PREPARATION OF CELLULOSE FROM WOOD PULP BY CONTINUOUS ACETYLATION

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INTRODUCTION

The position of cellulose acetate and triacetate in the world market is given every year by the American review *Textile Organon*[1]. *Table 1* sums up the figures published in June 1965 by this review and enables one to compare the worldwide development of yarn, fibre, tow produced from cellulose acetate and triacetate in relation to the production of non-cellulosic synthetic textiles. The production figures of the Eastern countries are not included in this table since they are not well known. The production of cotton textiles has been mentioned as a comparison. The increase in the production of synthetic textiles has been extensive, but the development of the production of cellulose acetate and triacetate textiles is also important.

The development of the production of cellulose esters designed for manufacturing plastics and cinematographic films is of importance. Cellulose esters designed for plastics and films are generally prepared from bleached linters and not from wood pulp. However, it is to be noticed that some cellulose producers have tried to prepare celluloses from wood pulp suitable for these end uses.

Generally the acetylation processes used are old batch processes and

Table 1. World production of yarn, fibre and tow from cellulose acetate, triacetate and synthetic products (millions of pounds)

Year	Cellulose acetate + triacetate			Synthetic fibres: polyamides, polyesters, acrylics, etc.			Cotton
	Fibre and tow†	*Filament yarn*	*Total*	*Fibre and tow*	*Filament yarn*	*Total*	
1955	83	397	480	182	398	580	20 926
1959	116	416	532	498	774	1 272	22 622
1960	226	429	655	637	926	1 563	22 372
1961	240	468	708	739	1 102	1 841	22 004
1962	249	536	785	976	1 407	2 383	23 384
1963	272	559	831	1 223	1 713	2 936	24 019
1964	311	646	957	1 568	2 154	3 722	24 597

Increase in textile production from 1955 to 1964 included (10 years)
Cotton   17%
Cellulose acetate + triacetate   100%
Synthetic fibres: polyamides, polyester, etc.   545%

† Cigarette tow included.

improvements for which are now limited. For this reason and in view of the expansion of the production of cellulose esters, the Societe Rhodiaceta decided, as far back as 1946, to develop a modern process of continuous acetylation.

CONTINUOUS ACETYLATION PROCESS OF RHODIACETA

This process has been patented in many countries[2]. As compared with the batch process, the main advantages of the continuous acetylation process are: (a) Important saving of labour. (b) Reduction in the quantity of acetic anhydride used. (c) Possibility of automating the manufacturing processes completely, which permits to obtain cellulose ester with more uniform analytical characteristics. (d) The surface necessary for capacities of production is twice smaller. (e) Possibility of using blends of cellulose, including linters.

However, since the process is highly mechanized, the power consumption is generally higher than that of batch acetylation operations. In order to simplify our report which is in fact limited to the use of cellulose from wood pulp for continuous acetylation, the continuous acetylation process has been divided into various stages which are briefly described here.

1. Dispersion

This is the only batch operation of the process. It comprises weighing the charge of cellulose followed by dispersion of this charge in a hydrapulper which is a conventional apparatus used in the paper industry (*Figure 1*).

The dispersion can be carried out either in water, or in aqueous acid issued from storage tanks. The time necessary for the dispersion of the charge of cellulose is about 10 min. The cellulosic suspension is then sent through a pump into storage tanks, from which the second stage of the process is continuously fed.

2. Displacement and acetylation

The cellulosic suspension issued from the storage tanks is sent through a pump into an equipment in which the water or the aqueous acetic acid used for the batch preparation of the cellulosic suspension is replaced by pure acetic acid. This operation is carried out on a multistage belt-type filter called "displacement filter" (*Figure 1*).

The cellulosic suspension is introduced in the filter; the 100 per cent acetic acid necessary for the displacement is introduced in the filter at the place indicated (*Figure 1*) and is recycled from one stage to another, in order to remove completely the water from the cellulose. The cellulosic band issued from the displacement filter is pressed with press-rolls, and then shredded in a conventional equipment, before being sent into the feed hopper of a continuous acetylation kneader. Each stage of the displacement equipment is run under a certain vacuum.

The stages 'dispersion' and 'displacement in continuous acetylation' are the only ones extensively investigated in this report. They are carried out on a conventional equipment of the paper industry.

