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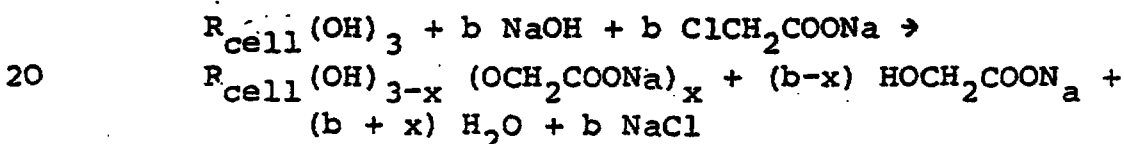
PROCESS FOR PREPARING AN ALKALI METAL
SALT OF CARBOXYMETHYL CELLULOSE

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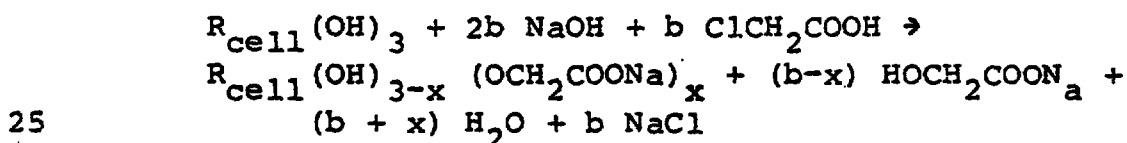
The present invention relates to a process for the preparation of alkali metal salts of carboxymethyl cellulose, sometimes referred to in the literature as alkali metal cellulose glycolates. The alkali metal salts of carboxymethyl cellulose, hereinafter sometimes referred to as "CMC", that are prepared by the process of this invention possess enhanced viscosity and fluid loss control characteristics when dispersed in an aqueous medium containing dissolved calcium ions.

Cellulose is a linear polymer of β -anhydroglucose units. Each anhydroglucose unit contains three hydroxyl groups. CMC is prepared by the reaction of some of the cellulose hydroxyls with sodium monochloroacetate, using sodium as a typical alkali metal, or monochloroacetic acid as follows:

Sodium Monochloroacetate



Monochloroacetic Acid



where b indicates reaction stoichiometry and x indicates the DS achieved in the reaction. The extent of the reaction of cellulose hydroxyl groups to form a derivative is called the "degree of substitution" (DS), and is defined as the average number of the three hydroxyl groups in the anhydroglucose unit which have reacted. Commercial products have DS values ranging from 0.4 to 1.4. The most common grade has a DS of 0.7 to 0.8.

CMC is commercially available in several different viscosity grades, generally ranging from 4500 centipoise

(B)

(cp) in a 1% by weight solution of CMC in deionized water to 10 cp in a 2% by weight solution. The various viscosity grades correspond to products having molecular weights from substantially 1,000,000 to 40,000.

5 Alkali metal or ammonium salts of carboxymethyl cellulose are water-soluble polymers. If calcium ion is present at a concentration normally found in hard water, these salts of carboxymethyl cellulose will not normally develop their full viscosity. At higher calcium ion con-
10 centrations, CMC precipitates from solution. CMC is, however, more tolerant of alkali metal ions in solution than are many other water-soluble polymers. The tolerance is greater if the cation is added to a CMC solution than if CMC is added to a cation solution.

15 The commercial production of CMC involves treatment of cellulose with aqueous sodium hydroxide, followed by reaction with sodium chloroacetate or monochloroacetic acid. A side reaction also occurs whereby the sodium
20 chloroacetate reacts with sodium hydroxide to give sodium glycolate and sodium chloride. Cellulose is a fibrous solid. Chemical cellulose which is useful for the manufacture of CMC is derived from cotton linters or wood pulp. To obtain uniform reaction, it is essential that all the
25 fibers be wetted with the aqueous NaOH. One process for accomplishing this is to steep sheeted cellulose in aqueous NaOH, and then to press out the excess. The sheets are then shredded and the sodium chloroacetate is added. Reactions are generally conducted at 50 to 70°C. In some
30 instances, a greater amount of NaOH is added, and the monochloroacetic acid is added as such, the sodium salt being formed in the presence of the cellulose.

