

EVALUATION OF ACETYLATION PULP

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INTRODUCTION

It is a well-known, although regrettable fact that no pulp can be fully characterized or evaluated by means of simple chemical and physical analysis. Complementary, time-consuming tests, in which the consumers process is more or less simulated, are necessary. This is true for dissolving pulps as well as for paper pulps, although in the latter case knowledge is slowly accumulating so that in the future chemical and physical analysis may be enough to evaluate a paper pulp. As to dissolving pulps, however, it is difficult to imagine with present knowledge how to do without some test of the reactivity of the pulp. For acetylation pulps the situation is further complicated by the fact that producers of cellulose acetate use so many different processes. The pulp producers cannot possibly simulate all of these processes in their tests but must confine themselves to some standardized procedure.

This communication describes a method, developed within our company, for evaluation of acetylation pulp and some applications of the method.

PRINCIPLE AND REPRODUCIBILITY OF THE METHOD

Cellulose acetate producers demand that a pulp should give a good filterability of the acetate solution at a high viscosity level. We therefore decided to base our method on the measurement of these two properties—filterability and viscosity.

As mentioned before, the choice of acetylation process is not a simple one. We have chosen to pretreat the pulp in glacial acetic acid and to acetylate after addition of methylene chloride as a solvent and sulphuric acid as a catalyst.

When it was found difficult to obtain reproducible results on solutions of precipitated cellulose triacetate, the filterability and viscosity were instead determined directly on the acetate dope. Samples were taken out at different time intervals and filterability was plotted against viscosity. A detailed description of the method is given in the Appendix.

As an illustration of the type of curve obtained and of the reproducibility of the method, *Figure 1* shows the results from eight acetylations of the same pulp.

SOME APPLICATIONS OF THE METHOD

Comparison with consumers judgement

Some cellulose acetate producers judge the quality of a pulp by means of an index proportional to the product of filterability and viscosity of the cellulose acetate produced from the pulp. In *Figure 2* three pulps of quality

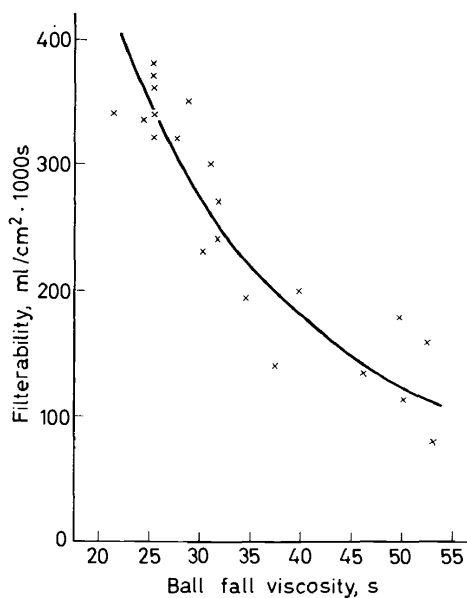


Figure 1. Filterability versus viscosity from eight acetylations of one pulp

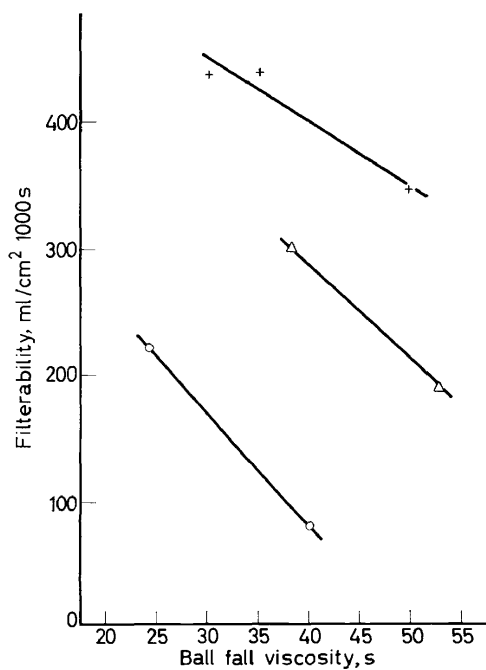


Figure 2. Filterability versus viscosity for three pulps of different quality index as given by cellulose acetate producer [Quality indexes: ○—○, 3; △—△, 4; +—+, 5]

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indexes 3, 4, and 5 respectively, as given by an acetate producer, are evaluated with our method. It is seen that the method grades the pulps in the correct order.

