

### *Permanently Amorphous Cellulose*

Amorphous cellulose may be produced by severe grinding of native cellulose in a ball mill.<sup>1,2</sup> The x-ray diffraction of the resulting powder indicates that it is in the amorphous state. Milling must be done dry. On wetting with water, the amorphous cellulose regains some of its lost order and gives an x-ray diffraction diagram corresponding to cellulose II.<sup>3</sup>

Amorphous cellulose can also be produced by anhydrous deacetylation of cellulose acetate.<sup>4</sup> Crystallinity is regained on wetting as with ball-milled cellulose.

In a recent investigation, the accessibility of amorphous cellulose,<sup>5</sup> as measured by hydrogen exchange methods, was found to be 89%. The accessibility measurement required that the cellulose be exposed to water vapor at 50% relative humidity. This is known to produce partial recrystallization of the amorphous cellulose. Therefore, there was some doubt as to whether the accessibility of 89% was for truly amorphous material or for partially recrystallized cellulose.

Some method of "fixing" the amorphous character of the cellulose was then sought. It was considered possible that the introduction of chemical crosslinks into the amorphous cellulose under anhydrous conditions would eliminate molecular reordering processes on subsequent addition of water. After much trial and error, such a method was found and is described in the present note.

Amorphous cellulose was prepared by the saponification of oil-free secondary cellulose acetate fiber (kindly supplied by Chemcell of Canada). The fiber was first Wiley-milled to 40-mesh. Deacetylation was carried out in a non-aqueous medium by use of 1% sodium methylate dissolved in anhydrous methanol. The saponified material was treated with glacial acetic acid to neutralize the alkali. The cellulose was washed with anhydrous methanol and dried in a vacuum oven at 70°C. overnight.

The amorphous cellulose was crosslinked with formaldehyde by a modification of the Wagner and Pacsu technique.<sup>6</sup> Ten parts of amorphous cellulose were sealed in a Pyrex tube with one part of solid paraformaldehyde and one part of finely powdered boric acid. The tube was shaken to mix the contents, placed in a metal shield, and baked at 125°C. for 24 hours. The contents of the tube were then removed and washed with boiling distilled water until free from formaldehyde and boric acid. The crosslinked amorphous cellulose was then dried in a vacuum oven at 70°C. Batches of up to 20 g. were made by the above procedure.

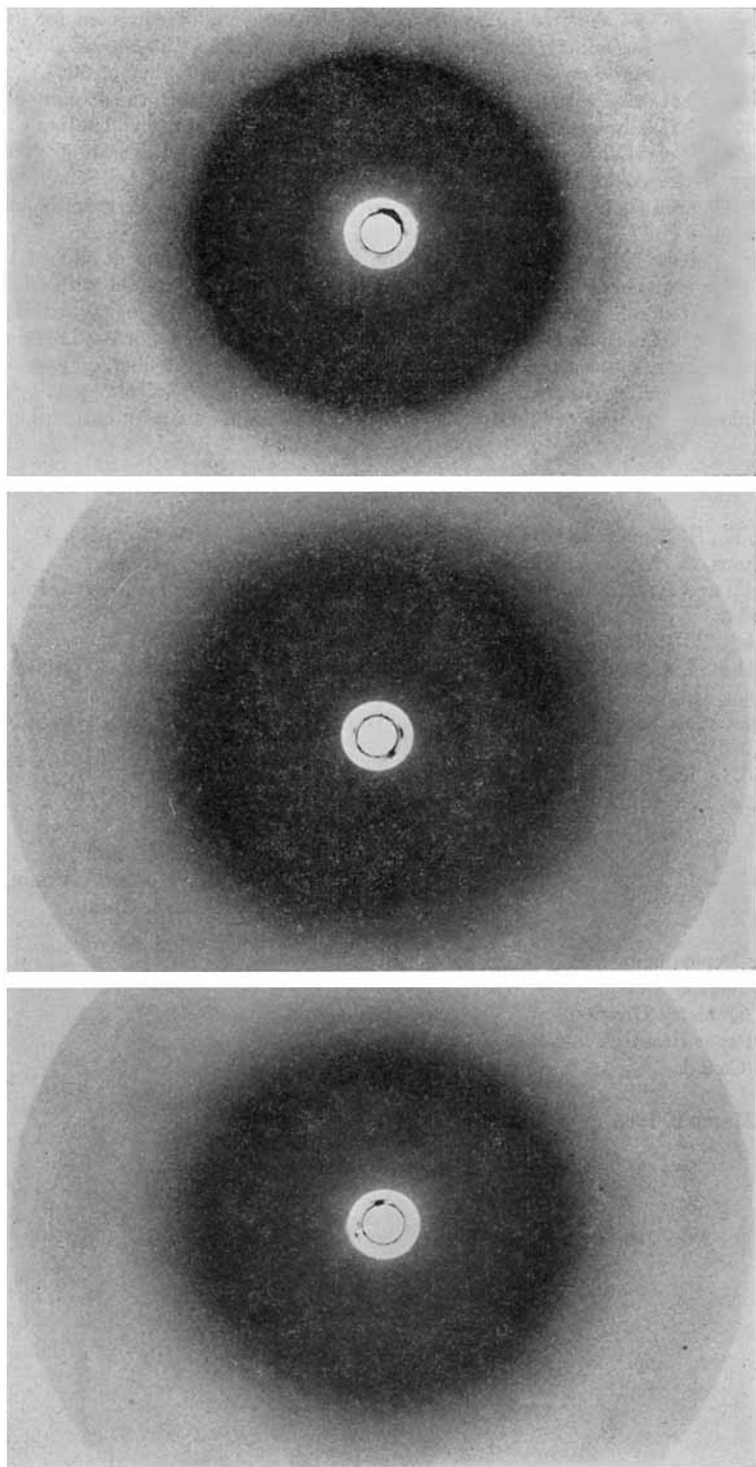
The formaldehyde content of the crosslinked material was measured by the method of Hoffpavir, Buckaloo, and Guthrie.<sup>7</sup> It was about 2% which is equivalent to one crosslink for every 9 glucose residues.

