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FORMALDEHYDE-CELLULOSE PRODUCTS
AND THE PROCESS OF MAKING SAME

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The present invention relates to cellulose derivatives and to the process of making same. It is an object of this invention to provide derivatives of cellulose which are soluble in dilute alkalis.

It is a further object of this invention to make available cellulose derivatives which are useful as textile sizing compositions.

It is an object of this invention to provide wash- and laundering-fast cellulose textile sizes.

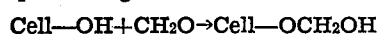
It is a further object to provide cellulose derivatives which may be dissolved in alkali solutions and spun into fibers in a suitable precipitating bath for the production of artificial silk or precipitated in the form of fibers or foils. It is also an object of this invention to provide paper sizing and modifying agents.

Other objects and advantages will become apparent from the more detailed description of the invention given hereinafter. Such detailed description should not be construed as limiting, but only by way of explanation and illustration, since numerous variations may be made by those skilled in the art without departing from the scope and spirit of the invention.

The derivatives of the present invention may be formed by the reaction of an alkali cellulose, as for instance, soda cellulose, potash cellulose, lithium cellulose, quaternary ammonium cellulose, and the like, with formaldehyde or formaldehyde-forming substances such as paraformaldehyde, hexamethylenetetramine, and the like.

The reaction may be effected in the cold in some instances and in others by the application of heat. We may first react cellulose with sodium hydroxide, for instance, to form soda cellulose. After aging the soda cellulose to a satisfactory degree, as explained below, it is mixed with the formaldehyde or formaldehyde-forming compound and heated.

In the reaction of the present invention it is suggested that the following reaction may occur. Representing cellulose as Cell—OH:



The above is given by way of possible explanation only and should not be construed as limiting since we do not wish to be limited by any theoretical explanation of the reaction.

The cellulose derivatives are soluble in alkalies with cooling or hot, according to the number of substituent groups. Thus we may make a derivative which is insoluble in alkali at ordinary temperatures but which is readily soluble by cooling the alkali suspension to about 0° C. Such

solutions are valuable as textile sizing agents. The solutions, usually of about 1% to 10% strength, are applied to cotton, linen or rayon goods on a padder, squeezed, dried and coagulated by using a solution of an acid, acid salt, or a precipitating concentrated salt solution.

The treated textile is washed thoroughly after coagulating and then dried. A firm hand is imparted to the fabric which is resistant to laundering and the ordinary cleansing agents. The finish may be applied at practically any convenient stage of processing such as before kier boiling, before dyeing, and the like.

Since the derivatives of the present invention contain reactive groups, they may be caused to undergo further reaction, as for instance with aldehydes, acids, phenols, amines and ammonia, hydroxylamine, hydrazine, hydrogen cyanide and the like. Thus if used as a sizing material, the derivatives of the present invention may be subjected to heat after coagulation which causes a further reaction of the reactive group, with subsequent cross-linking and curing of the derivative on the textile. On the other hand, a textile sized with the derivatives of the present invention may be treated with ammonia, amines or other reactive nitrogenous derivatives. Such treated sized textiles are then much more receptive to dyestuffs capable of dyeing wool, silk, hair, and the like.

Cellulose in its various forms may be used in the present invention. However, after forming the alkali or quaternary ammonium cellulose, we prefer to age it to secure some controlled degradation until the desired viscosity is attained.

The viscosity may be varied both by using different forms and sources of cellulose, by introducing more or less reactant and by degrading the cellulose to a greater or lesser degree.

In the reaction of the present invention we may use inert solvents if desired such as ethylene dichloride, carbon tetrachloride, benzene, ethyl ether, heptane, and the like.

When making the alkali cellulose, concentrations of from about 15% to 50% of alkali may be used. This is also true of the quaternary ammonium hydroxides. When using these latter materials solutions of the cellulose sometimes occurs. In such cases, the solutions may be diluted with alkali metal hydroxide solutions before reaction. Such quaternary ammonium hydroxides may be trimethyl benzyl ammonium hydroxide, tetraethyl ammonium hydroxide, diethyl dipropyl ammonium hydroxide, diethyl piperidinium

hydroxide, methyl pyridinium hydroxide and the like.

The proportions of reactants may be varied within very large limits of for instance from 5% to about 100% of the weight of the cellulose. For several reasons it may be desirable to use an excess of formaldehyde or formaldehyde-forming agent. For instance, in some cases a Cannizzaro reaction occurs very readily, or a resinification reaction occurs with subsequent partial exhaustion of the aldehydic reactant. On the other hand, a greater proportion of formaldehyde or formaldehyde-producing agent may be used to accelerate the reaction, which may then be terminated before completion if desired.

Therefore, the process of the present invention consists in allowing cellulose to react with an excess of a 15% to 50% aqueous solution of an alkali such as sodium hydroxide to form alkali cellulose. The amount of alkali amounts to from 2 to about 8 moles per $C_6H_{10}O_5$ group of cellulose. To this mixture is then added from 5% to about 100% (based on dry cellulose) of formaldehyde or formaldehyde-forming material as above defined and reacted for a period from 1 to about 5 hours. The reaction temperature is between about 40° and 100° C., higher temperatures being employed when a degraded product (that is, one producing a lower viscosity) is desired. Afterwards the reaction mixture is acidified, whereby the product is coagulated and can be filtered, washed and dried. The dried product is capable of dissolving in dilute aqueous alkali to form a homogeneous solution useful particularly as a wash-fast size for fabrics.

The following examples are given to illustrate the products and processes of the present invention. All proportions are in parts by weight.

