

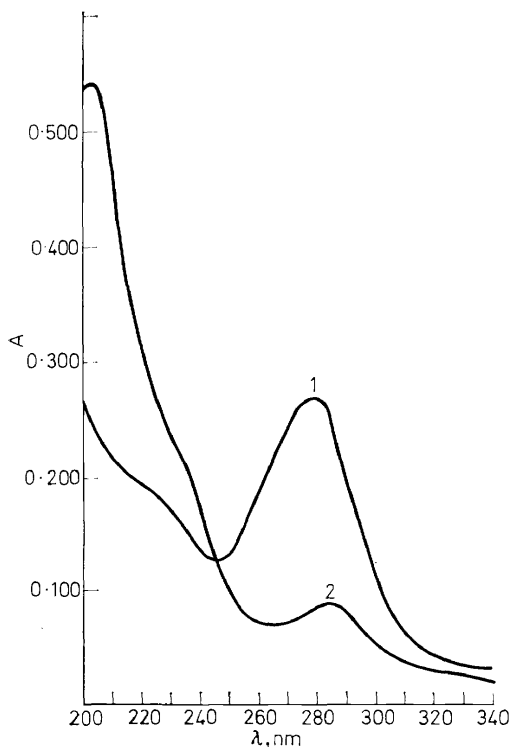
# SOME FACTORS CAUSING COLOUR IN ACETATE PULP AND CELLULOSE ACETATE

J. TURUNEN and K. TURUNEN

*Rauma-Repola Oy, Pulp Mill, Research Laboratories, Rauma, Finland*

## RESIDUAL LIGNIN

Many methods have been developed for determining the residual lignin in pulp. These methods are suited to the analysis of paper pulp and packing materials. In the latest methods attention has been paid not only to the precipitating lignin but also to low molecular lignin, which remains in solution in acid hydrolysis. The concentration of the acid soluble lignin is determined by the ultraviolet absorbance at a wavelength of 205 nm<sup>1-4</sup>. The absorbance maximum of the benzene ring of lignin occurs at this wavelength (*Figure 1*), and the concentration of soluble lignin can be calculated, for example, by a standard curve made with liginosulphonic acid.



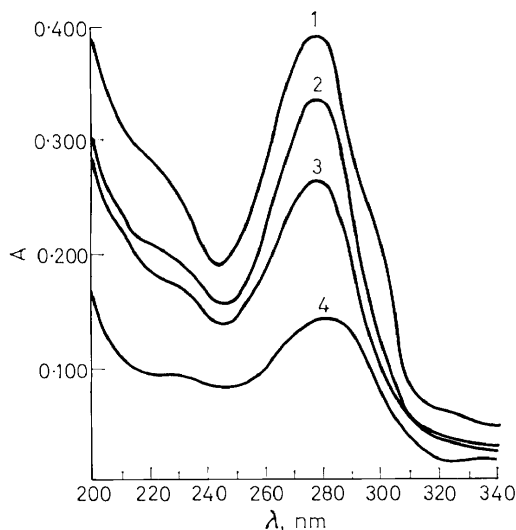
*Figure 1.* Ultraviolet spectra of acid hydrolysates prepared by the modified method of Jayme<sup>1</sup> [1, acetate pulp (concn. 6.250 g/l.); 2, barium liginosulphonate (concn. 15 mg/l.)]

However, there are so few aromatic impurities in acetate pulps and apparently also in the best viscose pulps, that we have not been able to find any method, which even when modified would work satisfactorily for determining residual lignin in acid solution. When such an amount of purified cotton linters is used, which gives a reliable absorbance value at 205 nm, the values obtained correspond to about half of the absorption for the hydrolysate of acetate pulps shown in *Figure 2*. Because the cotton linters contains apart from glucan only < 0.3 per cent of xylan we can assume that half of the hydrolysate absorbance of acetate pulp at 205 nm depends on its glucan component. The ultraviolet spectra of the hydrolysis products of different carbohydrates analysed are of similar appearance to the spectra of the hydrolysates of acetate pulps and all of them absorb at 205 nm (*Figure 3*).

The absorption intensity of xylose is, however, much higher than those of glucose and mannose. According to our estimations of the ultraviolet spectra the absorbance caused by xylan would be about a fifth or a quarter of that in acetate pulps. The remainder of the absorbance is derived from unknown material, perhaps of the aliphatic and aromatic degradation products of lignin.