Influence of drying conditions on filterability

The primary purpose of investigating drying conditions was to establish a suitable method to dry laboratory pulps in order to obtain reproducible filterability values, comparable to those furnished by mill drying. Pulp samples were taken from the wet end of the drying machine in the mill and sheeted in the laboratory. Half of the sheets were pressed at 2 kp/cm^2 . Drying was performed, either in the air at room temperature, or at 60°C

Table 1. Influence of drying conditions on filterability

<i>Drying conditions</i>	<i>Filterability at a ball fall viscosity of 24 s</i>
Room temp., unpressed sheets	280
Room temp., pressed sheets	280
60°C, 3 h, unpressed sheets	230
60°C, 3 h, pressed sheets	320
Machine dried sheets	380

for 3 h. Results are presented in Table 1. The results from air drying at room temperature proved to be low and badly reproducible. Drying of pressed sheets at 60°C gave the best results, which, however, were still a little low compared to the filterability of the mill dried pulp.

Product development and quality control

When the test method described in the present paper was introduced in our company more than ten years ago, the pulp from our mill showed a filterability of about 100 at a ball fall viscosity of 24 s. Today, pulps lower than 300 are considered unacceptable. This development would have hardly been possible without a good method of evaluation. Among the changes, partly based on laboratory research findings, made in the mill to create this result, the choice of conditions at the hot alkali extraction may be mentioned. In accordance with the view expressed by Richter¹, it proved to be very essential that not even a minute part of the pulp is allowed to be "cold alkali refined" in the hot alkali extraction step.

GEL PARTICLES AND FILTERABILITY

It is evident that filterability of dissolving pulps is closely connected with gel particles, originating from insufficiently reactive fibre parts. In viscose testing, particle counting is now a familiar and much used complementary method of characterization. For cellulose acetate solution only few investigations on particle counting have been reported^{2, 3}. We do not intend to introduce here any new results in this field but we intend to use the literature data for an admittedly rough, but interesting calculation which, as far as we know, has not been presented before.

If it is assumed that only particles larger than about $15\text{ }\mu\text{m}$ influence the filterability⁴, literature data²⁻⁴ show that the number of such particles in viscose or in cellulose acetate solution is about 10^3 – 10^4 per gram cellulose for an acceptable pulp. As the number of fibres per gram pulp is generally of the order of 10^6 – 10^7 † it can be calculated that there is one filter clogging particle per 10^2 – 10^4 fibres of original pulp. The result of this calculation must be a memento to those studying pulp reactivity in the microscope. It is also a support to the statement made in the introduction that dissolving pulp filterability will hardly ever be evaluated by simple chemical or physical analysis.

APPENDIX

Apparatus

1. Thermostated water bath provided with device for rotating six or eight glass bottles at a speed of approximately 15 rev/min.

2. Standard glass bottles, volume 1000 ml, with screw caps provided with rubber gaskets covered with thin sheets of polyethylene.

3. Propeller disintegrator.

4. Centrifuge for removal of excess acetic acid.

5. Thermostated water bath for cooling the samples of the acetylation mixture prior to filtration (20°C). The small bottles of glass are fixed on a slowly rotating axis in the bath.

6. Filtration equipment allowing filtering a solution of cellulose acetate without risk of evaporation of the volatile solvent. The apparatus consists mainly of a glass tube of about 40 cm length and an inner diameter of 15 mm. The filtering cloth, of the same quality as used for determination of viscose filterability, is fixed between two circular metal bricks with holes 7 mm in diameter. All gaskets are of polyethylene. The filtering pressure (2 kp/cm^2) is maintained using a nitrogen bomb. The amount of filtered solution can be read on a centimetre scale fixed outside the glass tube. The filtration equipment used is simply made of a water gauge glass fixed to a boiler.

Reagents

1. Acetic acid 99–100 per cent. On the arrival in the laboratory the water content of the acetic acid is determined and an equivalent amount of acetic anhydride is added and the solution is allowed to stand for about a week.

2. Acetic anhydride. All the acetic anhydride is distilled in the laboratory before it is used.

3. Methylene chloride.

4. Catalyst. The catalyst solution consists of sulphuric acid in acetic acid and must not be allowed to stand for more than three days. It consists of 80 g of sulphuric acid (100 per cent) per litre of solution. The strength of the sulphuric acid (*pro analysi*) is best determined by titrating a weighed sample against sodium hydroxide and the amount required for preparing the sample must also be accurately weighed.

