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11—THE STRUCTURE OF CELLULOSIC RAYONS. Part I. THE NON-DEGRADATIVE ACETYLATION AND DEACETYLATION OF CELLULOSE AND SECONDARY CELLULOSE ACETATE

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I. INTRODUCTION AND SUMMARY

The present paper is intended to be the first of a series describing an experimental study of the structure of cellulosic rayons, with particular reference to the chain length (degree of polymerisation) and chain length distribution of their molecules. Cellulose acetate rayons were the first to be examined, and difficulties soon arose owing to the fact that many of them differed slightly in acetic acid yield. It therefore became important to have available methods that could be used to change the degree of acetylation of a cellulose acetate without changing its degree of polymerisation, i.e., without causing any degradation. The use of such methods would enable materials of slightly different acetic acid yield to be compared with greater accuracy, either by bringing them all to the same acetic acid yield, or by studying the behaviour of a series of samples differing *only* in acetic acid yield, so that its effect could be eliminated from the comparison. With the extension of the work to the regenerated cellulose rayons the need for such methods became even more imperative, because it proved impracticable to use solutions of cellulose in the ordinary cellulose solvents for all the purposes of the investigation, and conversion to acetate by a non-degradative process would permit the application of methods similar to those developed for acetate rayon.

Most of the literature on methods of acetylation has been concerned with developments of the processes used in industry for the large-scale production of cellulose acetate, but as these generally make use of acids or acid-producing catalysts in the pre-treatments and the acetylation process they need not be considered here on account of the degradation involved. The methods to be discussed chiefly employ a mild catalyst such as pyridine with acetic anhydride as the acetylating agent. Zemplén and László[1] used a mixture of pyridine, chloroform, and the particular chloride for preparing glucose and cellobiose esters of higher fatty acids; Behrend and Roth[2] used acetic anhydride and pyridine for acetylating glucose; and Hess and Messmer[3] extended this method to the esters of higher fatty acids. Cellulose was esterified with acid chlorides of higher fatty acids in mixtures of pyridine and benzene by Grün and Wittka[4], Kita and his collaborators[5], and Pringsheim, Larand and Ward[6]; and with quinoline as catalyst by Karrer and Zega[7]. In these methods the acetylation was generally accomplished by refluxing the cellulose with the reagents for several hours.

The desirability of swelling the cellulose before acetylation was stressed by Elöd and Schmid-Bielenberg[8]; Hess and Ljubitsch[9] had previously used a swelling treatment in dilute sodium hydroxide solution, this being subsequently replaced by the acetylating medium pyridine and acetic anhydride, and the acetylation continued for about 40 days at a temperature below 70° C. The resulting triacetates were insoluble in organic liquids, and the opinion was expressed that the method reduced degradation to a minimum. Staudinger and Eilers[10] criticised the use of the usual acid catalysts, and found by employing a method similar to that of Hess that

triacetates from rayons were soluble in certain organic solvents and were not degraded, whilst triacetates from cotton or wood-pulp would do no more than swell in the solvents. More recently Staudinger and Daumiller[11] have made extensive use of this method of acetylation, and after hydrolysing the triacetates found no change in the degree of polymerisation as indicated by viscosity measurements.

Much of the recent work, with, however, little reference to the possible occurrence of degradation, has been done by Shettle and his co-workers[12]. In this work pyridine was always used as catalyst in preference to either quinoline or dimethylaniline, and, as acetylating agent, the acid chloride was generally used in the presence of benzene. The extent of the esterification was found to decrease in the order acetate, benzoate, palmitate, and stearate, and raw linters acetylated more easily than mercerised cotton, which itself acetylated more easily than viscose rayon. In Shettle's most recent publication[13] it is stated that a mixture of acetic anhydride and pyridine is the best acetylating agent, and the presence of benzene, chloroform, or carbon tetrachloride is undesirable.

The complete acetylation of technical secondary cellulose acetate has been discussed by Bernoulli, Schenk and Hagenbuch[14], and by Staudinger and Daumiller[11], who have stated that at room temperature aqueous pyridine and acetic anhydride quickly form the triacetate.

