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New Synthesis of Cellulosic Ion-Exchange Compounds

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Dear Sir:

The synthesis of cellulosic ion-exchange compounds was noted by Jurgens *et al.* [1]. Since then, cellulosic ion-exchange materials have found wide use in chromatographic columns. These cellulosic compounds have also been used as ion-exchange reagents for large bulky molecules that are not readily adsorbed into the matrix by the more conventional ion-exchange resins. These cellulose ion-exchange materials have generally been in fiber or floc form and, therefore, have been limited mostly to industrial batch-type operations or to chromatographic work [2, 3] where relatively low flow rates are tolerable. A second limitation of cellulose ion-exchange material has been relatively low capacities when compared to the conventional ion-exchange resins. The preparation, properties, and uses of cellulose ion-exchange compounds, mainly in fibrous or floc form, have been fully reported and summarized [4].

Head *et al.* [5] demonstrated that by cross-linking cellulose with a di-esterfied phosphate, an ion-exchange cellulose could be produced with a capacity higher than usual. Guthrie *et al.* [6] showed that the capacity and stability of cellulose ion-exchange compounds, in the fiber, yarn, cloth, or paper form, could be increased by cross-linking with formaldehyde. By cross-linking, the ion-exchange capacity of the cellulose could be increased before excessive swelling or solubilization occurred.

We have now developed a modification of Guthrie's procedures which permits the use of cellulosic cation-exchange compounds, both in particulate form for industrial columns and in membrane form. Our approach differs from that of Guthrie in that our starting cellulose material is not cross-linked in the formal sense. Thus,

the cellulose is not excessively embrittled. Rather than cross-linking the cellulose, our approach has been to parchmentize the cellulose in a unique way. Normal parchmentizing is done with sulfuric acid at temperatures somewhat lower than 23°C. Our method is to suspend or dissolve cellulose fibers in orthophosphoric acid and then use the resultant mixture as the parchmentizing medium.

When a cellulose sheet or fabric is passed through this medium, squeezed, and then rinsed in water, some of the suspended or dissolved cellulose in the acid precipitates or adheres to the fabric or paper. The fabric or paper simultaneously becomes a membrane. The end result is a membrane with a deposited surface of cellulose with an unusually high percentage of amorphous cellulose. Such a material or membrane has wet strength, purity, and normal parchment-membrane properties.

This new type of parchment product can be used as a starting material for the synthesis of cellulosic ion-exchange compounds. For example, our modification of Guthrie's carboxymethylation method was used on the previously described parchment. This carboxymethylation was repeated three successive times upon the same material. The final product had an ion-exchange capacity of 1.8 meq/g. By repeating the same experiment, but using a parchment produced in a normal manner, i.e., with sulfuric acid, the capacity was found to be only 1.3 meq/g.

Parchment ion exchangers described above can be friated at high temperatures. Such ion-exchange materials of particulate form have proved to be efficient ion-exchange reagents in commercial ion-exchange columns, the flow rate being at least 5 gal (US)/min/ft² with good cycling stability.

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