

### Sorption of Copper by Wood Constituents

Belford, Myers and Preston<sup>1</sup> have directed attention to the fact that cellulose and wood absorb copper ions and that they appear to be regularly spaced on a grid pattern not corresponding to the unit cell of cellulose. Bayley and Rose<sup>2</sup> consider that  $\alpha$ -cellulose has only a small cation binding power and that the complexes formed in wood consist of metal cations bound on the non-cellulosic constituents. Belford *et al.*<sup>3</sup> observed that in wood impregnated with preservatives containing copper-salts the middle lamella in particular stained very deeply with dithio-oxamide. In the work now reported the copper sorption of isolated wood constituents has been measured and the copper has been located in sections of treated wood by staining methods and electron microscopy.

'Milled wood lignin' prepared by the method of Björkman<sup>4</sup>, wood  $\alpha$ -cellulose (40 mesh) and purified cotton cellulose (40 mesh) have been examined for their copper binding capacity by the following method. A specimen of each material, 0.1–0.5 g, was shaken for 1 h in 5 ml. of 0.3 per cent copper acetate solution at about 20° C. The mixture was then filtered, the specimen washed with distilled water and the filtrate discarded. It was then washed three times with 10 per cent acetic acid and the combined acetic acid filtrates evaporated to dryness on a steam bath. The organic matter present was destroyed by heating on a hotplate with sulphuric–nitric acid mixture and the copper determined by the spectrophotometric rubenic acid (dithio-oxamide) method of Center and MacIntosh<sup>5</sup>. The results are given in Table 1. A similar test on the residual lignin after the acetic acid washing showed that it retained no significant amount of copper.

These copper sorptions of cellulose are much lower than those recorded by Belford, Myers and Preston<sup>1</sup> and consistent with those observed by Michie<sup>6</sup>, allowance being made for the different conditions by his equation (1). However, the absorption of copper by the milled wood lignin was, as shown in Table 1, much higher than for cellulose.

Table 1. COPPER SORPTION OF WOOD, CELLULOSE AND LIGNINS (GRAMS OF COPPER PER 100 G)

<i>Eucalyptus regnans</i> wood	0.033
Wood $\alpha$ -cellulose	0.040
Cotton—purified	0.038
<i>E. regnans</i> milled wood lignin	0.361
<i>E. goniocalyx</i> milled wood lignin	0.325
<i>E. regnans</i> methanol lignin	0.154
<i>P. radiata</i> compression wood milled wood lignin	0.258

It has been shown by me<sup>7</sup> that these milled wood lignins retained some uronic acid and that their infra-red spectra showed a band at 5.8 $\mu$  attributable to carboxyl groups. Milled wood lignin from compression wood was exceptional in that this band was absent. No such band was observed in the spectrum of methanol lignin<sup>8</sup>. However, it may be seen from Table 1 that a significant sorption of copper by both these lignins occurred.

Examination of the infra-red spectra of copper-treated milled wood lignins showed only a small reduction in intensity of the band at 5.8 $\mu$ . This indicates that, as would be predicted by Michie's equation for the conditions of our experiment, only a fraction of the carboxyl groups reacted with copper. Furthermore, there is extensive sorption of copper on lignin by some other mechanism. This suggests that groups other than carboxyl groups are also involved, but appears to be in accord with the view of Bayley and Rose that most of the copper sorption is on the non-cellulose constituents of the wood.

General confirmation of this conclusion has been obtained from the optical and electron microscopic examination of sections treated with a solution of copper sulphate. Fig. 1a shows a transverse section of *Pinus radiata* impregnated with copper sulphate and stained

with dithio-oxamide. Fig. 1b shows the same section photographed between crossed nicols. It can be seen that copper is observed in or external to the layer  $S_1$  of the secondary wall. An electron micrograph of a similar section of copper impregnated wood is shown in Fig. 2, the dark area indicating the presence of copper. It is apparent from the greater resolution in this picture that most of the copper was taken up by the primary wall  $P$  and intercellular layer. From ultra-violet absorption measurements, Lange<sup>9</sup> concluded that more than 70 per cent of the cell wall lignin is located in this region, so that these results are consistent with the suggestion that most of the copper taken up by the cell wall is attached to the lignin.

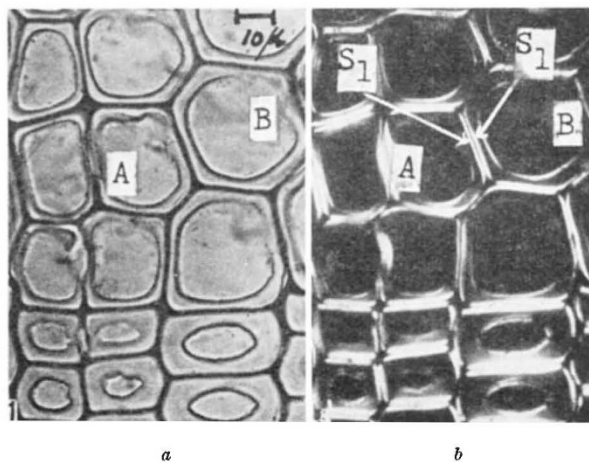


Fig. 1. Transverse section of *Pinus radiata* copper treated. (a) Stained with dithio-oxamide; (b) same section between crossed nicols

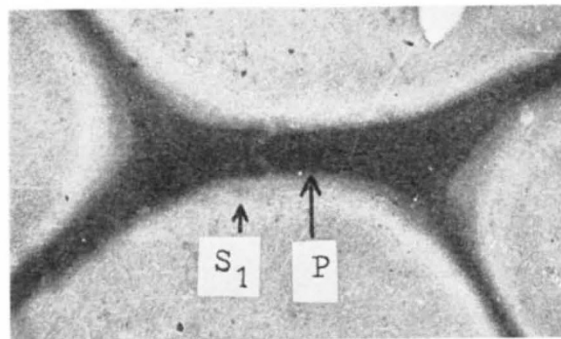


Fig. 2. Electron micrograph showing intercellular layer in copper-treated *Pinus radiata*

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<sup>1</sup> Belford, D. S., Myers, A., and Preston, R. D., *Biochim. Biophys. Acta*, **34**, 47 (1959).

<sup>2</sup> Bayley, C. H., and Rose, G. R. F., *Nature*, **185**, 313 (1960).

<sup>3</sup> Belford, D. S., Preston, R. D., Cook, C. D., and Nevard, E. H., *J. App. Chem.*, **9**, 192 (1959).

<sup>4</sup> Björkman, A., *Svensk. Papperstid.*, **59**, 477 (1956).

<sup>5</sup> Center, E. J., and MacIntosh, R. M., *Indust. Eng. Chem. (Anal. Ed.)*, **17**, 239 (1945).

<sup>6</sup> Michie, R. I. C., *Nature*, **190**, 803 (1961).

<sup>7</sup> Bland, D. E., *Holzforschung*, **15**, 102 (1961).

<sup>8</sup> Bland, D. E., *Biochem. J.*, **75**, 195 (1960).

<sup>9</sup> Lange, P. W., in *Fundamentals of Papermaking Fibres*, edit. by Bolam, F. (Tech. Sect. B.P. and B.M.A., 1958).