In comparing the ultraviolet absorption spectra of liginosulphonic acid and acetate pulp hydrolysates in *Figure 1* at 205 nm, we can calculate from the weights of the substances present that if 0.12 per cent of liginosulphonic acid is added to the pulp its absorbance would be doubled.

As comparatively many compounds absorb at 205 nm we tried to study the presence of the aromatic degradation products of lignin in acetate pulps and their extracts by using the infrared spectra, which are noticeably more specific than the ultraviolet spectra (*Figure 4*). Not one commercial grade of acetate pulp seems to have aromatic absorption in the region<sup>5</sup> 1600–1500cm<sup>-1</sup>.



*Figure 2.* Ultraviolet spectra of acid hydrolysates of three commercial acetate pulps and cotton linters. The method used is similar to that in *Figure 1*. Concentration in curves 1–4: 6.250 g/l. [1–3, acetate pulps; 4, cotton linters]

## SOME FACTORS CAUSING COLOUR IN ACETATE PULP

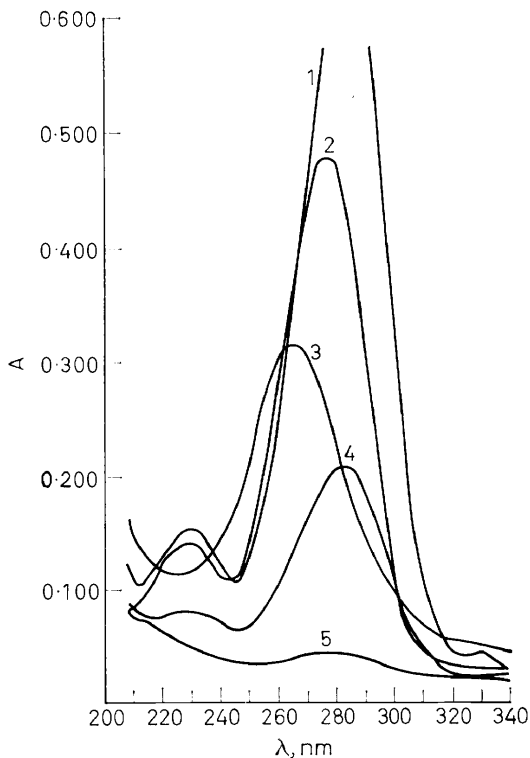


Figure 3. Ultraviolet spectra of acid hydrolysates of different model substances. The method used is similar to that in Figure 1 [1, 5-hydroxymethylfurfural (concn. 5 mg/l.); 2, xylose (concn. 150 mg/l.); 3, mannose (concn. 3.125 g/l.); 4, glucose (concn. 3.125 g/l.); 5, glucuronic acid (concn. 50 mg/l.)]

For this reason we measured infrared spectra of methylene chloride extracts of acetate pulps, also of those fractions of pulp, which were dissolved in steeping lye and isolated, and finally of that fraction<sup>6</sup>, which was dissolved in 0.5 per cent sodium hydroxide solution by heating at 100°C for 1 h.

The only aromatic absorption was found in the methylene chloride extract of an experimental pulp. However, this sample contained 0.3 per cent of extractable material and therefore the pulp was unsuitable for acetylation. The aromatic component of the extract might be derived from the neutral fraction of extractable material and not from lignin (cf. ref. 7).

Hydrolysates were prepared from pulps extracted by 0.5 per cent sodium hydroxide solution as well as from their dissolved fractions by using the modified method of Jayme<sup>1</sup>. Ultraviolet spectra of the hydrolysates are shown in Figure 5. Only 3.0–4.4 per cent of acetate pulps was dissolved in extractions. The original absorption peak of 280 nm was extended over the range 250–280 nm. Although the concentration of extract in the hydrolysates was 3.2 per cent of the concentration of the corresponding pulp, the absorption of the extract at 205 nm was stronger than that of the extracted pulp.