 Alternative processes have been developed wherein the steeping and pressing steps are eliminated by conducting the reaction in the presence of an inert water-
35 miscible diluent such as tertiary butanol, acetone, or isopropanol. At the end of the reaction, the excess alkali is neutralized and the crude product, which con-

tains sodium chloride and sodium glycolate, may be purified depending on the quality of the product desired.

The following United States Patents disclose various processes for preparing CMC: 2,148,952; 2,512,338;
5 2,513,807; 2,607,772; 2,715,124; 2,839,526; 3,069,409;
3,085,087; 3,088,943; 3,284,441; 3,498,971; and 4,063,018.

One of the most desirable properties of CMC for a wide variety of uses is its ability to impart viscosity and other special rheological properties to aqueous solutions. Most solutions of CMC are pseudoplastic. Most
10 products having a DS below 1.0 are also thixotropic. Thixotropy, or the lack of it, is a function not only of the degree of substitution, but also of the uniformity of substitution. Solution properties can be changed from
15 thixotropic to non-thixotropic with no change in DS by using special reaction schedules and by selection of raw materials. Uniformity of substitution also increases tolerance to acid systems and dissolved ions. The presence of salts in solution represses the disaggregation of
20 CMC, and therefore affects the viscosity and other properties.

In the drilling, mining, and other industries, drilling fluids are used to: carry the cuttings to the surface; clean and cool the drill bit; reduce friction between the
25 drill string and the sides of the borehole; maintain the stability of uncased sections of the borehole; prevent the inflow of fluids from the formations penetrated; and form a thin, low permeability filter cake on the sides of the borehole to prevent or decrease the loss of fluid from
30 the drilling fluid to the formations penetrated.

In order to prevent formation fluids from entering the borehole, the hydrostatic pressure of the mud column must be greater than the pressure of the fluids in the formation. As a result, drilling fluids tend to invade
35 the permeable formations. Solids in the drilling fluid are filtered out into the walls of the hole, forming a cake of relatively low permeability, through which only

filtrate can pass. Drilling fluids must be treated to keep the cake permeability as low as possible in order to maintain a stable borehole and to minimize filtrate invasion of, and damage to, potentially productive formations. High cake permeability results in thick filter cakes, which cause many problems.

CMC has been used for many years to reduce the filter loss, i.e. the volume of filtrate, of aqueous drilling fluids. Many cations, such as potassium and calcium, are advantageously present in drilling fluids to help stabilize the sides of the borehole and to prevent excessive breakdown of the cuttings before they are removed from the borehole. However, the presence of multivalent cations drastically affects the filtration characteristics of the drilling fluids just as they affect the rheological properties as discussed above.

The following U.S. Patents discuss the use of CMC in drilling fluids: 2,425,768; 2,536,113; 2,606,151; 2,957,822; 3,076,758; and 3,954,628.

Thus there is a need for an additive for use in decreasing the fluid loss of drilling fluids containing calcium ions. There is also a need for an additive for use in increasing the viscosity of aqueous fluids containing calcium ions.

It is an object of this invention to provide a process for the manufacture of CMC which possesses enhanced stability in aqueous solutions containing calcium ions.

It is another object of this invention to provide a CMC which possesses enhanced rheological characteristics in aqueous fluids containing calcium ions.

It is still another object of this invention to provide aqueous compositions containing calcium ions, particularly adapted for use as well working compositions, which possess enhanced rheological characteristics.

A further object of this invention is to provide a process for the manufacture of CMC which possesses

enhanced fluid loss control characteristics in aqueous fluids containing calcium ions.

We have discovered that CMC possessing improved rheological properties in CaCl_2 solutions can be prepared
5 by a wetted-solid process in which the causticization of the cellulose is conducted in an oxygen-reduced atmosphere at a temperature less than 35°C in a dispersant comprising an azeotropic mixture of isopropanol and water while the cellulose is intensively sheared at a solvent to cellulose
10 weight ratio in the range from 2/1 to 7.5/1.