In the present paper several factors affecting the acetylation of secondary acetate and regenerated cellulose rayons by means of acetic anhydride in the presence of pyridine are considered. It is shown that the rayons are not degraded when this method of acetylation is employed, and the dependence of solubility on the degree of esterification is briefly discussed. A non-degradative method of hydrolysing secondary cellulose acetates while in solution, in order to eliminate non-random effects due to a heterogeneous process, or to samples having different molecular orientations, is also given.

II. EXPERIMENTAL METHODS

(a) Method of Acetylation

Partial acetylation of cellulose proceeding in a heterogeneous system always results in a non-random distribution of acetyl groups, and so makes any theoretical treatment difficult. It is therefore desirable to acetylate in a homogeneous system, especially when intermediate degrees of acetylation are required. It is at all events invariably better that the final product should dissolve in the acetylation mixture, so that precipitation may secure as homogeneous a product as possible.

The method generally adopted for the esterification of secondary cellulose acetates was to dissolve the air-dry material (1 gram) in pure pyridine (30 c.c.), to acetylate with acetic anhydride (20 c.c.) for various times and then to precipitate the samples in water. The white flocculent solids formed were filtered through sintered glass funnels, washed free from pyridine and acetic anhydride, and air-dried. In an alternative procedure, the materials were refluxed together, samples being removed at intervals for precipitation and washing.

For the acetylation of viscose rayon the following procedure was adopted. The air-dry rayon (1 gram) was swollen in 20 c.c. of the swelling mixture, and the swollen fibres were filtered, washed in pure pyridine, and acetylated for various times in a mixture of pyridine (30 c.c.) and acetic anhydride (20 c.c.). The whole was then poured into water and the acetylated material filtered, washed free from the acetylation mixture, and dried. Similar experiments in which the cellulose was refluxed with the esterification mixture are recorded.

(b) Method of Homogeneous Hydrolysis

To prepare a hydrolysed cellulose acetate a 2 per cent. solution of secondary acetate rayon in acetone was made and N/10 aqueous sodium hydroxide solution sufficient to cause the requisite amount of hydrolysis was slowly added with stirring. The homogeneous liquid was then generally left for about 20 hours at room temperature in order to ensure completion of the hydrolysis, and the solution was poured into water. The solid was filtered off through a sintered glass filter, washed free from acetone and sodium acetate, and dried at 40° C.

(c) Determination of Acetic Acid Yield

Acetic acid yield was determined in accordance with the procedure outlined in a previous publication[18], but for convenience and completeness details of the method are included here.

About 0·4 gm. of the acetylated sample was dried for 3 hours at 110° C. and hydrolysed over-night at room temperature with 10 c.c. of an approximately normal solution of potassium hydroxide made up in equal volumes of water and methyl alcohol. The amount of alkali consumed and hence the acetic acid liberated was estimated by adding 10 c.c. of approximately normal sulphuric acid, leaving for half an hour, and then titrating the excess acid with N/10 sodium hydroxide, phenolphthalein being used as indicator. The concentrations of the approximately normal solutions were such that blank determinations made in the absence of cellulose acetate gave a small positive titre with the N/10 alkali, which was allowed for in the calculation. The acetic acid yield is defined as the weight in grams of acetic acid produced from 100 g. of dry cellulose acetate on hydrolysis, and is calculated from the following relation:

$$\text{Acetic acid yield} = \frac{0{\cdot}6 \times f \times (T - t)}{W}$$

where f = factor of the N/10 NaOH,
T = titre,
t = blank titre,
and W = dry weight of cellulose acetate used.

The values recorded for the acetic acid yield of all the acetylated samples considered are the means of duplicate determinations.