The acetylation kneader is a very peculiar reaction vessel which has especially been designed by the Societe Rhodiaceta. We shall give no detailed information about acetylation, which is a classical reaction. At the outlet
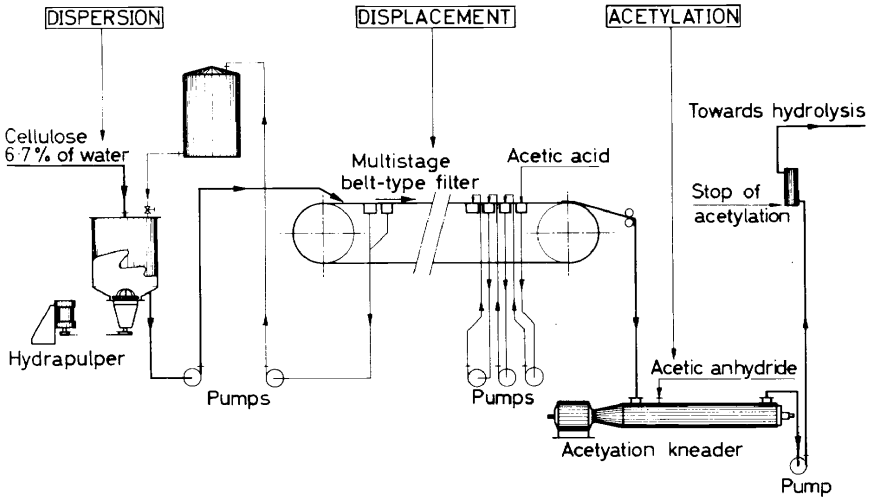
Figure 1. Diagrammatic sketch of the continuous acetylation process of Rhodiaceta showing stages 1 and 2.

of the kneader, the acetic syrup is sent, through a pump, into a device designed for stopping the acetylation reaction. A certain amount of water is introduced, in order to eliminate the excess of anhydride and to bring a certain percentage of water into the collodion entering the next stage of the process.

3. Hydrolysis and continuous precipitation of acetic syrup

Hydrolysis is carried out in the presence of a certain amount of water in a series of vertical vats (*Figure 2*). The internal disposition of these vats is
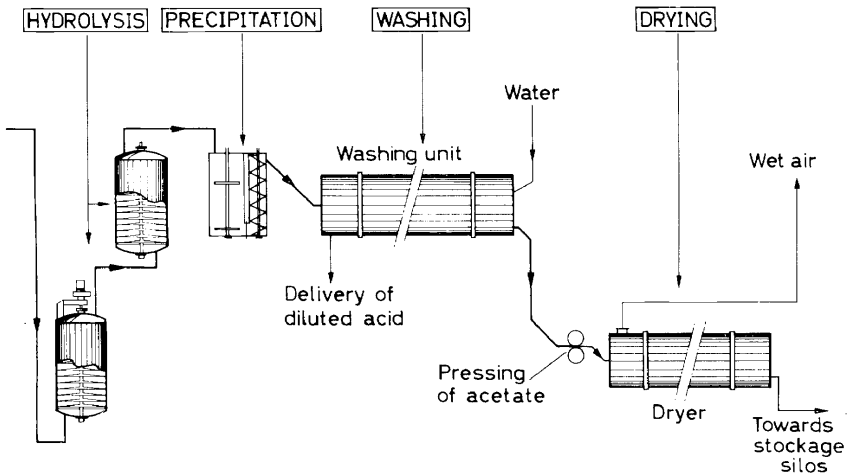

Figure 2. Diagrammatic sketch of the continuous acetylation process of Rhodiaceta showing stages 3, 4 and 5

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particularly important because it is indispensable for the syrup to circulate systematically and spend the same time in the vat in order to obtain a perfectly homogeneous product.

Each vat is fitted with a jacket, so that it can be either cooled or heated. The acetic syrup at the outlet may contain a cellulose acetate with an acetic acid content between 54 and 55 per cent according to the requirements of the spinning plants processing this cellulose ester. The syrup is then precipitated.

4. Ripening and washing of the precipitated cellulose acetate

The suspension of cellulose ester in aqueous acetic acid issuing from the precipitating vat is sent into a ripening rotary drum, and then collected in a storage tank, from which the washing rotary filter is fed (*Figure 2*). All these operations are carried out continuously; the washing machine is fed with water and delivers a diluted acid which is recovered and concentrated in special units not described in this report.

5. Pressing and drying

At the outlet of the rotary washing unit, the cellulose acetate drained is passed through a press. Then it is sent through a pneumatic conveyer into the feed cyclone of a rotary dryer. Dry cellulose acetate is continuously sent through a pneumatic conveyer into a storage tank.

CHARACTERISTICS OF CELLULOSE USED FOR CONTINUOUS ACETYLATION

A cellulose designed for acetylation, according to a continuous or batch process should be checked from the point of view of its reactivity, whether it is obtained from wood pulp or from linters. This problem has been worked out by many investigators and in particular by Richter[5].

As regards continuous acetylation, two particular characteristics of cellulose should be investigated, since the size of some apparatus depends on them. For instance, the reactivity of a cellulose may interfere in the determination of the size of the continuous acetylation vessel, while the permeability of cellulose is of great importance for determining the characteristics of the displacement unit

For the determination of the reactivity of cellulose we have developed a laboratory acetylation method using a Dewar vessel. Details of this method will be published elsewhere in due course. Also included will be a method for measuring the permeability of celluloses. We shall limit our present study to the influence of the permeability of wood pulp on sizing displacement units designed for continuous acetylation.