This invention provides a process for preparing an alkali metal salt of carboxymethyl cellulose having a yield of at least 130 ml of 15 centipoise fluid containing 4% calcium chloride, per g. of said alkali metal salt, which
15 comprises reacting cellulose with an alkali metal hydroxide in the absence of air at a temperature less than 35°C in an aqueous solution containing from 84.9% to 88.9% by weight of isopropanol, and at an isopropanol-water solution: cellulose weight ratio from 2:1 to 7.5:1, and reacting
20 the resulting alkali metal cellulose with monochloroacetic acid containing less than 2% by weight of dichloroacetic acid, wherein the amount of alkali metal hydroxide is such that the alkali metal hydroxide to monochloroacetic acid molar ratio during the subsequent carboxymethylation of
25 the cellulose is greater than 2.00 to 1.

A preferred embodiment of the process of this invention comprises :

(a) forming a slurry of swollen cellulose by intensively shearing and agitating a mixture of high molecular
30 weight cellulose, isopropanol and water;

(b) removing oxygen from the reaction vessel;

(c) pressurizing the reaction vessel with an inert gas;

(d) adding alkali metal hydroxide, while maintaining the temperature of the aqueous isopropanol solution
35 less than 35°C ;

(e) forming alkali metal cellulose by reacting the

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alkali metal hydroxide with the cellulose while maintaining the temperature of the aqueous isopropanol solution at less than 35°C;

(f) forming an alkali metal salt of carboxymethyl cellulose by adding monochloroacetic acid and carboxymethylating the cellulose at a temperature of from 55 to 90°C;

(g) removing isopropanol from the vessel by azeotropic distillation; and

10 (h) drying and pulverizing the alkali metal salt of carboxymethyl cellulose;

wherein the concentration of isopropanol in the aqueous isopropanol solution in step (e) is from 84.9% to 88.9% by weight, the aqueous isopropanol solution to cellulose weight ratio in step (f) is from 2:1 to 7.5:1, the amount of alkali metal hydroxide in step (d) is such that the alkali metal hydroxide to monochloroacetic acid molar ratio in step (f) is greater than 2.00 to 1, the monochloroacetic acid contains less than 2% by weight of dichloroacetic acid, and the molar ratio of dry cellulose: alkali metal hydroxide: monochloroacetic acid in step (f) is from 1:1.725-2.415:0.85-1.15.

The isopropanol can conveniently be in the form of an azeotropic solution of isopropanol and water at 0.98 bars, i.e., 86.9% by weight isopropanol, 13.1% by weight water hereinafter sometimes referred to as "azeotrope".

Optionally the concentration of water in the isopropanol-water solution in step (a) can be less than that required to form the azeotrope, and a solution of sodium hydroxide in water can be added in step (d), provided that the combined concentration of isopropanol and water added in steps (a) and (d) is such that the azeotrope is formed and is present thereafter in step (e).

Also optionally, the solid sodium hydroxide can be mixed with the azeotrope and added as such in step (d) provided that the azeotrope/dry cellulose ratio is maintained in the required range of from 2:1 to 7.5:1,

preferably from 3:1 to 6:1.

The product obtained by the process of this invention exhibits enhanced rheological and fluid loss control properties in aqueous systems containing soluble calcium salts and having a pH less than 10. The preferred products obtained by the process of this invention have a drilling fluid yield of at least 130 ml/g, most preferably at least 150 ml/g, when evaluated in a 4% by weight CaCl_2 solution. A drilling fluid yield of X ml/g indicates that 1 gram of CMC will produce X ml of a drilling fluid having an apparent viscosity of 15 cp, as measured by API Procedure RP 13B.

In practicing the process of this invention, the cellulose starting material is added to an isopropanol-water solution in a suitable reaction vessel and intensively sheared and agitated to wet the cellulose. The vessel is then evacuated to remove air (oxygen) from the vessel and the vessel is pressurized with an inert (non-oxygen containing) gas, preferably nitrogen. It is preferred that the reaction vessel be capable of: (1) being heated and cooled, such as by passing a fluid through a jacket surrounding the interior of the vessel; (2) being evacuated and pressurized; and (3) imparting high shear and agitation to the cellulose at the desired cellulose concentration.