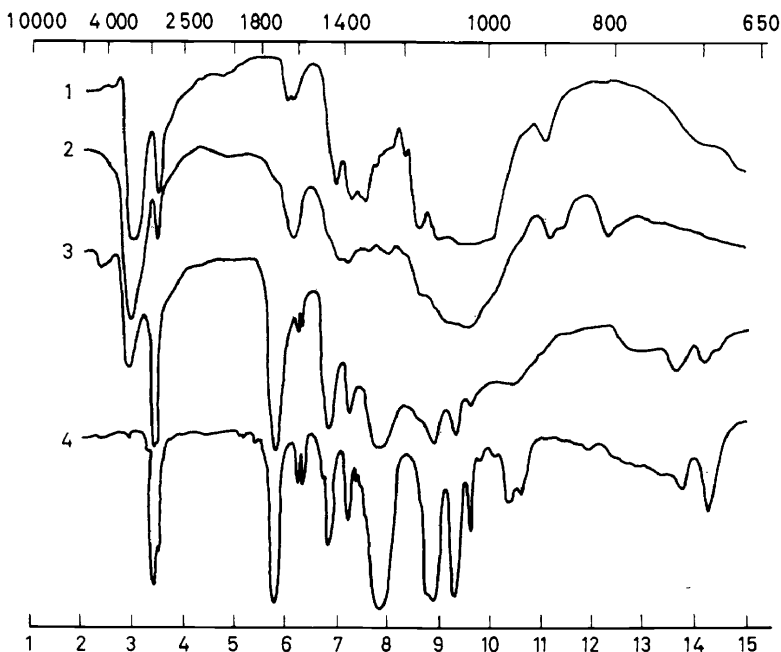


Figure 4. Infrared spectra [1, acetate pulp; 2, low molecular fraction of mercerized acetate pulp; 3, methylene chloride extract of pulp; 4, fraction of neutral substance isolated from pine tall oil]

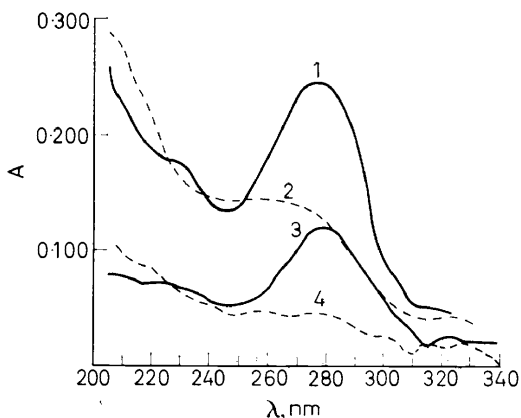


Figure 5. Ultraviolet spectra of acid hydrolysates after 0.5 per cent NaOH extraction. The weights refer to the quantities of organic material hydrolysates made with the modified method of Jayme<sup>11</sup> [1, acetate pulp (concn. 6.250 g/l.); 2, alkali extract of acetate pulp (concn. 200 mg/l.); 3, cotton linters (concn. 6.250 g/l.); 4, alkali extract of cotton linters (200 mg/l.)]

Kleinert<sup>6</sup> has found that the biggest part of alkali-lignin grafted on acetate pulp was extracted with 0.5 per cent sodium hydroxide solution.

On the basis of the foregoing we can say that the quantity of the aromatic degradation products of lignin is very small in commercial acetate pulps and cannot exceed one tenth per cent. We have not yet been able to measure

## SOME FACTORS CAUSING COLOUR IN ACETATE PULP

exactly its effect on producing colour in cellulose acetate but it can be studied by the method described in the following section. For the present we cannot be certain about the presence of aliphatic degradation products of lignin and their effect on the colour of cellulose acetate.

### POTENTIAL EFFECT OF DIFFERENT COMPOUNDS ON THE COLOUR

In the drying of cellulose or cellulose acetate flake low molecular weight inorganic and organic compounds migrate to the surface of the flake with the water. They concentrate on the surfaces where the evaporation is greatest especially on the corners and edges of flakes. This phenomenon is typical of the larger flakes (*Figure 6*). These compounds change the local pH and may



*Figure 6.* The staining of a point of a triacetate flake

catalyse the hydrolysis, oxidation and polymerization of organic substances in the flake thus assisting the formation of coloured compounds. If the acetate is precipitated for example as a thin filament, which is later cut into very short pieces, the surface of the particles can be stained evenly at a high temperature (e.g. 140°C), but no “staining centres” are formed (*Figure 7*).