In the batch acetylation processes, wood cellulose introduced in the reaction vessel has an average water content of about 6·7 per cent. This water consumes a certain quantity of acetic anhydride, according to the reaction:

$$\begin{array}{c} CH_3CO \\ \diagdown \\ O + H_2O \longrightarrow 2\ CH_3COOH \\ \diagup \\ CH_3CO \end{array}$$
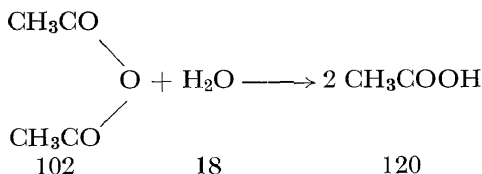
$$\quad 102 \qquad\qquad 18 \qquad\qquad\qquad 120$$

One kg of cellulose with a water content of 6·7 per cent consumes about 400 g of 100 per cent acetic anhydride.

After the displacement stage of the continuous acetylation process, 1 kg of 100 per cent cellulose is impregnated with pure acetic acid (1·6–1·9 kg) and water (0·008–0·0095 kg). This quantity of water represents an acetic anhydride consumption of 0·053–0·063 kg during the acetylation stage. Hence, the anhydride saving due to the use of the continuous acetylation process is about 0·340 kg/kg of cellulose used.

DISPERSION AND DISPLACEMENT STAGES

The wood pulps designed for acetylation are generally supplied as bales made of sheets piled up, with an average water content of about 6·7 per cent. The dispersion of the cellulose sheets may be carried out at a temperature automatically controlled (a) either in water; or (b) in aqueous acetic acid.

Reactivation carried out in water is a little better[4], but necessitates the use of a greater quantity of acetic acid during the operation of displacement, or the use of a displacement unit comprising a larger number of stages. In practice, it seems preferable to use dispersion in an aqueous acetic acid medium. Reactivation depends on the following parameters: (i) water content of the aqueous acetic acid; (ii) temperature at which dispersion is carried out; and (iii) time of contact between the charge of cellulose and acetic acid until the cellulose impregnated with acetic acid is introduced into the reaction vessel.

The efficiency of the displacement unit depends also on various factors relating to celluloses, mentioned hereunder.

Permeability to acetic acid of cellulose from wood

The theory of the laminar flow of a liquid through a porous medium was proposed in 1856 by Darcy who expressed it by the following relation:

$$V = \frac{B_0}{E} \times \Delta p \qquad (1)$$

This relation has been written, further, under the form:

$$V = \frac{B_1}{\mu E} \times \Delta p \qquad (2)$$

where Δp is depression under the layer of cellulose of thickness E; μ the viscosity of the liquid; V the flow speed; and B_1 is the permeability. Permeability depends on fibre nature, on the section (flat or circular), on surface condition, and way of piling, etc.

Equation (2) shows in addition that the flow speed is proportional to pressure and is inversely proportional to the viscosity of the liquid.

This relation has been used by Campbell[5] in a statistical research about the permeability[6] under the form:

$$V = \frac{1}{RM} \times \frac{\Delta p}{\mu} \qquad (3)$$

where M is the weight of cellulose per unit surface; and R is the specific resistance per unit weight of fibrous mass to the passage of the displacing liquid. This factor depends on the fibre nature and piling fibres, since as shown in *Figure 3* the size of cellulosic fibres from conifers or from leafy trees such as beech or eucalyptus is very different.
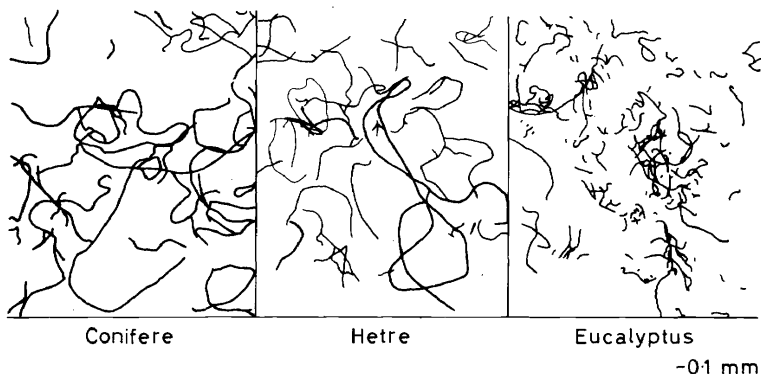

Conifere   Hetre   Eucalyptus

-0·1 mm

Figure 3. Cellulosic fibres from conifers, hetre and eucalyptus

The problem of permeability has been surveyed by Scheagis and Rarchlen[7]. Meadly[8] worked out equations for a turbulent pattern in which the resistance to filtration is proportional to the square of the speed of passage through cellulose. In practice, when the depression varies between 35 and 140 cm of water, flow is a transition between these flow patterns. It is better to carry out practical measures for each type of cellulose.

Our method for the determination of permeability explained in the experimental part of the section gives the time necessary for the passage of 1 000 litres of acetic acid under a depression of 35 cm of water, through 1 m² of a layer of cellulose (3 kg of pure cellulose/m²). For instance, it is found that this time for wood pulps is as follows: from conifer, 300 –600 sec; from beech 600–1 200 sec; and from eucalyptus 1200–2 000 sec.

Of course, the output of a displacement system, consisting of a belt-type filter, shown in *Figure 1* is closely related to the permeability of the cellulose used.