The amount of the isopropanol-water solution utilized is such that the combined total amount of isopropanol and water added throughout the etherification process is sufficient to provide a weight ratio of isopropanol-water solution to dry cellulose of from 2:1 to 7.5:1. The combined total amount of isopropanol and water includes the isopropanol and water added initially, as well as any isopropanol and water added with the alkali metal hydroxide and the monochloroacetic acid.

Thereafter the cellulose is causticized by adding a suitable alkali metal hydroxide, preferably sodium hydroxide, while maintaining the temperature at less than

35°C. It is critical in the process of this invention that the concentration of isopropanol in the isopropanol-water solution during causticization of the cellulose be $86.9 \pm 2\%$ by weight, preferably from 85 to 88% by weight.

5 The causticization of the cellulose is conducted for a period sufficient to form the alkali cellulose. Generally, causticization will be complete after 30 minutes from the time when all alkali metal hydroxide has been added, although longer alkalization times can be utilized. The

10 temperature may be maintained at less than 35°C by controlling the rate of addition of the sodium hydroxide, circulating water or other fluid through the jacket of the reaction vessel, if present, and periodically evacuating the vessel, thus evaporating a portion of the isopropanol-

15 water solution (evaporative cooling).

Monochloroacetic acid (hereinafter sometimes referred to as MCA) is added to the alkali cellulose and the temperature is raised to the range of from 55 to 90°C for a period sufficient to convert all of the MCA into the

20 carboxymethyl cellulose ether and into alkali metal glycolate. Generally a reaction time of 30 minutes is sufficient, although longer times can be utilized. The MCA is conveniently added to the vessel in the form of a solution in water or in an isopropanol-water solution.

25 Subsequently the isopropanol and water are removed from the CMC, and the CMC is pulverized to form the novel viscosifiers of this invention. Preferably the isopropanol is removed from the CMC by heating and evacuating the reaction vessel and collecting the azeotrope for re-

30 cycling in the process. The water-wet CMC remaining can then be dried to obtain a moisture content less than 15% by weight, preferably from 5 to 10% by weight. Alternatively, the water-wet CMC, after removing the azeotropic solution of isopropanol and water, can be sprayed with

35 water to increase the moisture content of the CMC to from 40 to 65% by weight. Subsequent drying and pulverizing of this water-wet CMC produces a more dense product which

is easier to handle. It is preferred that additional water be added to the reaction vessel before removing the azeotropic solution from the vessel. This keeps the CMC in a relatively free-flowing, non-dusting state during azeotrope removal, thus preventing dust carryover with the azeotrope vapour. It also prevents excessive mechanical stress on the reactor mixer elements, and facilitates product discharge from the vessel. The amount of additional water added before azeotrope removal is such that the water-wet CMC remaining after azeotrope removal will contain from 20 to 30% by weight of water.

Purified grades of CMC can be prepared, if desired, by washing the CMC with aqueous alcohol solutions, preferably methanol, of about 75% by weight, to remove the alkali metal chloride and alkali metal glycolate from the CMC.

The amount of alkali metal used is varied, depending upon the desired degree of substitution (D.S.) of carboxymethyl groups on the cellulose; however, the alkali metal hydroxide to monochloroacetic acid molar ratio must be greater than 2 to 1 to obtain CMC having the superior rheological characteristics in calcium chloride solution as required by this invention.

For a technical grade CMC in which the by-products of the reaction remain in the product, it is preferred that the molar ratio of the cellulose (dry): alkali metal hydroxide: MCA be in the range from 1:1.725-2.415:0.85-1.15 and that the molar ratio of alkali metal hydroxide to MCA be in the range from 2.03 to 1 to 2.1 to 1. The upper limit on the caustic to MCA ratio is necessary since the excess caustic will raise the pH of the aqueous solutions to which the technical grade CMC is added. As will be explained hereinafter, the superior viscosity characteristics of the CMC of this invention in calcium chloride solutions is dependent upon the pH of the solutions.