X-ray patterns for the amorphous cellulose and the crosslinked amorphous cellulose are shown in Figure 1. Included is the pattern for regenerated cellulose obtained by boiling the amorphous cellulose in distilled water for five minutes and drying in a vacuum oven at 70°C. It is quite clear that boiling in water caused the amorphous cellulose to revert to cellulose II. In contrast, the crosslinked amorphous cellulose retained its amorphous pattern even after the prolonged aqueous treatment required to remove the formaldehyde and the boric acid.

Similar preparations were made by crosslinking amorphous cellulose produced by ball-milling cotton linters in a Spex Mixer Mill. However, milled samples were rather impure due to the accretion of metallic residues generated in the milling process.

Accessibilities were measured by the tritium exchange method of Sepall and Mason.<sup>8</sup> Measurements were made at 100% relative humidity. The regenerated cellulose gave an accessibility of 79% in good agreement with previous results for other regenerated celluloses.<sup>5,8</sup>

The accessibility of the crosslinked amorphous cellulose was 83% of the original —OH content of the cellulose. If formaldehyde crosslinks by formation of a methylene ether, then each Cell—O—CH<sub>2</sub>—O—Cell bridge eliminates two hydroxyl groups which would be potential exchangers in uncrosslinked cellulose. The formaldehyde content of 2%



*A* *B* *C*  
Fig. 1. X-ray diffraction patterns for: (A) amorphous cellulose; (B) crosslinked amorphous cellulose; (C) regenerated cellulose.

is equivalent to 7% of the free hydroxyls. Thus the accessibility corrected for loss of —OH groups by crosslinking was 90%. This value confirms the accessibility of 89% previously measured on amorphous cellulose at a relative humidity of 50%.<sup>5</sup> It is interesting to note that in spite of the amorphous diffraction pattern the accessibility was not 100%. This is a further demonstration of the absence of a quantitative correlation between crystallinity as measured by x-ray diffraction and accessibility determined by hydrogen exchange. An analogous result was reported by Sepall and Mason<sup>8</sup> who showed that birch xylan which gives an amorphous x-ray diagram is only 52% accessible.

The degree of swelling was measured by the dilatometric technique developed by Minhas.<sup>9</sup> The crosslinked material swelled in water by 200% compared with 100% for the regenerated cellulose. Thus, crosslinked amorphous cellulose behaves rather like a hydrophilic gel in contrast to the regenerated cellulose in which the ordered regions, impervious to water, act as a restraint on the swelling tendency of the fiber. From the accessibility and swelling results, it would be anticipated that the chemical reactivity of the crosslinked amorphous cellulose will be considerably higher than for conventional celluloses.

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