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CARBODIIMIDE-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 alkalies.

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 cellulosic 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 film and foils.

It is an object of this invention to provide paper sizes and modifying agents.

Other objects and advantages will become apparent from the more detailed description of the invention set forth 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 present invention.

The derivatives of the present invention may be formed by the reaction of an alkali cellulose derivative, as for instance, soda cellulose, quaternary ammonium cellulose, potash cellulose, lithium cellulose and the like, with disubstituted carbodiimides. The reaction may be effected in the cold, in some instances, and in others by the application of heat; that is, between ice temperature and boiling.

Instances of carbodiimides which may be used in the process of the present invention are N,N'-dimethyl carbodiimide, N,N'-diethyl carbodiimide, N,N'-diphenyl carbodiimide, N,N'-dioctyl carbodiimide, N-ethyl-N'-propyl carbodiimide, N-ethyl-N'-methoxy-ethyl carbodiimide, N-methyl-N'-carboxyethyl carbodiimide, N-methyl-N'-phenyl carbodiimide, and the like. I may first react cellulose with sodium hydroxide, for instance, to form soda cellulose. After aging the soda cellulose to a satisfactory viscosity, it is mixed with cooling with the carbodiimide. Reaction is effected either in the cold or the reaction mixture is allowed to warm up and further heating applied up to 100° C. or less.

Thus the carbodiimides of the present invention may be represented by

$$R—N=C=NR'$$

where R and R' may be alkyl, aryl, alkaryl,

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aralkyl, olefinyl, alkynyl, alkenyl, carbocyclic, dicyclic, and the like.

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

$$\text{Cell—OH} + \text{R—N=C=N—R'} \longrightarrow \text{Cell—O—}\overset{\overset{\text{N—R}}{\|}}{\text{C}}\text{—NHR'}$$

Thus isomers could be formed which in some cases, at least, or under suitable conditions rearranged to the urea, thus:

$$\text{Cell—O—}\overset{\overset{\text{N—R}}{\|}}{\text{C}}\text{—NHR'} \longrightarrow \text{Cell—}\overset{\overset{\text{R}}{|}}{\text{N}}\text{—CONHR'}$$

The above is given by way of possible explanation only and should not be construed as limiting. However, it is an object of this invention to provide a process of making isourea derivatives of cellulose.

The cellulose derivatives of this invention are soluble in dilute alkalies or in water according to the kind and number of substituent groups. Thus, I 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, etc. 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 amido and isourea groups, they may be caused to undergo further reaction, as for instance with aldehydes, acids, halogens and the like. Thus, when used as a textile sizing material, the coagulated size may be treated with formaldehyde, or other aldehyde, in order to effect curing and fixation of the size. Furthermore, textiles sized with the compositions of the present invention are much more receptive to dyestuffs by reason of the isourea groups.

Cellulose in its various forms may be used in the present invention. However, after forming the alkali or quaternary ammonium cellulose, I prefer to age it to secure some controlled degradation until the desired viscosity is obtained. The viscosity may be varied both by using different

forms and sources of cellulose, and by degrading the cellulose to a greater or lesser degree.

In the reaction of the present invention, I may use inert diluents if desired, such as ethylene dichloride, carbon tetrachloride, benzene, ethyl ether, dioxan, heptane, and the like. When making the alkali cellulose, concentrations of from 15% to 50% of alkali may be used, although greater or lesser concentrations can be employed. I usually prefer to employ concentrations of about 30% to 40%. This is also true of the quaternary ammonium hydroxides. When using these latter materials, solution 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, etyhl piperidinium hydroxide, methyl pyridinium hydroxide and the like. The amount of quaternary ammonium or alkali hydroxide is from about 3 to 8 moles per $C_6H_{10}O_5$ group of cellulose.

The proportions of reactants may be varied within wide limits of, for instance, from 5% to 100% or more of the cellulose. For several reasons it may be desirable to use an excess of carbodiimide. For instance, in some cases a large excess of carbodiimide may be used and the reaction terminated short of completion, if desired.

As well as utilizing the carbodiimide given above, I may also use carbodiimides containing other substituents such as halogen, cyano, carboxy, aldehyde, acyl, keto, nitro and the like.