The effect whereby dissolved substances are concentrated at the surface of the flake is comparable to chromatography, where water is used as a developing liquid. We have made use of this phenomenon when studying the potential colour forming ability of different ions and compounds in pulp and cellulose acetate. Triacetate, for example, was ground to a degree of 60 mesh and used as supporting substance in thin-layer chromatography. The chromatograms were dried in an oven for 2 h at a temperature of 140°C. Now, if the compound was colour imparting, spots would appear either in ordinary or in ultraviolet light (*Figure 8*). The efficiency of different compounds can be estimated by a visual test and agrees well with previously reported colour reversion tests on cellulose or cellulose acetate<sup>9,10</sup>.

The strongest colouring substances were inorganic acids and sodium hydroxide. The effect of calcium hydroxide was very small. Inorganic salts stained especially cellulose powder if one of the ions could sublime after the

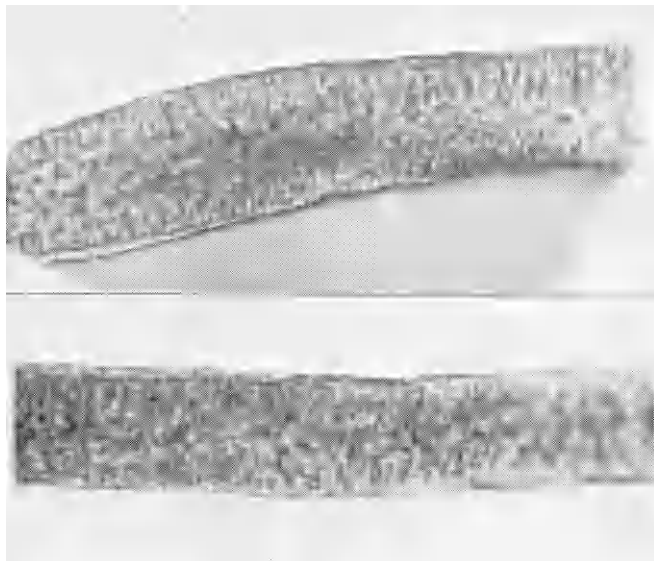


Figure 7. The even staining of a filament piece of diacetate at high temperature (140°C). In the upper figure is the untreated filament piece

hydrolysis of the salt. Uronic acids and their lactones are obviously the most dangerous of the organic compounds. Pentoses had only relatively weak effect, a little lower than that of lignosulphonic acid.

By using other developing liquids it might be possible to accomplish a run so that the spots do not migrate with the liquid front, and the intensity of the spots can be measured by densitometer. We have observed in our tests that cellulose is considerably easier to stain than triacetate. These studies are being continued.

### EXPERIMENTAL

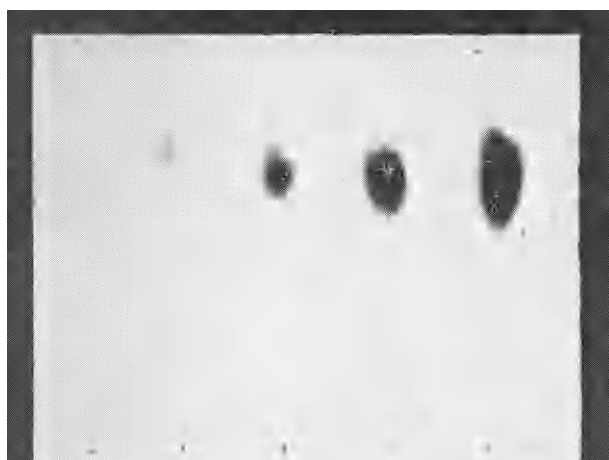
The cotton linters used was The Buckeye Cellulose Corp. Cotton Linter Pulp "Premium acetate grade". The other acetate pulps were American and European commercial qualities if not otherwise stated. The model substances used were MA grade of the Mann Research Laboratories Inc. or *pro analysi* of Fluka AG. Before hydrolysis or other treatments the pulps were extracted always with methylene chloride. The acetate pulps and other samples were hydrolysed by the method of Jayme<sup>1</sup> except that the quantities of the samples varied and that the 15 min heating period was omitted. In this way the repolymerization of lignin degradation products was avoided.