An example of calculation for a belt-type displacement filter is given below; this system seems to be the more rational, but other "leaching" systems can also be used[9].

Diffusion rate and calculation of the number of stages

The number of stages of the displacement unit calculated according to the permeability to acetic acid is useful in determining the equipment dimensions.

We shall now study the mass balances of the displacement and the means available for calculating the number of stages of a unit. If p is the weight in kg/h of 100 per cent cellulose entering or leaving the displacement unit;

and P the weight in kg/h of solid matter, with a degree of dryness entering or leaving each stage, we have

$$P = p/s \qquad (4)$$

If w is the weight of the liquid present

then $w = P - p = (p/s - p)$

or
$$w = p \frac{(1 - s)}{s} \qquad (5)$$

In the following calculations, we shall assume that there is no by-passing between the various stages of the displacement unit; and we call W as the weight in kg/h of acetic acid passing through each stage.

Figure 4 shows the mass transfer in a multistage displacement unit, as well as mass balances for every stage. The titre of the acetic acid used as a solvent is nearly 100 per cent. We asume that w and W are constant, and that an equilibrium is reached at every stage, although this is not exactly true in practice.
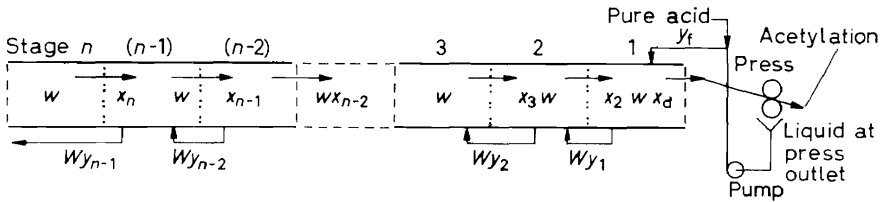

Figure 4. Mass transfer in a multistage displacement unit and mass balance at every stage

In *Table 2* y_f is the water content of the aqueous acid entering the stage 1; $y(n - 1)$ is the water content of the aqueous acid entering the stage n; x_n is the water content of the acid impregnating the cellulose leaving the stage n; and x_d is the water content of the acid impregnating the cellulose leaving the stage 1.

The mass balance of the stage $n - 1$ gives the relation:

$$x_n = x_{n-1} + \frac{W}{w} \left[(y_{n-1}) - (y_{n-2}) \right] \qquad (6)$$

Then, knowing the relation W/w, it is possible to calculate by recurrence or to determine on a graphic the number of stages.

In fact, since the cellulosic fibre size is very small, diffusion is nearly instantaneous. Under these conditions, the liquid leaving a stage is in equilibrium with the liquid impregnating the cellulose leaving the same stage, so that:

$$y_1 = x_d \quad y_2 = x_1 \; .. \; y_{n-1} = x_{n-1}$$

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Table 2. Mass balance per hour for 100 kg of cellulose [Cellulose dryness at every stage: 25%]

	Cellulose leaving stage n	Cellulose leaving stage 2	Acid leaving stage 1	Acid entering stage 1	New acid	Acid leaving press	Cellulose entering press (dryness 25%)	Pressed cellulose (dryness 37%)
100% Cellulose	100 k	100 k	0	0	0	0	100 k	100 k
Acid Water	276 k 900 23 k 100 $x_n = 0.077$	297 k 300 2 k 700 $x_2 = 0.009$	427 k 850 2 k 150 $y_1 = x_d = 0.005$	429 k 05 0 k 95 $y_f = 0.0022$	299 k 7 0 k 3	129 k 350 0 k 650	298 k 500 1 k 500 $x_d = 0.005$	169 k 150 0 k 850
Total Weight of liquid	300 k w	300 k w	430 k W	430 k W	300 k	130 k	300 k w	170 k

$$\frac{W}{w} = \frac{430}{300} = 1.433$$

The number of stages may be calculated according to the method of Backer[10], expressed by the relation:

$$1/f = 1 + a_n \Sigma_1^n a^{n-1} \tag{7}$$

$$a = \frac{y_{n-1}}{x_d} \quad f = \frac{x_d}{x_f} \quad A_n = \frac{x_d}{x_1}$$

or according to the method of McCabe and Smith[11] expressed by the relation:

$$(n - 1) = \frac{\log \dfrac{x_n - y_{n-1}}{x_d - x_f}}{\log \dfrac{x_n - x_d}{y_{n-1} - y_f}} \tag{8}$$

The notations of this form are those used for *Table 2*.

There are also graphical methods which have been described in the report of Robert N. Rickles[9]. In the balance, shown in *Table 2*, we assumed that, at each stage of unit, cellulose dryness is 25 per cent. In fact, dryness often is between 18 and 25 per cent but the method of calculation is the same.