(d) The Determination of Fluidity

The determination of the fluidity of cotton cellulose in cuprammonium hydroxide solution has been considered in detail by Clibbens and Geake[15] and Clibbens and Little[16]; the application of the method to the regenerated cellulose rayons has been described by Ridge, Parsons and Corner[17]. Cuprammonium hydroxide solution hydrolyses cellulose acetate to cellulose (cellulose recovered from a cuprammonium solution of cellulose acetate had an acetic acid yield of 1·3 per cent.), and hence it is possible to determine the fluidity of cellulose acetate by a method similar to those used for cotton and the regenerated celluloses. It will be obvious, however, that since acetic acid is split off when cellulose acetate is dissolved in cuprammonium a weight of cellulose acetate greater than that of cellulose must be dissolved in order to produce a solution of given cellulose concentration. The actual amount of acetate required to produce a 2 per cent. solution of cellulose is given by the relation

$$W = 2V\left(\frac{1}{100 - m} \times \frac{142{\cdot}9}{142{\cdot}9 - A}\right)$$

where W = weight of cellulose acetate in gm.,
V = volume of viscometer in c.c.,
m = per cent. moisture content (gm. water per 100 gm. air-dry cellulose acetate),
A = per cent. acetic acid yield of cellulose acetate.

For the purpose of the work described in this paper, however, most of the fluidities of cellulose acetates have been determined in solutions containing 1 per cent. of cellulose, in order to economise on materials.

The acetic acid split off from the cellulose acetate of course neutralises part of the cuprammonium hydroxide, and so alters the composition of the solvent. It will be shown later that this has a definite but small effect on the fluidity, so that for ordinary purposes it is sufficiently accurate to dissolve the cellulose acetate directly in the solvent rather than first hydrolyse it to cellulose.

The fluidity is calculated as for cotton or regenerated cellulose rayons by the formula:

$$F = \frac{C}{T - (k/T)}$$

where F = fluidity of solution, in reciprocal poises,
C = viscometer constant,
k = kinetic energy constant,
T = time of outflow in seconds.

(e) Purity of the Pyridine employed

Impure pyridine resulted in products which were not white, and for all this work a refined grade was dried over solid sodium hydroxide and distilled in an electrically heated all-glass apparatus fitted with a reflux return head. A water-white product boiling between 114° and 114·5° C. was obtained.

(f) Cellulosic Materials used

The samples were in yarn form except No. 2, which was available as a sliver of cut staple fibre; all were freed from oil, soap, or other foreign matter before use. The materials were chosen so as to be reasonably representative of the various types of rayon in production.

(1) *Seraceta.*—Secondary acetate rayon produced by Messrs. Courtaulds Ltd. Yarn denier 140, filament denier 5.

(2) *Celanese FS.*—A regenerated cellulose rayon made by the hydrolysis of acetate rayon, stretched to give high strength. Produced by Messrs. British Celanese Ltd. Filament denier 1.

(3) *Bemberg.*—A regenerated cellulose rayon made by the cuprammonium process by Messrs. British Bemberg. Yarn denier 150, filament denier 1·5.

(4) *"A" Quality Viscose Rayon.*—A regenerated cellulose rayon made by the viscose process by Messrs. Courtaulds Ltd. Yarn denier 100, filament denier 5.

(5) *Tenasco.*—A regenerated cellulose rayon of high tensile strength made by the viscose process by Messrs. Courtaulds Ltd. The fluidity of this material is lower than that of (4). Yarn denier 265, filament denier 2.

Figures for the fluidity and acetic acid yield (where applicable) of these materials are given with the results of the acetylation experiments in which they were used.

III. EXPERIMENTAL RESULTS

(a) Effect of Added Acetic Acid on the Fluidity of Celluloses

Although due allowance for the weight of combined acetic acid was made in obtaining the solutions in cuprammonium hydroxide yet it was desirable to study the effect of this liberated acetic acid on the fluidity of the solution, since it changes the composition of the solvent. Accordingly, glacial acetic acid, equivalent in amount to that released from certain cellulose acetates, was added to cuprammonium hydroxide solutions of viscose or secondary acetate rayons, and the fluidities of the solutions determined.

The results, presented in Table I, show a small but definite reduction in fluidity. This has been found for most of the preparations to be described.

Table I

	Sample	Fluidity in 2% solution (*a*)	(*b*)
(1)	Viscose rayon	8·8, 8·9	9·5
(2)	Viscose rayon+acetic acid equivalent to secondary acetate rayon (53%)	6·8, 6·6	8·2
(3)	Viscose rayon+acetic acid equivalent to triacetate (62·5%)	—	7·6
(4)	Seraceta	10·3	—
(5)	Seraceta+acetic acid equivalent to triacetate	8·8	—

(b) The Effect of Acetylation and of Hydrolysis on the Fluidity

In order to establish the non-degradative action of the acetylation method two samples of Seraceta and two of viscose rayon were acetylated for ten days, at room temperature and at 60° C. respectively, then carefully hydrolysed out of contact with air with N-potassium hydroxide in alcohol-water solution, and finally re-acetylated as before. At each stage the fluidity of 1 per cent. solutions was determined and the results are expressed in Table II.