Example 1.—100 parts of soda cellulose containing 30.4 parts of cellulose and 69.6 parts of aqueous 20% sodium hydroxide solution and aged for 96 hours were mixed with 162 parts of a 37% formaldehyde solution. The mixture was homogenized and reacted for 5 hours at 70° C. The reaction mixture was then diluted with water and treated with sufficient acetic acid to coagulate the cellulose derivative. The material thus obtained was washed several times with water and finally with acetone. A white fluffy product was formed which dissolved readily in dilute sodium hydroxide solution to give a solution of medium viscosity.

Example 2.—99.7 parts of soda cellulose containing 30 parts of cellulose and 69.7 parts of 20% sodium hydroxide solution were mixed with 16.2 parts of a 37% formaldehyde solution. The soda cellulose had been aged for 48 hours. The mixture was thoroughly homogenized and reacted for 3 hours at a temperature of 70° C. A white material was obtained which was acidified with acetic acid, washed thoroughly with water and acetone, and dried. A white powdery material was obtained which was soluble in cold 5% to 10% sodium hydroxide solution. A 4% solution thus made had a medium viscosity.

Example 3.—100 parts of soda cellulose containing 30% of cellulose and 70% of 20% aqueous sodium hydroxide and aged for 48 hours, were mixed with sufficient aqueous formaldehyde solution (16.2 parts) to furnish 1 part of formaldehyde to 5 parts of cellulose. The mass was thoroughly mixed in order to insure complete homogenization and was then reacted at 50° C. for 5 hours. The reaction product was mixed with water, acidified with glacial acetic acid, and thoroughly washed with warm water. The mate-

rial was dried and a white fibrous product was obtained which was soluble in dilute aqueous sodium hydroxide solution on cooling.

Example 4.—A solution of the formaldehyde-cellulose derivative of Example 3 was made by mixing 4 parts of this material with 40 parts of 20% aqueous sodium hydroxide and 56 parts of crushed ice. The solution was clear and fairly viscous. A piece of cotton broadcloth was immersed in the solution, the excess solution removed by squeezing and the cloth dried. The fabric was then passed through a bath containing 10% sulfuric acid and finally washed and dried. A firm hand was imparted to the cloth. This was not diminished to any appreciable extent upon laundering.

Example 5.—100 parts of alkali cellulose containing 30% cellulose, 15% NaOH and 55% water and aged for 114 hours were reacted with 27 parts of a 37% formaldehyde solution at 80° C. for 2 $\frac{3}{4}$ hours. The material was then neutralized and washed thoroughly with water and dried. A fluffy fibrous material was obtained which was soluble in 10% sodium hydroxide solution with cooling.

Example 6.—36.6 parts of soda cellulose containing 10 parts of cellulose and 26.6 parts of 20% sodium hydroxide solution were mixed with 27 parts of a 27% solution of formaldehyde. The material was thoroughly homogenized and then reacted for 5 hours at 70°–75° C. The reaction mixture was neutralized with acetic acid, washed with water and dried. A white fibrous derivative was obtained which was soluble in 8% sodium hydroxide solution with cooling to give a viscous solution of 4% strength.

Example 7.—49 parts of soda cellulose containing 15 parts of cellulose and 34 parts of 20% sodium hydroxide solution were aged for 72 hours. The aged material was treated with 40 parts of an aqueous solution of hexamethylenetetramine containing 60 parts of hexamethylenetetramine in 100 parts of water. The mixture was thoroughly homogenized and reacted for 5 hours at 70° C. At the end of the reaction period the material was acidified with acetic acid, washed with water and acetone, and dried. A white powdery fibrous cellulose derivative was thus obtained, which was soluble in dilute alkali solution. A 4% solution exhibited low viscosity.

We claim:

1. The process of making a formaldehyde-cellulose compound which is soluble in aqueous alkali solutions which comprises reacting an alkali-cellulose prepared from a 15% to 50% aqueous solution of an alkali and containing from 2 to about 8 moles of alkali hydroxide per $C_6H_{10}O_5$ group of cellulose, with from 5% to about 100% of formaldehyde based on the cellulose, at a temperature between about 40° C. and 100° C.

2. The process of making a formaldehyde-cellulose compound which is soluble in aqueous alkali solutions which comprises reacting an alkali-cellulose prepared from a 15% to 50% aqueous solution of an alkali and containing from 2 to about 8 moles of alkali hydroxide per $C_6H_{10}O_5$ group of cellulose, with from 5% to about 100% of formaldehyde based on the cellulose, at a temperature between about 40° C. and 100° C.; and thereafter coagulating the formaldehyde-cellulose compound and recovering the same by filtering, washing and drying.

3. The process of making a formaldehyde-cellulose compound which is soluble in aqueous alkali solutions which comprises reacting a soda-cellulose prepared from a 15% to 50% aqueous

solution of sodium hydroxide and containing from 2 to about 8 moles of NaOH per $C_6H_{10}O_5$ group of cellulose, with from 5% to about 100% of formaldehyde based on the cellulose, at a temperature between about 40° C. and 100° C.; and thereafter coagulating the formaldehyde-cellulose compound and recovering the same by filtering, washing and drying.

4. A formaldehyde-cellulose compound soluble in aqueous alkali solutions and consisting of the 10

coagulated, washed and dried reaction product of an alkali-cellulose and formaldehyde, the alkali-cellulose being prepared from a 15% to 50% aqueous solution of an alkali containing from 2 to 8 moles of alkali hydroxide per $C_6H_{10}O_5$ group of cellulose and the formaldehyde being from 5% to 100% of the weight of the cellulose.

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