In *Table 3* is given the mass balance of the displacement, not in a belt-type filter as for the preceding balance, but in a Hildebrandt extractor (*Figure 5*), in which cellulose dryness does not exceed 9 per cent (cf. Rickles[9]).
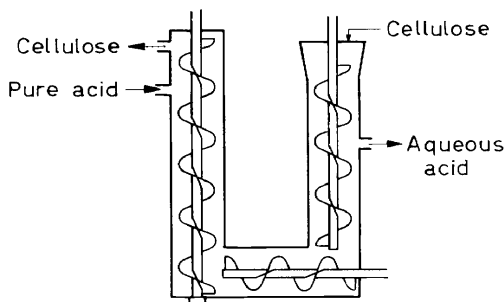

Figure 5. Hildebrandt extractor

In such an extractor equipment, that is to say continuous and not divided, the number of stages corresponds to the so-called H.T.U. (Height Transfer Unit) in chemical Engineering. For every stage, a length so-called H.T.U. (Height Transfer Unit) is determined. The total length of the equipment is then equal to the product N.T.U. × H.T.U. The curves shown in *Figure 6* have been drawn with the help of *Table 3*. Curve 1 is an experimental curve corresponding to the mass balances in *Table 2*. Curve 2 represents the calculations based on a cellulose dryness of 18 per cent. Curve 3 shows the removal of a product different from water added to cellulose.

Table 3. Displacements in a Hildebrandt extractor

	Cellulose sent to acetylation	Cellulose before pressing (dryness 9%)	Acid leaving press	New Acid	Acid entering stage 1	Acid leaving stage 1	Cellulose stage 1 (dryness 9%)
Cellulose	100 k	100 k	0	0	0	0	100 k
Acid Water	169 k 150 0 k 850 $x_a=0.005$	995 k 5 k 00 $x_a=0.0050$	825 k 85 4 k 15	454 k 545 0 k 455 $y_a=0.001$	1 280 k 405 4 k 605 $y_f=0.0039$	1 185 k 75 6 k 425 $y_1=0.005$ x_a	993 k 180 6 k 820 $x_1=0.00682$
Liquid total	170 k	1000 k w	830 k 00	455 k	1 285 k w	1 285 k w	1 000 k w

$$W/w = 1{\cdot}285$$

The examination of these curves shows that water is not displaced with the same facility as other matters. This phenomenon is well known and results as a consequence from preferential hydrogen bonds between OH of cellulose and OH of water.
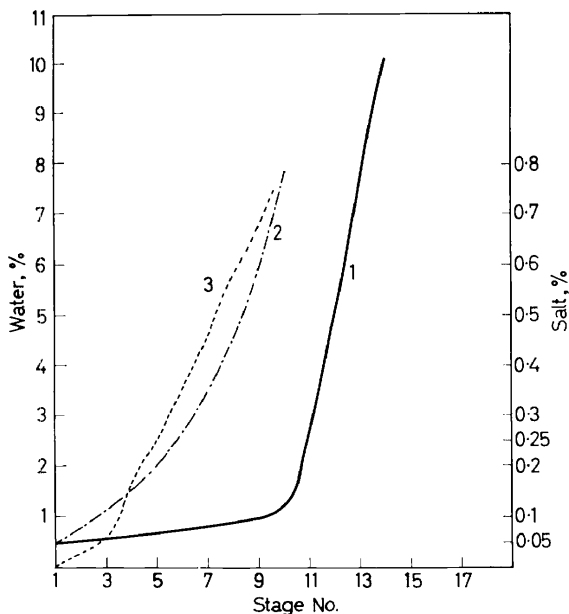

Figure 6. Curves indicating mass balances (1), cellulose dryness (2), and removal of a product different from water (3).

Giles and Jain[13] report that in aqueous solution, methanol is not absorbed by cellulose. Then in the curve 1, the practical output of 9 stages out of 13 is very small. As a result, instead of setting the maximum water content on cellulose impregnated with acetic acid to 0·005, it would be better to set it to only 0·009. Under these conditions, the consumption of anhydride for removing water is still satisfactory.

The difficulties in eliminating the last traces of water contained in cellulose at the end of the displacement may also be explained with the help of the following heterogeneous reaction

$$CH_3COOH + Cel{-}OH \longrightarrow Cel{-}O{-}COCH_3 + H_2O$$
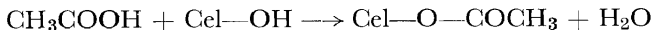
mentioned by Hiller[14] as an example, or by the fact that air which passes through the cellulosic layer leaves behind the moisture it contains.

Determination of stage dimensions

When a belt-type filter is used as displacement equipment, the theoretical surface of each stage is a function of permeability of cellulose, depression under each stage and viscosity of acetic solutions. Viscosity of acetic acid–

water mixtures depends on temperature and ratio[12]. As a rule, a displacement filter should be designed for using acetylable cellulose commonly available in the international market, i.e. cellulose from conifers.

In the method for the determination of the permeability of cellulose to acetic acid, the relation $T = 51\cdot3\ t$ (seconds) enables the determination of the time T necessary for the passage of 1 000 litres of acetic acid at 25°, density d, through a layer of cellulose containing 3 kg of 100 per cent cellulose/m², under a depression of 35 cm of water; t is the time in seconds necessary for 880 ml of acetic liquid to pass through a cellulose layer of 4·52 dm² according to the method.