For a purified grade of CMC in which the by-product of the reaction and the neutralized excess caustic have

been removed from the product, there is no upper limit on the molar ratio of alkali metal hydroxide to MCA, although excessive amounts are wasteful and costly. For purified grades, the molar ratio of dry cellulose: MCA
5 can be greater than for technical grade CMC, such as from 1:0.85 to 1:1.5.

The monochloroacetic acid used in the process of this invention must not contain more than 2% by weight of dichloroacetic acid. Larger amounts of dichloroacetic
10 acid in the MCA produce a CMC having reduced rheological and fluid loss characteristics in calcium chloride solutions.

As noted, it is critical in practicing the process of this invention to conduct the causticization of the
15 cellulose in the absence of oxygen, at a temperature less than 35°C, in an aqueous solution containing from 84.9 to 88.9% by weight of isopropanol, at an isopropanol-water solution to cellulose weight ratio from 2 to 1 to 7.5 to 1, and in the presence of sufficient alkali metal hydroxide
20 to ensure that the alkali metal hydroxide to MCA molar ratio during the etherification of the alkali cellulose is greater than 2.00 to 1. For unpurified CMC, the molar ratio of alkali metal hydroxide to MCA must not exceed 2.1 to 1. Additionally, the monochloroacetic acid must not
25 contain more than 2% by weight of dichloroacetic acid. This combination of variables results in the production of a CMC which exhibits enhanced rheological and fluid loss characteristics in aqueous calcium chloride solutions. Such solutions are of value as drilling, workover and
30 completion fluids in the oil and gas industry.

The concentration of isopropanol in the solution initially charged to the reactor is advantageously greater than that required to form the azeotrope, i.e. greater than 86.9% by weight, provided that additional water is
35 later added such that the required amount of water is present during the causticization of the cellulose (11.1 to 15.1% by weight of water, preferably 12 to 15% by

weight).

The CMC produced by the process of this invention is characterized as having superior rheological characteristics in aqueous calcium chloride solutions at a pH less than 10.0 as will be indicated in the Examples below. The CMC will have a yield of at least 130 ml/g of 15 cp fluid containing 4% by weight calcium chloride, preferably at least 150 ml/g. The CMC at a concentration of 5.7 g/l in 4% by weight calcium chloride solution will produce a fluid having an apparent viscosity of at least 10 cp.

The invention is illustrated by the following non-limiting Examples.

The reaction vessel utilized in conducting the following Examples was a jacketed vessel capable of use at high temperatures and pressures ranging from full vacuum to 5 bars. The mixing of ingredients was accomplished by means of four ploughs connected to a horizontal shaft and one chopper (a whirling blade with its shaft perpendicular to the horizontal shaft). This type of reactor allows intensive mixing and chemical reaction at much higher solids to liquid ratios than are possible in most other types of reactions.

The CMC manufacturing process consisted of the following steps, unless otherwise indicated:

(1) The desired amount of cellulose and isopropanol solution were added to the vessel and mixed intensively for 15 to 20 minutes while circulating cooling water through the jacket;

(2) The vessel was evacuated to 0.95 to 0.98 bars and thereafter pressurized with nitrogen while mixing;

(3) The desired amount of sodium hydroxide, either 99% by weight solid prills or a 48-50% by weight aqueous solution, was added at a controlled rate to keep the causticization reaction temperature below 35°C while mixing;

(4) The causticization reaction was allowed to continue for 20 to 90 minutes at a temperature less than 35°C while mixing;

(5) Monochloroacetic acid was added while mixing either as a 50% by weight solution in azeotrope or as an 80% by weight aqueous solution, and the temperature was allowed to increase due to the heat of reaction;

5 (6) The vessel was heated by circulating hot water through the jacket and the etherification reaction was conducted at a temperature in the range of from 64 to 77°C for a period of from 30 to 40 minutes, while mixing;

(7) The isopropanol/water azeotrope was distilled
10 from the vessel under a vacuum of 0.98 bars (86.9% isopropanol, 13.1% water, by weight); and

(8) Thereafter the CMC, which contains from 15 to 25% by weight of water was dried to a moisture content less than 15% by weight, preferably from about 5 to 10% by
15 weight moisture.