It is an object of this invention to make isoureas of cellulose by the reaction of an alkali cellulose with a carbodiimide. The cellulose isoureas of this invention have a variety of uses besides those described above. For instance, they may be spun into fibers and used in textiles or they may be coagulated in the form of foils and films. In some cases, when a highly substituted cellulose is used, it is expected that solution may be effected with acids due to the basic character of the isourea group. In some cases when the substituent groups are correct in number and kind the cellulose may be dissolved in organic solvents and used as coating compositions and moldings. The latter are especially useful since they may be made thermosetting.

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

Example 1.—N,N'-diamyl carbodiimide was prepared by heating 7.5 parts of symmetrical diamyl thiourea in 40 parts of dioxan with 30 parts of yellow mercuric oxide and 10 parts of anhydrous sodium sulfate at 70° C. for 30 minutes. The mercuric sulfide and salts were filtered off and the solution which was obtained was mixed with 66.5 parts of soda cellulose containing 15 parts of cellulose and 51.5 parts of 33% sodium hydroxide solution. The mixture was heated at 70°–75° C. for 2 hours, then acidified with acetic acid, washed with water and acetone, and dried. A white fibrous cellulose derivative was obtained which was soluble in 10% sodium hydroxide solution.

Example 2.—5 parts of diamyl carbodiimide-cellulose were mixed with 30 parts of 33% sodium hydroxide solution, 40 parts of water and 30 parts of crushed ice. This solution contained 5% of cellulose derivative and 10% sodium hydroxide. There was then added 7.5 parts of 33% sodium hydroxide solution, 80 parts of water and 62.5 parts of crushed ice. A clear solution was obtained consisting of 2% cellulose derivative and 5% sodium hydroxide. Broadcloth was treated with this solution, squeezed, dried and treated with 10% sulfuric acid solution. After coagulation, the cloth was washed thoroughly in water and dried. A firm hand was imparted to the cloth and better draping qualities.

Example 3.—N,N'-diamyl carbodiimide was prepared by heating 3.5 parts of symmetrical diamyl thiourea in 35 parts of dioxan with 10 parts of yellow mercuric oxide and 10 parts of anhydrous sodium sulfate for 1 hour under reflux condenser. The black mercuric sulfide and salts were removed by filtration and the solution mixed with 66 parts of soda cellulose containing 15 parts of cellulose and 51 parts of 33% sodium hydroxide solution. The mixture was heated at 80° C. for 2 hours. It was then acidified with acetic acid, washed with water and acetone, and dried. A white fibrous material resulted which was soluble in dilute sodium hydroxide solution on cooling.

Example 4.—N,N'-dioctyl carbodiimide was prepared by refluxing for 1 hour 5 parts of symmetrical di-n-octyl thiourea with 10 parts of yellow mercuric oxide, 10 parts of anhydrous sodium sulfate, 30 parts of dioxan and 14 parts of benzene. The black mercuric sulfide and salts were removed by filtration and the solution mixed with 35 parts of soda cellulose, containing 10 parts of cellulose and 25 parts of 33% sodium hydroxide solution. The mixture was heated at 70° C. for 3 hours. It was acidified with acetic acid, washed with water and acetone, and dried. A gray friable powder was formed. This was soluble in dilute sodium hydroxide solutions.

Example 5.—N,N'-diphenyl carbodiimide was prepared by refluxing a mixture of 5 parts symmetrical diphenyl thiourea, 30 parts of dioxan, 10 parts of lead carbonate, and 10 parts of anhydrous sodium sulfate. The heating was carried on for 1 hour. The lead sulfide and salts were filtered off and the solution mixed with 35 parts of soda cellulose containing 10 parts of cellulose and 25 parts of 33% sodium hydroxide solution. The mixture was heated at 70° C. for 2½ hours, then acidified with acetic acid. The cellulose derivative was washed with water and acetone, and dried. A fluffy white fibrous mass was obtained which was soluble in dilute sodium hydroxide solution on cooling.