For a belt-type filter, 1 m wide, working with a layer of cellulose containing 3 kg of 100 per cent cellulose/m² we call V the translation speed in m/h of the layer of cellulose; P the weight in kg/h of dry cellulose to be processed; and $P = 3V$.

The throughput of liquid through a stage is given by a mass balance similar to that of the *Table 2*, i.e. $W = 430$ kg/h for 100 kg of 100 per cent cellulose.

For a weight P of 100 per cent cellulose, the flow D of liquid through a stage will be:

$$\frac{430\ P}{100} = D \text{ in kg/h} \tag{9}$$

If $S =$ theoretical surface of a stage; $T =$ permeability index of cellulose in seconds, the theoretical throughput D in kg/h for a stage will be:

$$D = \frac{1\ 000\ d \times 3\ 600 \text{ seconds} \times S}{T} = 3\ 600\ 000 \times \frac{dS}{T} \tag{10}$$

When equating the relations (9) and (10), we have:

$$3\ 600\ 000\ \frac{dS}{T} = 4\cdot3\ P \tag{11}$$

$$S = \frac{4\cdot3\ P \times T}{3\ 600\ 000\ d} \tag{12}$$

Example:
If $P = 320$ kg/h, $T = 600$, $d = 1\cdot045$

$$\text{theoretical } S = \frac{4\cdot3 \times 320 \times 600}{3\ 600\ 000 \times 1\cdot045} = 0\cdot22 \text{ m}^2$$

In fact, the liquid which passes through an empty stage is subjected to a pressure loss dp_0 which should not be underrated in a commercial unit, so that, in the above example, the depression will be: $dp + dp_0 = 35 + dp_0$ cm of water. The preceding calculation has been made for 100 per cent acetic acid at 25°C.

Table 4. Calculation of a displacement unit, stage by stage

Average dryness of acetic cellulose in the different stages		*Belt-type filter*		*Hildebrandt extractor*
		(25%)	(18%)	(9%)
Value of W/w		1·433	1·285	1·285
y_f-water content of the liquid entering stage 1		0·0022	0·0029	0·0039
Stage No.	*Water content of the liquid contained in the cellulose leaving the stage*	*Consumption of new acid per 100 kg of 100% cellulose*		
		300 kg	300 kg	455 kg
1	x_d	0·0050	0·0050	0·0050
2	x_1	0·0090	0·0076	0·0068
3	x_2	0·0147	0·0109	0·0092
4	x_3	0·0229	0·0152	0·0122
5	x_4	0·0347	0·0202	0·0160
6	x_5	0·0516	0·0266	0·0210
7	x_6	0·0758	0·0350	0·0274
8	x_7	0·1050	0·0458	0·0356
9	x_8		0·0597	0·0462
10	x_9		0·0776	0·0597
11	x_{10}			0·0771

As regards stages fed with aqueous acetic acid, the viscosity and sometimes the resins content of the liquid should be taken into account. For determining the real surface of a stage, a coefficient of safety should be applied.

With a belt-type filter, 1 m wide, working with a layer of 3 kg of 100 per cent cellulose/m², the translation speed should be:

$$P = 3V$$

$$V = \frac{320}{3} = 106·7 \text{m/h.}$$

DETERMINATION OF THE REACTIVITY OF CELLULOSES IN A DEWAR VESSEL

Objective

Draw the temperature–time curve of an acetylation carried out in a silvered Dewar vessel under acetylation conditions closely related to those of continuous acetylation. Measure the filterability and the viscosity of the acetic dope obtained. This method may be applied to linters and wood pulps.

Equipment

(i) An agitator with a six-bladed propeller and a shaft made of stainless steel, reference 8264 of the catalogue (Prolabo, 12 rue Pelée, Paris 11°), fitted on a motion and a transmission, reference 8440. (ii) A 220 V universal motor, reference 8261, and a starting rheostat, reference 8262 of the same catalogue Prolabo. The rotation speed of this agitator is 1 100 rev/min.

(iii) A cylindrical vessel, 150 mmϕ, 3 000 ml. capacity. (iv) A Büchner funnel made of porcelain, 110 mm ϕ, mounted on a rigid holder and fitted with a twilled filter cloth, preferably made of vinyl chloride, or else of cotton. (v) A pressing assembly comprising a stainless steel perforated plate with orifices of 3 mm distance from centre to centre 8 mm, and on it a tripod stand which may support a charge of 40 kg. (vi) A vacuum bottle. (vii) A Dewar vessel. (viii) A thermometer, $-10°$ to $+150°$C scale, with a 8 mm rod. (ix) Two measuring bottles each fitted with a thermometer to regulate the temperature of the reagents. (x) A rotational viscometer. (xi) A filtration equipment with standard flannelette.

Reagents

(i) Acetic acid, solidification point 16°C. (ii) Solution of acetic acid, solidification point 16·4°C containing 11·8 g/l. of chemically pure 95 per cent sulphuric acid. (iii) Pure anhydride at 98 per cent. (iv) Acetylation-stopping liquor—acetic acid, 900 g; triethanolamine, 25 g; water quantity necessary to bring the volume to 1 000 ml.