The cellulose utilized in the Examples was a high molecular weight, purified grade of cotton linters obtained from the Buckeye Cellulose Corp., ER 4500, in the form of sheets, chips (6.35 x 6.35 mm), or flakes.

20 The monochloroacetic acid utilized was obtained from American Hoechst, and contained a maximum of 0.5% by weight of dichloroacetic acid.

Example 1A

7.854 Kg of Buckeye Cellulose Corp. cotton linter chips ER 4500 (99% by weight of alpha cellulose), containing 6.4% by weight of water were mixed with 36.774 Kg of a solution containing 86.9% by weight of isopropanol and 13.1% by weight (azeotrope) water for 19 minutes at a temperature in the range from 14 to 19°C. The vessel was evacuated to 0.98 bars and pressurized with nitrogen to 3 bars while mixing for 8 minutes. 3.723 Kg of sodium hydroxide beads were added while mixing and cooling for 13 minutes at a temperature in the range of from 15 to 24°C. The causticization reaction was then conducted for 47 minutes while mixing at a temperature in the range of from 15 to 20°C. Monochloroacetic acid was added as a 50% by weight solution (azeotrope) over a mixing period of 18 minutes during which the temperature increased to 45.5°C. The batch was heated to 65°C in 9 minutes and the etherification reaction conducted at a temperature in the range from 65 to 70°C for 33 minutes, while mixing. Thereafter the azeotrope was removed under 0.98 bars vacuum at a temperature from 43 to 91°C, and the CMC dried at 65 to 83°C to a moisture content of 8.2% by weight. Analysis of this technical grade CMC showed a D.S. of 0.87 and a purity of 77.6% dry basis. It contained 17.1% by weight of sodium chloride and 5.6% by weight of sodium glycolate, dry basis. The reaction was conducted at a molar ratio of cellulose: NaOH: MCA of 1:2.03:1.

Example 1B

The CMC produced in Example 1A was washed with an 80% by weight methanol solution (20% by weight water) to remove the sodium chloride and sodium glycolate byproducts, thus producing a purified grade of CMC.

Example 2

A procedure similar to Example 1A was conducted utilizing Buckeye Cellulose Corp. purified cotton linters in flake form.

Comparative Example A and B

A procedure similar to Example 1A was conducted utilizing the same cellulose in pulp form and in the form of a floc obtained by milling the chips of Example 1A through a Raymond mill having a 3.175 mm screen.

Example 3

A procedure similar to Example 1A was conducted at a molar ratio of cellulose: NaOH: MCA of 1:2.05:1.

Comparative Example C

10 A procedure similar to Example 3 was followed except that the concentration of isopropanol in the isopropanol/water mixture initially added to the vessel was 77.0% by weight.

Comparative Example D

15 A procedure similar to Example 3 was followed except that the concentration of isopropanol in the isopropanol/water solution originally added to the vessel was 94.0% by weight.

Comparative Example E

20 A procedure similar to Example 3 was followed except that the sodium hydroxide was added to the reactor as a 50% by weight solution in water which resulted in an isopropanol/water concentration of 84.5%/15.5% in the reactor during the causticization reaction.

Example 4

25 A procedure similar to Example 3 was followed except that the concentration of isopropanol in the solution initially added to the vessel was 85.4% by weight and the causticization time was 960 minutes.

Example 5

30 A procedure similar to Example 1A was followed except that the concentration of isopropanol in the solution initially added to the vessel was 94.6% by weight and the sodium hydroxide was added to the reactor as a 50% by weight solution in water, resulting in an isopropanol/water concentrations of 86.9/13.1% by weight (azeotrope) in the reactor during the causticization reaction.

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Example 6

A procedure similar to Example 1A was followed except that the MCA was added to the reaction vessel as an aqueous solution containing 20% by weight water.

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Example 7

A procedure similar to Example 5 was followed except that the MCA was added to the reaction vessel as an aqueous solution containing 20% by weight water.

Comparative Example F

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A procedure similar to Example 1A was conducted at a molar ratio of cellulose: NaOH: MCA of 1:2.0:1. The CMC had a D.S. of 0.72.

