated that the ash consisted principally of calcium and to a lesser extent of magnesium, iron, aluminum, and zinc. In addition, the first fraction contained 0.11 percent of SO_4.

Further examination of this material indicated that it could be separated into an acetone-soluble fraction, a chloroform-soluble fraction, and a fraction which was insoluble in both solvents. It is of interest to note that the last of these fractions contained a large proportion of the total ash.
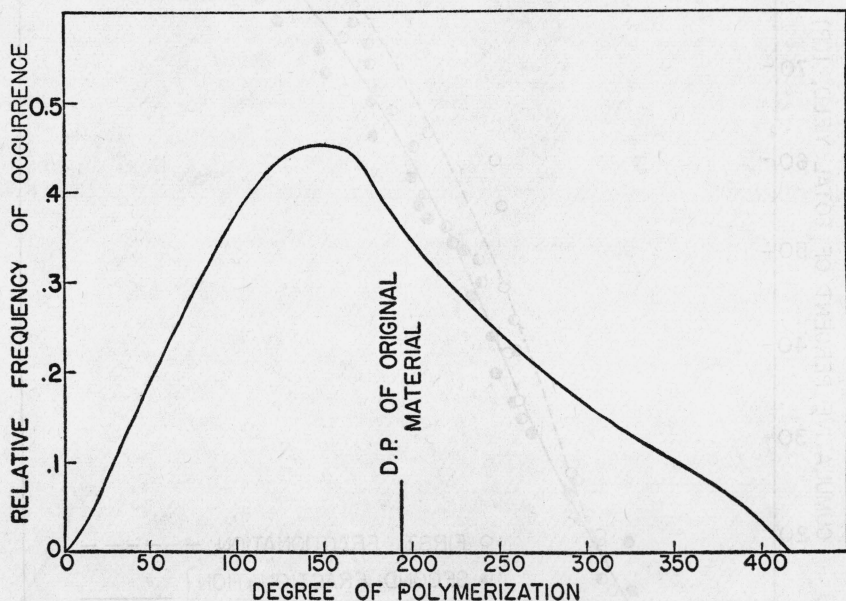
FIGURE 2.—*Differential distribution curve for the cellulose acetate used in this work.*
The first fractions are omitted.

The properties of the remaining fractions are shown in table 2. With the exception of the first fraction, the ash contents are in all cases very low. Similarly, with the exception of the three fractions of lowest *DP*, the acetyl contents are also identical with that of the starting material within the experimental error. The somewhat high acetyl contents of these three fractions may be explained by the presence of an extra esterifiable hydroxyl group on the glucose residue on one end of each chain. The influence of this extra functional group is not noticeable except in the fractions of very low *DP*, when it becomes an appreciable proportion of the total number of hydroxyl groups. The results therefore indicate that with the exception of the first fraction, the separation has apparently been primarily with respect to chain-length.

TABLE 2.—*Properties of the starting material and the fractions of cellulose acetate*

Fraction	Specific viscosity at—		DP	Acetyl content	Ash content	Melting point [a]
	25.1° C	60.6° C				
				Percent	*Percent*	*° C*
Starting material	0.498	0.362	194	38.6	0.06	250
1				38.6	.33	
2	1.019	.687	380	38.5	.06	255
3	0.921	.626	345	38.5	.03	253
4	.770	.531	291	38.5	.07	255
5	.699	.473	262	38.5	.07	255
6	.630	.428	236	38.3	.04	257
7	.550	.390	211	38.4	.03	254
8	.520	.347	194	38.5	.03	253
9	.429	.313	167	38.6	.03	248
10	.382	.271	146	38.5	.02	255
11	.335	.239	129	38.7	.02	247
12	.303	.223	118	38.6	.05	248
13	.197	.156	81	38.9	.02	246
14	.171	.128	68	39.0	.00	242
15	.074	.058	30	39.3	.04	237

[a] We are indebted to F. D. Pilgrim and W. O. Kearse, of the Tennessee Eastman Corporation, for making the melting-point measurements reported in this table.

As further means of characterizing the fractions, a number of solubility measurements were made, the results being shown in figure 3.
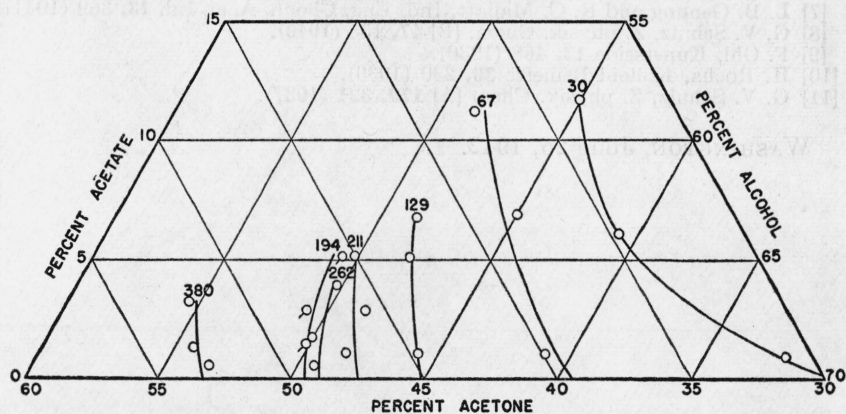
FIGURE 3.—*Phase diagram, showing some of the solubility relationships of the cellulose acetate and several of its fractions.*
Fractions, ○; starting material, ○. For complete description, see text. The number above each curve represents the *DP* of the material.

The procedure involved the titration with absolute ethyl alcohol of solutions of different concentrations of the acetate samples in acetone at 21° C. The weight composition of the solution when the first permanent cloud appeared is represented by a point on the diagram. The results indicate that a better separation can be obtained in dilute solutions, since the curves are more widely separated in the region of low concentrations. In addition, the wider relative separation of the curves for materials of lower *DP*'s indicates that more thorough fractionation would be expected for the materials of lower molecular weight. These results are consistent with the conclusions reached by Schulz on theoretical grounds [8, 11]. The curve for the starting material is, of course, displaced from the position that would be

occupied by a fraction of corresponding average *DP*, since it contains a large proportion of materials of high molecular weight. It is interesting to note, however, that this displacement is considerably less than might have been expected. Thus, the curve for the starting material might perhaps have been expected to fall near that for the fraction of *DP* 380, since some of this fraction is in the starting material. The fact that it does not, indicates that the presence of smaller chains apparently increases the solubility of the long-chain material.

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WASHINGTON, June 26, 1942.