Table II

	Seraceta				Viscose			
	Sample I		Sample II		Sample I		Sample II	
	Acetic acid yield	Fluidity 1% solution	Acetic acid yield	Fluidity 1% solution	Acetic acid yield	Fluidity 1% solution	Acetic acid yield	Fluidity 1% solution
Original	53·8	28	53·8	28	0·0	24	0·0	24
Acetylated material ...	60·8	27	62·5	26	62·0	23	60·8	24
Hydrolysed material...	4·8	28	4·1	30	1·6	25	1·9	25
Re-acetylated material	57·9	28	59·6	26	59·8	23	58·2	24

The validity of the technique described for homogeneous hydrolysis has also been investigated by determining the fluidity of samples of Seraceta hydrolysed in solution to various extents. The samples were not soluble in acetone below an acetic acid yield of 52 per cent., but all dissolved in pyridine. The changes in fluidity shown in Table III indicate that little degradation has occurred.

Table III

Sample		Acetic acid yield	Fluidity in 1% solution
Seraceta		54	28·0
Partially hydrolysed Seraceta	1	52	26·1
	2	47	29·6
	3	46	27·4
	4	44	27·1
	5	43	30·8

(c) The Acetylation of Secondary Acetate Rayons

Samples of a commercial secondary acetate rayon were dissolved in pyridine, acetic anhydride was added, and the acetylation carried out in thermostats at 25 and 60° C. The results in Table IV show that the rate of acetylation is not much influenced by temperature in this range, and subsequent work on secondary acetates was therefore done at 25° C.

Table IV

		Time of acetylation (hours)						
		0	¼	1	2	6	24	96
Acetic acid yield ...	25° C.	53·8	56·8	59·9	60·6	60·9	61·6	61·8
	60° C.	53·8	60·3	60·6	61·3	60·9	61·6	61·8

Further series of acetylated samples were prepared, chiefly for the purpose of obtaining acetylated celluloses covering a range of acetic acid yields and characterised by a random distribution of acetyl groups along molecules of constant mean chain length. In each experiment of the second series 50 gm. of secondary acetate were further acetylated; the fluidities given in Table V show that no degradation has occurred in the preparation of the acetylated samples, which were all white flocculent solids.

Table V

Time of acetylation (hours)	0	$\frac{1}{60}$	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{2}$	1	4	7	21	27
Acetic acid yield ...	53·8	54·1	57·0	57·3	58·6	59·8	60·6	60·3	61·5	61·5
Fluidity (1% solution)	28·0	26·5	27·2	28·9	26·2	26·2	24·8	26·3	26·4	27·9
Time of acetylation (hours)	0	$\frac{1}{15}$	$\frac{1}{12}$	$5\frac{3}{4}$	240	...	...	...	...	...
Acetic acid yield ...	53·8	57·5	58·3	59·4	62·5	...	...	...	...	...
Fluidity (2% solution)	9·3	8·7	9·0	7·5	7·3	...	...	...	...	...

It was at first considered that the slowness of the acetylation when the acetic acid yield approaches that of the triacetate (62·5 per cent.) might be due to the presence of water causing simultaneous hydrolysis. Accordingly, phosphorus pentoxide was introduced into the acetylation mixture, but no improvement was effected.

It is interesting to observe the solubility changes as the acetic acid content of a cellulose acetate rises without change in chain length. Table VI shows these effects qualitatively.

Table VI

Solvent	Acetic acid yield									
	53·8	54·1	57·0	57·3	58·6	59·8	60·3	60·5	61·5	62·5
Acetone	S	S	S	S	S	P	P	P	P	P
Dioxane	S	S	S	S	S	S	S	S	P	P
Pyridine	S	S	S	S	S	S	S	P	P	P
Chloroform	P	P	S	S	S	S	S		S	S
Methylene chloride and alcohol:—										
90 : 10, by vol.	S	S	S	S	S	S	S	S	S	S
70 . 30, by vol.	S	S	S	S	S	S	S	S	S	S

S = Soluble. P = Partially soluble.