† Spruce wood, e.g., contains about 2×10^6 fibres (tracheids)/g, birch 10^7 fibres/g.

Preparation of sample

The pulp is torn into pieces of *c.* 2×2 cm and is allowed to condition in the open air overnight. Moisture content is determined on a separate sample.

Pretreatment

The pulp (30 g bone-dry basis) is transferred to the glass bottle and 625 ml acetic acid is added. The bottles are allowed to rotate in the water bath for 2 h at 38°C . The acetic acid is then drained off and the pulp centrifuged; during the latter operation it is best kept in a cloth. After the centrifugation the pulp holds exactly double the amount of acetic acid, the weight of the wet (with acetic acid) sample will thus be $30 + 60 = 90$ g, and is corrected by addition of acetic acid. The sample is then completely disintegrated in 625 ml of methylene chloride, which thus is mixed with the acetic acid already present in the pulp. The liquid then has the following composition: 840 g methylene chloride ($625 \text{ ml} \times 1.34$); 60 g acetic acid; 2.1 g water (assuming 7 per cent humidity in the pulp), totalling 902 g.

Acetylation

The disintegrated pulp is slightly drained on a Büchner funnel and placed in the tared acetylation bottle on a balance. The drained mixture of methylene chloride and acetic acid is again added until the contents of the bottle weighs exactly 428 g. The excess is used for washing the filtering apparatus, etc. The mixture in the acetylation bottle will then have the following composition:

30 g cellulose

$$\frac{840 \times 398}{902} = 370 \text{ g methylene chloride}$$

$$\frac{60 \times 398}{902} = 27 \text{ g acetic acid}$$

$$\frac{2.1 \times 398}{902} = 1 \text{ g water}$$

Total: 428 g mixture.

To this mixture is added 115 ml of acetic anhydride ($115 \times 1.087 = 125$ g) in which the required amount of catalyst (5 ml) has been mixed in advance. The mixture is carefully stirred by a glass rod and the bottle vigorously shaken. The pressure is released by opening the screw cap after shaking the bottle. Exactly 15 min after the pretreatment is stopped the bottle is again put into the water bath and allowed to rotate at the same temperature (38°C). After a couple of hours the dope becomes clear and samples may be examined in the microscope for residual fibres. The viscosity may be measured by determining the time of flow through a very simple viscosimeter

consisting of a 10 ml pipette of which the end has been cut. This determination is carried out in order to decide the time for taking the first sample for filtration. When it is time to do that, about 60 ml of the acetylation mixture is poured into a 250 ml flask of glass and allowed to cool in the 20° thermostat bath for about 10 min. From each acetylation bottle totally three filtration samples are taken with an interval of exactly 30 or 45 min.

Filtration

The filtration is started exactly 15 min after the sample has been taken out of the acetylation bottle. Immediately after the solution has been transferred to the filtration apparatus the viscosity is determined by measuring the time for a steel ball ($\frac{1}{8}$ in.) to fall 30 cm. Then the lid is screwed on and the pressure is applied. The filtering time for 2, 4, 6, 8 cm, etc. is determined by reading on a stop watch and on the centimetre scale fixed on the glass tube. The filtration is generally stopped after a filtering time of about 120–300 sec.

Calculation of the filterability

If the quotient t/v is plotted against t , where t is the filtering time and v the volume filtered during this time, an approximately straight line is generally obtained after a short time. The equation for this line may be written as follows:

$$\frac{t}{v} = k \times t + \left(\frac{t}{v}\right)_0$$

The slope k and the ordinate t/v at $t = 0$ are determined graphically or calculated from two points on the line.

The filtration of the acetate solution is best expressed in the volume filtered on a certain time per unit area. To get a suitable size of the figure the filtering area has been set to 1 cm² and the theoretical filtering time to 1000 sec.

The filterability is reported in ml/cm² and 1000 sec filtration time at two different viscosities, 24 and 40 s respectively. These figures are best obtained by plotting filterability for the three samples taken out of every acetylation against viscosity and interpolating the curve thus obtained.

References

- ¹ G. A. Richter. *Tappi* **40**, 429 (1957).
- ² L. R. Parks and K. A. Jurbergs. *J. Appl. Polymer Sci.* **4**, 193 (1960).
- ³ B. Philipp and K.-H. Bischoff. *Faserforschung und Textiltechnik* **16**, 46 (1965).
- ⁴ E. Treiber. *J. Polymer. Sci.* **51**, 297 (1961).