Comparative Example G

15 A procedure similar to Example 1A was repeated except that the temperature was allowed to increase to 51°C during the causticization reaction.

Example 8

20 A procedure similar to Example 3 was repeated except that the temperature was allowed to increase to 30.5°C during the causticization reaction. The CMC had a D.S. of .74.

Comparative Example H

25 A procedure similar to Example 1A was repeated except that the vessel was not evacuated and pressurized with nitrogen, i.e., it was conducted in the presence of air at atmospheric pressure.

30 These CMC samples were evaluated as viscosifiers at a concentration of 5.72 g/l at a comparable moisture content of 8% by weight, in an aqueous solution containing 4% by weight of calcium chloride.

The reaction conditions for all of the above examples are given in Table 1 and the form of the materials used in the examples are given in Table 2, in which all percentages of components are by weight.

Table 1

Example No.	Cellulose/Alcohol Mixing		Reactor Evacuation		Nitrogen Addition		NaOH Addition		Causticization		MCA Addition		Heating		Etherification	
	Time Min.	Temp. °C	Time Min.	Vacuum Bars	Time Min.	Pressure Bars	Time Min.	Temp. °C	Time Min.	Temp. °C	Time Min.	Temp. °C	Time Min.	Temp. °C	Time Min.	Temp. °C
1	19	14-19	5	0.98	3	1	13	15.5-24	47	15-20	18	18-45.5	9	65.5	33	65.5-70.5
2	15	16-27	2	0.98	6	1	14	16-20.5	45	14.5-24	21	23-47.5	11	65.5	31	65.5-72
3	15	13-25.5	3	0.965	4	1	15	14.5-30	42	16-30.5	16	16.5-51	12	66	29	64.5-76
4	16	7.5-19.5	1	0.98	5	1	13	8-21.5	960	14.5-25	15	25-47.5	8	66.5	31	66.5-72.5
5	16	14.5-19	2	0.98	3	1	16	13-22	27	14-21	13	20-43	9	65.5	31	65.5-71.5
6	15	18-26	2	0.95	8	1	12	14.5-20	54	15.5-22	13	22-41	8	65.5	30	65.5-71
7	15	15-25	5	0.95	4	3	19	14-18	44	14-21.5	10	18-36.5	10	65.5	30	65.5-70.5
8	15	17-23	4	0.98	7	1	13	17-21	42	16-30.5	10	30.5-50.5	12	65.5	30	65.5-70.5
A	16	18-23	4	0.98	6	1	11	10-21.5	39	15-21.5	22	21.5-50	4	66	31	66-71.5
B	85	9.5-12	2	0.98	3	1	10	11.5-23.5	31	16.5-22.5	21	22.5-45.5	6	65.5	32	65.5-70.5
C	18	11-23	2	0.98	3	1	15	9-21.5	38	14-20.5	13	19.5-23	19	66	31	66-69.5
E	17	8-26.5	2	0.98	1	3	13	10-19	41	14.5-21.5	13	22-42	7	65.5	40	65.5-72.5
F	16	22-26.5	—	0.98	3	2	8	28-33	32	25.5-30	15	29-50	12	66	30	66-72
G	15	27-38	6	0.95	7	1	8	39-41.5	31	39.5-51	20	51-71.5	—	—	30	69-70
H	18	18-24.5	0	—	0	1	11	18-21.5	32	18-26	22	25-51.5	11	66	30	66-72.5