It is well known that secondary cellulose acetates are soluble in acetone, but not completely soluble in chloroform, whilst the triacetates dissolve in chloroform, but not in acetone. The acetic acid yield ranges in which these properties hold are, however, less well known. Table VI shows that solubility in acetone is retained up to about 59 per cent. acetic acid yield whilst solubility in chloroform is possible for all acetic acid yields above 57 per cent. There is thus a small region of acetic acid yield in which acetone solubility and chloroform solubility are both exhibited. It is also seen from the table that methylene chloride mixed with alcohol can be a solvent for materials at all stages of acetylation between 53·8 and 62·5 per cent.

In order to investigate the possibility of using a substantially quicker method of acetylation, experiments were conducted in which pyridine solutions of acetate rayon were boiled under reflux with acetic anhydride in an all-glass (Monax) apparatus. Portions of the solution were removed at intervals, precipitated into distilled water, filtered through sintered glass funnels, washed free from the acetylation mixture, and dried. Timing of the acetylation was begun at the onset of boiling. The results are expressed in Table VII.

It is clear that in all the experiments substantially complete acetylation without degradation was achieved. In whiteness and fibrous nature of the acetylated sample, however, the treatment with 20 c.c. of acetic anhydride plus 30 c.c. of pyridine was by far the best, the other mixtures giving rise

to hard and sometimes yellowish products. As expected, all the products were completely soluble in chloroform (the typical cellulose triacetate solvent), almost completely soluble in pyridine, and about 50 per cent. soluble in acetone. From these results it appears that by using the same acetylation mixture and the same ratios of liquid to acetate rayon as those employed for acetylation at room temperature, complete esterification can be accomplished in two hours by conducting the reaction under reflux.

Table VII

Composition of acetylation mixture per gm. Seraceta	Time of acetylation (hours)	Acetic acid yield, %	Fluidity in 1% solution
	0	53·8	28·0
10 c.c. Acetic anhydride, 40 c.c. pyridine	1	62·6	27·0
	2	61·8	29·4
	3	62·0	26·7
20 c.c. Acetic anhydride, 30 c.c. pyridine	1	61·8	25·0
	2	62·6	28·2
	3	62·0	27·3
40 c.c. Acetic anhydride, 10 c.c. pyridine	1½	62·3	25·8
	2	61·6	27·5
	3	61·0	27·9

(d) The Acetylation of Viscose Rayon

The rate of acetylation of air-dry viscose rayon by acetic anhydride in the presence of pyridine is exceedingly slow, but it can be accelerated by a pre-treatment of the material with a reagent that produces swelling of the cellulose. Such swelling is produced, for example, by water, or to a still greater extent by solutions of the strong alkalis, and the rate of acetylation of viscose rayon was observed to be greatly increased by pre-treatment with sodium hydroxide solutions of suitable concentration. Systematic investigations were not, however, pursued along these lines since a sufficient acceleration of the process, with fewer possible complications, was achieved by a pre-treatment of the viscose rayon with a solution of water in the weak base, pyridine, which is a component of the acetylation mixture.

In this connection preliminary measurements were made of the swelling of cellulose in different mixtures of pyridine and water. Regenerated cellulose sheet, previously freed from plasticiser by immersion in many changes of distilled water, was employed in these swelling experiments instead of viscose rayon for reasons of convenience. Although it was realised that (quantatively) the results could not hold for viscose rayon yet it was expected that their application in a general way would be permissible. The increase in weight of the cellulose sheet was used as a measure of the swelling, and was determined after swelling to equilibrium at 25° C. in various mixtures of water and pyridine. The results presented in Fig. 1 show that very little swelling