Example 6.—Ethylene carbodiimide was prepared by heating 5 parts of ethylene thiourea, 30 parts of dioxan, 10 parts of yellow mercuric oxide and 10 parts of anhydrous sodium sulfate to 90° C. for 1 hour. The salts were filtered off and the resulting clear, colorless solution mixed with 35 parts of soda cellulose, containing 10 parts of cellulose and 25 parts of 33% sodium hydroxide solution. The mixture was heated at 70° C. for 2½ hours. The product was acidified, washed with water and acetone, and dried. A white, fluffy fibrous material was secured which was soluble in dilute sodium hydroxide solutions.

Example 7.—N,N'-diethyl carbodiimide was prepared by heating under reflux for 1 hour a mixture of 7.5 parts of symmetrical diethyl thiourea, 10 parts of yellow mercuric oxide, 10 parts of anhydrous sodium sulfate and 33.5 parts of benzene. The salts were removed by filtration and the resulting clear solution mixed with 66 parts of soda cellulose, containing 15 parts of cellulose and 51 parts of 33% sodium hydroxide solution. The mixture was heated for 2 hours at

65°–70° C. The reaction product was acidified, washed with water and acetone and dried. A white powder was obtained which was soluble in dilute sodium hydroxide solutions.

I claim:

1. The process of making a cellulose derivative which is soluble in dilute aqueous alkali solutions which comprises reacting alkali cellulose with a di-hydrocarbon radical-substituted carbodiimide wherein the substituting radicals each have less than 9 carbon atoms.

2. The process of making a cellulose derivative which is soluble in dilute aqueous alkali solutions which comprises reacting soda cellulose in aqueous medium with a di-hydrocarbon radical-substituted carbodiimide wherein the substituting radicals each have less than 9 carbon atoms.

3. The process of making a cellulose derivative which is soluble in dilute aqueous alkali solutions which comprises reacting, at between ice temperature and boiling, soda cellulose and a di-hydrocarbon radical-substituted carbodiimide wherein the substituting radicals each have less than 9 carbon atoms, in aqueous medium, the amount of carbodiimide being from 5% to about 100% of the cellulose and the soda cellulose being formed from a sodium hydroxide solution of 30% to 40% concentration and with the amount of sodium hydroxide from 3 to about 5 moles per $C_6H_{10}O_5$ group of cellulose; and thereafter coagulating the reaction mixture and recovering the carbodiimide-cellulose product by filtering, washing and drying the same.

4. Process for the manufacture of new cellulose derivatives which are soluble in dilute aqueous alkali solutions which comprises acting upon alkali cellulose in the presence of an alkali hydroxide with a di-hydrocarbon radical-substituted carbodiimide wherein the substituting radicals each have less than 9 carbon atoms.

5. The process of making a cellulose derivative which is soluble in dilute aqueous alkali solutions which comprises reacting alkali cellulose with diamyl carbodiimide.

6. The process of making a cellulose derivative which is soluble in dilute aqueous alkali solutions which comprises reacting alkali cellulose with dioctyl carbodiimide.

7. The process of making a cellulose derivative which is soluble in dilute aqueous alkali solutions which comprises reacting alkali cellulose with diphenyl carbodiimide.

8. A cellulose compound soluble in dilute aqueous alkali solutions comprising the reaction product of a di-hydrocarbon radical-substituted carbodiimide wherein the substituting radicals each have less than 9 carbon atoms, and alkali cellulose.

9. A cellulose compound soluble in dilute aqueous alkali solutions comprising the coagulated, washed and dried reaction product of a di-hydrocarbon radical substituted and soda cellulose, the carbobiimide wherein the substituting radicals each have less than 9 carbon atoms, being reacted in the proportion of 5% to 100% of the cellulose and the soda cellulose being formed from a 30% to 40% sodium hydroxide solution with from 3 to 8 moles of NaOH per $C_6H_{10}O_5$ group of cellulose.

10. A cellulose compound soluble in dilute aqueous alkali solutions comprising the reaction product of diamyl carbodiimide and alkali cellulose.

11. A cellulose compound soluble in dilute aqueous alkali solutions comprising the reaction product of dioctyl carbodiimide and alkali cellulose.

12. A cellulose compound soluble in dilute aqueous alkali solutions comprising the reaction product of diphenyl carbodiimide and alkali cellulose.

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