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ETHERIFICATION OF CELLULOSE

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1 Claim. (Cl. 260—152)

This invention relates to a process of etherifying cellulose, and more particularly, to such a process wherein grinding of the cellulose may be completely avoided.

In Hahn U. S. Patent 1,819,600, granted August 18, 1931, the process of etherifying cellulose is disclosed and claimed, wherein the cellulose is ground and then added without further grinding to a slurry of caustic alkali in an inert liquid, intimately mixed therewith, and then etherified. That process was a material improvement over the prior art processes because it avoided grinding the cellulose with caustic alkali.

An object of the present invention is to provide an improved process of the same general type disclosed in the above mentioned Hahn patent, but in which process all grinding of the cellulose may be avoided. The grinding of the cellulose is an expensive step and also has a tendency to degrade the cellulose, which may be slightly objectionable in preparing a very high grade product. Other objects of the invention will be apparent from the description given hereinafter.

The above objects are accomplished according to the present invention by converting cellulose to an alkali cellulose, then mixing the alkali cellulose with a slurry of caustic alkali in an inert liquid and then etherifying the alkali cellulose in known manner.

The cellulose may be converted to an alkali cellulose by treatment with a caustic alkali solution and by thus forming an alkali cellulose and then mixing with a caustic alkali slurry, the mixture is sufficiently homogeneous to obtain uniform etherification without the necessity of grinding the cellulose at any stage of the process. Where cellulose is mixed directly with the caustic alkali slurry without being first converted into an alkali cellulose, it has been found necessary to grind the cellulose in order to get uniform etherification.

As is well known in the art, it is necessary to maintain certain ratios of water and caustic alkali to cellulose during the etherification step in order to obtain economical operation and a product of desired properties. In carrying out the present invention, the cellulose may be treated with a restricted quantity of caustic alkali solution containing the amount of water desired, prior to etherification, and the whole mass after treatment may be mixed with the caustic alkali slurry, or alternatively, the cellulose may be treated with an excess of caustic alkali solution and the excess removed by pressing the cellulose, and the resulting alkali cellulose then mixed with the

caustic alkali slurry. In either case, alkali cellulose is mixed with a slurry of caustic alkali in an inert liquid and then etherified.

The following examples are given to illustrate the present invention, parts being given by weight:

Example 1.—One hundred parts of cotton linters (in board form) are steeped in an excess of 50% caustic soda solution and pressed to a weight of 475 parts. The resulting alkali cellulose is shredded and then added, either directly or after ageing, to an autoclave. Six hundred parts of a slurry of 200 parts of caustic soda in 400 parts of benzene, prepared by grinding these materials together in a ball mill, 500 parts ethyl chloride and 400 parts benzene are added to the alkali cellulose, and the mixture agitated and heated for six hours at 150° C. The ethyl cellulose thus formed is recovered in known manner.

Example 2.—One hundred parts of cellulose are impregnated with 200 parts of 50% caustic soda solution. Nine hundred parts of a slurry of 300 parts of caustic soda and 600 parts of benzene, prepared as described in Example 1, are added and the mixture is kneaded or shredded until it is uniform. The resulting alkali cellulose is charged into an autoclave together with 500 parts of ethyl chloride and 200 parts of benzene, and the mixture agitated and heated for five hours at 150° C. A high grade of ethyl cellulose is prepared in this manner.

Example 3.—One hundred parts of high alpha cellulose from wood pulp is impregnated with 400 parts of 50% caustic soda solution and the resulting alkali cellulose is kneaded or shredded with 600 parts of a slurry of 200 parts of caustic soda and 400 parts of toluene, prepared as described in Example 1, until the mixture is uniform. This will require only a short period of about 15–30 minutes. The mixture is then charged into an autoclave along with 600 parts of benzyl chloride and is agitated and heated for eight hours at 125° C., a high grade of benzyl cellulose being formed at the end of this treatment.

The above examples have been given merely to illustrate the present invention which is of broad application. Caustic potash and other caustic alkalies may be used in place of caustic soda and any other inert liquid such as xylene, chlorobenzene, chlorotoluene, Hi-flash naphtha, unsaturated hydrocarbons of the type of amylene, dimethyl ether, diethyl ether and glycol diethyl ether, may be used in place of benzene or toluene; from 1–3 parts by weight of inert liquid to one

part by weight of solid caustic alkali may be used in the slurry. Also additional inert liquid up to 10 parts by weight per one part by weight of cellulose may be added to the reaction mixture in addition to the inert liquid in the slurry. The additional inert liquid has the advantage of increasing the fluidity and miscibility of the reaction mass, but that advantage is somewhat offset by the disadvantage of decreasing the liquid concentration of the etherifying agent to some extent.