Mode of operation

Weigh 13·5 g of cellulose. The cellulose should have stayed for at least 30 min in a mixture of sulphuric acid and water, ratio 1:3, at a temperature between 20 and 25°, in order to bring the water content to 6–7 per cent. Pour the cellulose into the cylindrical vessel fitted with the Prolabo agitator, in which 1 000 ml. of aq. acetic acid (90 per cent HOAc) have previously been poured. After disintegrating, pass the suspension in the porcelain Büchner previously tared, and then suck off for 3 min under a vacuum of 200 mm of mercury. Pour 5 successive parts of 400 ml. of pure acetic acid on the cellulose cake, and suck off under vacuum after each pouring. After the last addition, the cake is not sucked off, but only allowed to drain off. Place the perforated plate and the charge of 40 kg on the cellulose cake. Press for 5 min. Weigh the Büchner funnel in order to determine the weight of the cake impregnated with acid. Pour the necessary amount of pure acetic acid on the cellulose to bring the weight to 80 g. The cake is placed in the Dewar vessel and shredded with the thermometer. This operation requires 5 min. Pour 40 ml. of the solution of sulphuric acid and pure acetic acid, cooled back to such a temperature, that the mass is maintained at 25°. This operation requires a certain practice from the operator.

For 10 min the mass is continuously stirred with the thermometer. Then 42 ml. of anhydride is added, the mixture cooled to 25°C in a thermostat and the chronometer is started. The temperature is noted every minute. The thermometer is used as stirring rod. When the temperature levels out the final temperature is noted after waiting for 4 min. The acetylation-stopping liquor (75 ml.) is then poured in and carefully mixed.

The reactivity of a cellulose is defined by the average temperature increase per minute, measured on the linear part of the curve.

Examination of the acetic collodion

After removing bubbles at 40°C for 1·5 h, measure: (a) the viscosity at 15°C with a rotational viscosimeter, the moving device rotating at 12 rev/min

and fitted with a ball, 14 mm diameter; (b) the filterability through standard flannelette, under a pressure of 1 kg/cm². The measure is carried out at 30°C through a standard flannelette, 1·76 m² surface.

The characteristics of an acetylable wood pulp of medium quality are: acetylation time, 13–15 min; temperature increase in the linear part of the curve, 2·8 to 3·3°C; viscosity at 15°C, 200–300 c.g.s. units; filtration, 50–80 ml.

Determination of the permeability of cellulose to acetic acid

The permeability of a cellulose to acetic acid is determined by the time that 880 ml. of pure acetic acid require to pass through a definite layer of cellulose under controlled vacuum.

Reagents and equipment

Distilled water at 20°C. Pure acetic acid, solidification point 16°C. Prepare two amounts of acid: 2 000 ml. and 880 ml. Cellulose with a normal humidity of 6–7 per cent, 135 g.
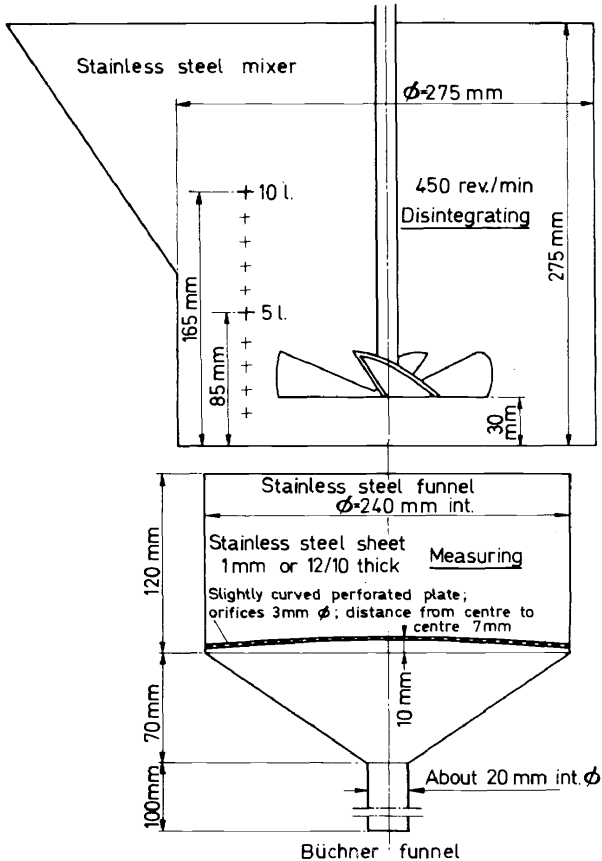

Figure 7. Arrangement of disintegrating and measuring operations during permeability determination.

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Mixer: cylindrical vessel, 275 mm diam, 300 mm high, with a propeller, 400 rev/min; length of the propeller about 180 mm. All parts made of stainless steel. (*Figure 7* top) Büchner-type funnel, made of stainless steel, 240 mm diam, 115 mm useful height, fitted on a 2 l. vacuum bottle. (*Figure 7* bottom) A vacuum corresponding to 35 cm of water column is drawn in the funnel. The bottom of the funnel is covered with a stainless steel wire gauze. The funnel cross-section is 4·52 dm².