The ultraviolet spectra were measured partly with the Beckman ultraviolet spectrophotometer, model DK 2, and partly with the Unicam spectrophotometer, model SP 500, with 10 mm far-u.v. silica cells. The infrared

SOME FACTORS CAUSING COLOUR IN ACETATE PULP



10      20      50      100      200  $\mu$ g  
tri.a.      Lignosulfonic acid      304



10      20      50      100      200  $\mu$ g  
tri.a.       $H_2SO_4$       297

Figure 8. Thin layer chromatograms on cellulose triacetate. Upper figure: 10–200  $\mu$ g amounts of lignosulphonic acid. Lower figure: 20–200  $\mu$ g amounts of sulphuric acid

spectra were measured partly in Åbo Akademi with a Perkin–Elmer infrared spectrograph, model 021, and partly in Helsinki University with a Perkin–Elmer infrared spectrograph, model 237. In Åbo Akademi special technique was used, which will be published elsewhere<sup>8</sup>.

The alkali extraction of pulps with 0.5 per cent sodium hydroxide solution was carried out by the method of Kleinert<sup>6</sup>. The extracted cellulose was

washed with water and dried. The cooled extract and washings were neutralized with 1 N hydrochloric acid to pH 7, evaporated in vacuum at 50°C to dryness and dried at 70°C in vacuum to constant weight. The sodium chloride containing the extracted organic substance was ground and the organic component was hydrolysed as described above before measuring the u.v. spectra. The blank was prepared by applying the same hydrolytic conditions to the corresponding quantity of pure sodium chloride.

The cellulose or acetate flake was ground with a Wiley mill (intermediate model) to the degree of 60 mesh. The thin layer plates were prepared by the method of the Firma Macherey, Nagel & Co.<sup>11</sup>. When using triacetate powder it is particularly necessary to add 5 per cent alcohol to the water used as developing liquor. The plates were dried for 30 min at room temperature and then for 2 h at 140°C. Photographs in u.v. light were taken in a "Fluotest" apparatus. The fluorescent ink consisted of 2,7-dichlorofluorescein dissolved in water-alcohol-glycerol mixture (5:5:1).

### SUMMARY

In this work we have tried to estimate the presence and the amount of residual lignin in acetate pulps. Aromatic degradation products of lignin could not be found by infrared spectrography with the apparatus used in any commercial products or in their methylene chloride and alkali extracts. On ultraviolet absorbance measurements we can conclude, that the amount of aromatic degradation products of lignin in these pulps cannot exceed one tenth percentage.

The potential colour forming ability of different compounds was analysed with thin layer chromatography using cellulose powder and cellulose triacetate powder as a supporting material. The strongest colouring substances were inorganic acids and sodium hydroxide. The effect of calcium hydroxide was very small. Uronic acids are obviously the most dangerous of the organic compounds. Cellulose triacetate had considerably higher resistance than unacetylated cellulose.

*We wish to thank Rauma-Repola Oy for permission to publish this study. Our thanks are also due to Prof. H. H. Bruun, Åbo Akademi, and doc. J. J. Lindberg, Helsinki University and their colleagues for the preparation and interpretation of the infrared spectra.*

### References

- 1 G. Jayme, H. Knolle and G. Rapp. *Papier* **12**, 464 (1958).
- 2 L. M. Marraccini and T. N. Kleinert. *Holzforschung* **13**, 43 (1959);  
T. N. Kleinert and C. S. Joyce. *Pulp Paper Mag. Can.* **58**, No. 5, 154 (1957).
- 3 B. Kyrklund and I. Palenius. *Paperi Puu* **46**, 513 (1964).
- 4 V. Lorås and F. Löschbrandt. *Norsk Skogind.* **15**, 302 (1961).
- 5 L. J. Bellamy. *The Infrared Spectra of Complex Molecules*. Methuen & Co. Ltd., London, 1958, 71.
- 6 T. N. Kleinert. *Holzforschung* **19**, 179 (1965).
- 7 H. H. Bruun *et al.*, to be published.
- 8 R. Sjöholm, to be published.
- 9 W. H. Rapson and J.-C. Corbi. *Pulp Paper Mag. Can.* **65**, No. 11, T-459 (1964);  
J.-C. Corbi and W. H. Rapson. *Pulp Paper Mag. Can.* **65**, No. 11, T-467 (1964).
- 10 L. R. Parks and L. H. Sperling. *J. Appl. Polym. Sci.* **8**, 2239 (1964).
- 11 E. Stahl. *Dünnschicht-Chromatographie*, Springer-Verlag, Berlin, 1962, 34.