The slurry of caustic alkali and inert liquid is conveniently produced by grinding solid caustic alkali in the inert liquid in a ball mill, although other grinding apparatus of course may be used. The slurry is relatively stable and there is practically no tendency to settle out even after standing for several hours. Since it is relatively fluid, it can be advantageously transported through pipe lines by means of pumps. The particles of caustic alkali are in an extremely fine state of subdivision compared with any of the commercial powdered caustic alkalies, or compared with caustic alkalies powdered in the absence of the inert liquid. Furthermore, the extremely fine particles of caustic alkali in the slurry show no tendency to clump together, whereas the dry powdered caustic alkali shows a strong tendency to form lumps which possess the same disadvantages as unpowdered caustic in the etherification process, namely, non-uniform concentration of alkali throughout the reaction mass.

Various types of cellulosic material may be used advantageously in the present process besides cotton linters or high alpha cellulose from sulphite pulp. In fact, practically any cellulose of good quality produced from wood, bagasse, or other cellulosic materials, may be used.

As will be obvious to those skilled in the art, a wide variety of etherifying agents may be used, among which may be mentioned not only ethyl chloride and benzyl chloride, but etherifying agents such as methyl chloride, ethylene chlorohydrin, ethylene chloride, crotyl chloride, cyclohexyl chloride, amyl chloride, lauryl chloride, propyl chloride, and the like.

In carrying out the process, it is advantageous to treat the cellulose with a caustic alkali solution having a concentration of from 18-50%, but it is to be understood that the present invention is applicable to any alkali cellulose regardless of how produced. The alkali cellulose prior to the addition of solid caustic alkali should contain 0.45 to 36.0 mols of water and 0.04-10.0 mols of caustic alkali for each mol of cellulose, although it is preferred to use 4.5 to 36.0 mols of water and 2.0-10.0 mols of caustic alkali per mol of cellulose for best results. It is advantageous to use high concentrations of caustic alkali solution in treating the cellulose, since higher concentrations minimize the formation of heat when the solid caustic alkali is added to the alkali cellulose. As will be obvious to those skilled in the art, the quantities of solid caustic alkali, inert liquid, and etherifying agent, as well as the conditions of time and temperature during the etherification, may be varied depending on the characteristics desired in the resulting cellulose ether. In the "mol" proportions given throughout the specification and claims, a mol of cellulose is taken as 162 for the monoglucose unit as is customary.

The total caustic alkali, including that originally added as caustic solution and that added

in slurry form, should amount to not more than one mol per mol of water in the reaction mixture where there is a high ratio of water to cellulose, for example, 4 parts by weight of water to one part by weight of cellulose. At lower ratios, for example, 2 parts by weight of water to one part by weight of cellulose, a caustic: water ratio of two mols to one may be used. At still lower ratios of water to cellulose, for example, one-half part by weight of water to one part by weight of cellulose, a higher caustic: water ratio may be used, i. e., 4 mols of caustic per mol of water. In general, it may be stated that the higher the ratio of water to cellulose, the lower is the ratio of caustic to water, and it is to be understood that the invention is by no means limited to the above ratios of caustic alkali, water, and cellulose in the reaction mixture, since those skilled in the art will be familiar with the ratio suitable for use to produce ethers of desired properties.

The etherifying agents may be varied from approximately 5 mols per 100 grams of cellulose upwards even to as high as 20 mols; using as high a proportion as 20 mols of etherifying agent per 100 grams of cellulose accelerates the reaction and the excess etherifying agent may be recovered. Suitable ratios of etherifying agent to cellulose are known in the prior art.

The cellulose ethers produced according to the present invention may be used for any of the purposes for which cellulose ethers or esters are now used, such as for plastics, molding compositions, lacquers and other coating compositions, interlayers for safety glass, artificial fibers, film for photographic or other purposes, and the like.

An advantage of the present invention resides in the elimination of the necessity for grinding cellulose or alkali cellulose at any stage in the process. In processes heretofore known, an ether satisfactory from the standpoint of viscosity, uniformity of etherification, film properties, plastic properties, et cetera, could not be obtained without grinding cellulose alone, or alkali, cellulose with solid caustic, at some stage in the process. In prior art processes involving intimate admixture of cellulose and caustic by means of grinding, the optimum properties of the cellulose ether were not obtained. The present process improves on all prior art processes by obtaining practically the optimum properties in the product. The elimination of this grinding of cellulose or alkali cellulose effects a very material economy in the process and, furthermore, avoids any danger of obtaining an inferior cellulose ether due to degradation of the cellulose by grinding.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claim.

I claim:

Process of etherifying cellulose comprising the steps of converting the cellulose to an alkali cellulose containing 4.5 to 36.0 mols of water and 2.0 to 10.0 mols of caustic alkali per mol of cellulose, mixing the alkali cellulose with a slurry of caustic alkali in an inert liquid, and then etherifying the alkali cellulose.

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