Accessories

A stainless steel level reference-gauge, 32 mm high, with 4 feet, placed on a circle, 66 mm diam, according to *Figure 8* annexed to this method.
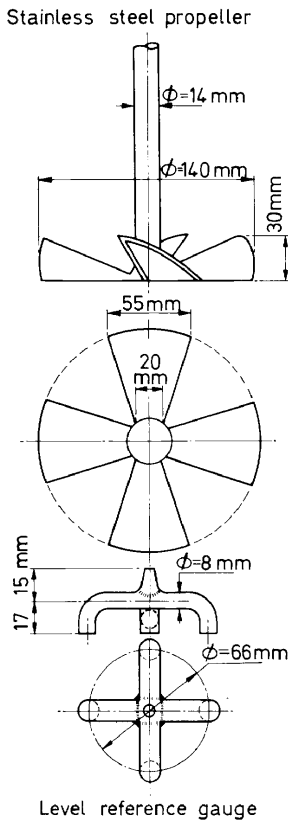

Figure 8. Stainless steel propeller and level reference gauge used for the determination of permeability

A perforated plate, with orifices of 3 mm, distance from centre to centre 7 mm, is placed on the layer of cellulose to prevent deformation during measuring.

Mode of operation

Measuring is preferably carried out by two operators.

(*a*) *Dispersion*

Cellulose (135 g) to be examined is disintegrated in 5 l. of distilled water in the above-described mixer. Disintegrating time, 15 min, or more if necessary. The dispersion obtained is then placed in a longotte in order to remove the excess water through slight squeezing. The squeezed cellulose is weighed to determine the weight of water present. Let p be the weight of water in grams; 4 100 litres: of pure acetic acid are introduced along with $(900 - p)$ g of water, and then the squeezed cellulose is introduced into the mixer.

The propeller is started up and cellulose dispersed in 5 l. of 82 per cent acetic acid. After 15 min of agitation, the proper distribution of the fibres is checked.

(b) *Spreading out*

At the time 18 min. 30 sec., the vacuum bottle is disconnected from the vacuum-circuit, the suspension of disintegrated cellulose is rapidly poured into the Büchner funnel, and distributed as regularly as possible, in order to obtain an homogeneous layer without applying any pressure on it. The vessel is rinsed with 1 litre of 82 per cent acetic acid, which is then poured into the Büchner funnel at the time 21 minutes. Between the 25th and the 26th minutes, the vacuum to be drawn during measuring is set at 35 cm of water-column. The small level reference-gauge shown in *Figure 8* is then put on the layer of cellulose, and the perforated plate placed above. At this moment there is no depression under the Büchner funnel.

(c) *Measuring*

At the 27th minute, 2 000 ml. of pure acetic acid at 20°C are poured, and the perforated plate removed. A vacuum of 35 cm of water is rapidly drawn and the chronometer started when the layer of liquid is flushed with the top of the level reference gauge. The second operator pours the 880 ml of pure acetic acid prepared separately. The chronometer is stopped when the liquid is again flushed with the top of the level reference gauge.

Results

Let t be the average time indicated by the chronometer and taken by 880 ml of acetic acid to cross through the layer of cellulose. The time T taken by 1 000 litres of acetic acid to cross through a surface of 1 m^2 bearing 3·1 kg of cellulose with a water content of 7 per cent is given by $T = 51·3t$. As a rule, $t = 4$–16 sec.

References

[1] *Textile Organon, Statistics* **36**, 105 & 111 (June 1965)
[2] U.S. Patents: 2 731 747, 2 778 820, 2 790 796, 2 801 237, 2 854 445, 2 854 446
[3] E. Richter. *Tappi*. 429 (1957)
[4] C. J. Malm, K. T. Barkey, L. C. May and E. B. Lefferts. *Industr. Engng. Chem.* **44**, p. 2 904 (1952)
[5] W. B. Campbell. *Convention Issue, Pulp Paper Magazine Can.*, 103 (1947)
[6] J. C. Fritz. Determination of filtration resistance on a paper machine. *Tappi* **48** No. 3, March 1965, p. 99 A
[7] P. Schaegis and L. Raichlen. *Génie chimique*, **94**, 89 (October 1965)
[8] C. K. Meadly. *Canad. J. Chem. Engng* December 1962 p. 256

9 R. N. Rickles. *Chem. Engng*, **72,** 157 (March 1965)

10 F. M. Baker. *Chem. and Met. Engng* (No. 42), 669 (1935)

11 MacCabe and Smith. *Unit operations of chemical engineering*, McGraw Hill, New York (1956), p. 760.

12 J. H. Perry. *Chemical Engng Handbook* McGraw Hill, New York (1964), 4th ed. p. 3–199.

13 C. H. Giles, S. K. Jain, and A. S. A. Hassan. *Chem. and Ind.* 629 (1955)

14 L. A. Hiller. *J. Polymer Sci.* **14,** 555 (1954)