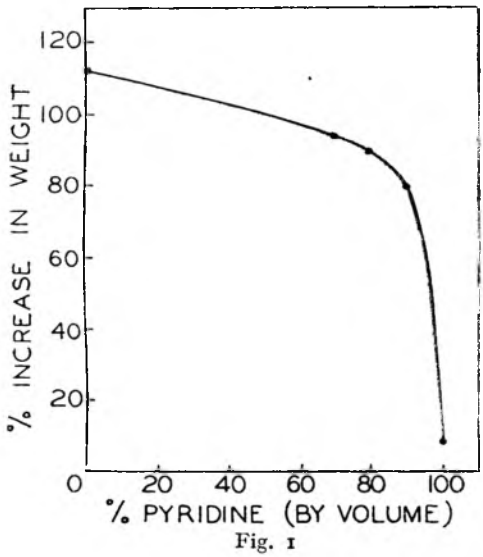

Fig. 1

occurs in pure pyridine, but that a mixture containing only 20 per cent. of water produces nearly as much swelling as pure water.

Experiments were then made to determine the effect on the degree of acetylation of the time and temperature of pre-treatment and of acetylation, for a given acetylation mixture (pyridine-acetic anhydride) and the following three pre-treatments:

(i) 100 per cent. pyridine.

(ii) 80 per cent. pyridine, subsequently removed by washing with 100 per cent. pyridine.

(iii) 80 per cent. pyridine, subsequently replaced by 90 per cent. pyridine, and this again replaced by 100 per cent. pyridine.

The following general conclusions were drawn from the results.

(*a*) Acetylation proceeds more rapidly at 60° than at 25° C.

(*b*) No real difference between the effects of swelling at 60° C. and 25° C. on the rates of subsequent acetylation was observed, and, further, no improvement occurred by prolonging the swelling beyond two hours.

(*c*) As expected, the use of 100 per cent. pyridine as a pre-treatment proved to be of no value. For instance, after acetylating for 48 hours at 60° C., an acetic acid yield of only 5 per cent. was obtained.

(*d*) The pre-treatments (ii) and (iii) above gave practically identical results in the acetylation, and values of about 50 per cent. acetic acid yield were obtained in 48 hours at 60° C. However, a further 150 hours were required to complete the acetylation to the triacetate stage.

(*e*) It was found that an acetic acid yield of over 60 per cent. was required before the material dissolved in the acetylation mixture.

It appeared, therefore, that a triacetate could be produced by pre-swelling in 80 per cent. pyridine at room temperature for any time greater than 2 hours followed by acetylation at 60° C. for 10 days.

Various changes were made in the technique in an attempt to hasten the acetylation process. For instance, acetyl chloride was substituted for acetic anhydride as acetylating agent, but proved to be less effective. The catalyst pyridine was replaced by dimethylaniline, which was used with both acetic anhydride and acetyl chloride, both dry and air-dry viscose rayon being used. The results were on the whole unsatisfactory; the acetylation of the air-dry rayon proceeded farther than that of the dry material.

Table VIII

Swelling for 1 hour			Swelling for 24 hours		
Time of acetylation (hours)	Acetic acid yield (%)	Fluidity in 1% solution*	Time of acetylation (hours)	Acetic acid yield (%)	Fluidity in 1% solution
Acetylation with 10 c.c. acetic anhydride + 40 c.c. pyridine per gm. viscose rayon :—					
8	46·4	28·1	6	60·9	23·7
12	51·8	28·4	12	53·9	21·7
Acetylation with 20 c.c. acetic anhydride + 30 c.c. pyridine per gm. viscose rayon :—					
3	61·6	22·7	3	60·4	23·3
6	62·2	22·3	6	62·3	22·8
12	60·5	23·8	12	61·7	23·2
Acetylation with 40 c.c. acetic anhydride + 10 c.c. pyridine per gm. viscose rayon :—					
6	56·0	22·9	6	62·4	24·0
12	56·8	29·3	12	62·4	22·7

* The fluidity of the untreated viscose rayon was 23·9

Experiments have also been conducted in which the swollen viscose rayon is boiled under reflux with the acetylation mixture. The apparatus and acetylating solutions were the same as those described for the reflux acetylation of Seraceta (above), but in addition the air-dry yarn was pre-swollen in a pyridine/water solution (80 per cent. pyridine, 20 per cent. water) at room temperature for 1 and 24 hours. The swelling solution was

removed by filtering through sintered glass filters and the yarn washed in pure pyridine before adding the acetylation medium. (Thus two series of results were obtained and are given in Table VIII). Viscose rayon or swollen viscose rayon being pure cellulose was not soluble initially in the acetylation mixture, but during the course of the esterification it gradually dissolved. No sample was taken for analysis until the whole of the viscose was in solution in order to eliminate any effect of chain length fractionation.

It can be seen from this table that on the whole the mixture composed of 20 c.c. of acetic anhydride and 30 c.c. of pyridine is the best for causing the greatest acetylation together with the least degradation; these samples were also the most white and fibrous. In this connection, swelling for 24 hours seems to produce little improvement over swelling for 1 hour. Further, the samples treated with 20 c.c. of acetic anhydride plus 30 c.c. of pyridine dissolved in the acetylation mixture in a shorter time than those having other treatments. For subsequent acetylation work on other fibres this treatment, together with swelling for 1 hour in the usual mixture was chosen as the most likely to yield useful results from the preparative point of view.

All samples dissolved completely in chloroform, and none dissolved completely in acetone or pyridine.

(e) Acetylation of Other Rayons

Celanese FS, Bemberg rayon, and Tenasco proved to be most difficult to acetylate. By pre-swelling in 80 per cent. pyridine solution followed by acetylation at 60° C. the first two attained an acetic acid yield of only 59 per cent. in ten days, but five weeks were needed for the Tenasco to reach this figure.

On account of these unfavourable results an improvement was attempted by acetylation under reflux in the manner previously described.

The air-dry samples were swollen in 80 per cent. pyridine in water solution for 1 hour at room temperature and then acetylated under reflux with the most favourable mixture: 20 c.c. acetic anhydride plus 30 c.c. pyridine per gram material.

Table IX shows that these samples can be almost completely acetylated with but little change in fluidity although it would seem undesirable to prolong the acetylation to the longest times noted.

Table IX

	Time of acetylation (hours)	Acetic acid yield %	Fluidity in 1% solution
Celanese FS	0	1·0	29·5
	10	62·3	28·1
	15	62·9	27·0
	24	61·2	27·9
Bemberg rayon	0	0	12·0
	6	60·0	12·1
	12	60·2	12·5
	24	60·6	15·2
Tenasco	0	0	14·5
	7	61·0	13·2
	12	60·6	15·2
	24	57·0	18·2

IV. GENERAL INSTRUCTIONS FOR THE COMPLETE ACETYLATION OF RAYONS

It is emphasized at the outset that complete solution in the acetylation mixture is essential before the sample is precipitated. After each of the acetylations described it is necessary to pour the clear liquid slowly into water, to filter through sintered glass funnels, and to wash the preparation free

from the acetylation mixture with distilled water. Details are given for 1 gram of cellulosic material.

(*a*) *Secondary Cellulose Acetate.*—Dissolve the air-dry material in 30 c.c. of pure pyridine, add 20 c.c. of acetic anhydride and acetylate for ten days at room temperature. Alternatively, the whole may be boiled under reflux in an all-glass apparatus for 2 hours. Both methods give white products.

(*b*) *Viscose Rayon.*—Swell the air-dry material over-night at room temperature in 20 c.c. of a mixture of 16 c.c. of pyridine and 4 c.c. of water. Filter the fibres, wash in pure pyridine, and acetylate at 60° C. for 10 days with a mixture of 30 c.c. of pyridine and 20 c.c. of acetic anhydride. The product is not quite white. By conducting the esterification under reflux for 6 hours a white product which is fully acetylated is formed. It is permissible here to reduce the time of swelling to 1 hour.

(*c*) *Other Cellulosic Rayons.*—The method at 60° C. described above for viscose rayon may be used, but often does not give complete esterification. Acetylation under reflux as described in (*b*) above is probably the most suitable, although an acetylation time of about 10 hours may be required. These samples will be almost white.

The data on the swelling of regenerated cellulose sheet in aqueous pyridine were supplied by Dr. R. J. B. Marsden, of these laboratories. Part of the experimental work was done by Mr. G. C. Gibbons and Miss E. Martin.

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