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Table 2

Isopropanol Solution			NaOH		MCA	Molar		Weight Ratio		Causticization Isopropanol Conc.		5.7 g/l CMC in 4% CaCl ₂
Example No.	% IPA	% Water	%	%	%	Stoichiometry	Total Liquid/ Dry Cellulose	% IPA	% Water	Apparent Viscosity/cp.		
1A	86.9	13.1	99	50	50	1/2.03/1	5/1	86.9	13.1	13.1	16.5	
2	86.9	13.1	99	50	50	1/2.03/1	5/1	86.9	13.1	13.1	13.5	
3	86.9	13.1	99	50	50	1/2.05/1	5/1	86.9	13.1	13.1	11.0	
4	85.4	14.6	99	50	50	1/2.05/1	5/1	85.4	14.6	14.6	11.5	
5	96.4	3.6	50	50	50	1/2.02/1	5/1	86.9	13.1	13.1	19.0	
6	86.9	13.1	99	80	80	1/2.03/1	5/1	86.9	13.1	13.1	10.5	
7	96.2	3.8	50	80	80	1/2.03/1	5/1	86.9	13.1	13.1	13.0	
8	86.9	13.1	99	50	50	1/2.05/1	5/1	86.9	13.1	13.1	16.5	
A	86.9	13.1	99	50	50	1/2.05/1	5/1	86.9	13.1	13.1	5.0	
B	86.9	13.1	99	50	50	1/2.03/1	5/1	86.9	13.1	13.1	2.5	
C	77.0	23.0	99	50	50	1/2.05/1	5/1	77.0	23.0	23.0	2.0	
D	94.0	6.0	99	50	50	1/2.05/1	5/1	94.0	6.0	6.0	2.0	
E	86.9	13.1	48	50	50	1/2.05/1	5/1	84.5	15.5	15.5	2.0	
F	86.9	13.1	99	50	50	1/2.00/1	5/1	86.9	13.1	13.1	2.0	
G	86.9	13.1	99	50	50	1/2.03/1	5/1	86.9	13.1	13.1	7.5	
H	86.9	13.1	99	50	50	1/2.03/1	5/1	86.9	13.1	13.1	2.0	

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Comparison of the data in Tables 1 and 2 indicates the following:

- 5 (1) Examples 1, 2, A, B - The type of cellulose suitable for the preparation of CMC having superior viscosity characteristics in calcium chloride solutions is very critical. The cellulose must be of high molecular weight and must not have undergone sufficient chemical or mechanical degradation to substantially reduce the rheological characteristics of the CMC. Any cellulose which
10 produces a CMC which exhibits an API RP 13B apparent viscosity greater than 10.0 cp when evaluated in a 4% by weight calcium chloride solution, when produced by the process of this invention, is sufficient for use in preparing the superior CMC viscosifiers of this invention;
- 15 (2) Examples 1A, 4, C, D, E - The concentrations of isopropanol and water in the reaction medium during the causticization of the cellulose is critical and must be controlled to $86.9 \pm 2\%$ by weight of isopropanol;
- 20 (3) Examples 1A, 5, 6, 7 - The concentration of isopropanol in the isopropanol/water solution before causticization should be maximized for best results;
- (4) Examples 1A, 3, F - The molar ratio of sodium hydroxide to monochloroacetic acid must be greater than 2 to 1 to obtain superior rheological characteristics in
25 calcium chloride solutions.
- (5) Examples 1A, 8, G - The temperature during the causticization of the cellulose must be kept below 35°C in order to obtain a CMC having superior rheological characteristics in calcium chloride solutions; and
- 30 (6) Examples 1A, H - The CMC must be prepared in the absence of oxygen so as to eliminate the oxidative degradation of the cellulose.

The rheological characteristics of the CMC samples from Example 1A and 1B were compared with those of several
35 commercial CMC products in a 4% by weight calcium chloride solution. The data obtained, given in Table 3 below, indicate the superior viscosification properties of the CMC produced by the process of this invention.

Table 3

Performance of Various OMC in 4% by weight CaCl_2 Solution

Sample Mark	1	2	3	4	5	6	7	8	9	10	11	12	13	14
High Viscosity OMC, g/l														
Example 1A	5.7	8.6	0	0	0	0	0	0	0	0	0	0	0	0
Example 1B	0	0	4.3	5.7	0	0	0	0	0	0	0	0	0	0
DRISPAC	0	0	0	0	17.1	22.8	0	0	0	0	0	0	0	0
AKU STAFLO	0	0	0	0	0	0	17.1	22.8	0	0	0	0	0	0
Gabrosa HVT-70	0	0	0	0	0	0	0	0	5.7	8.6	0	0	0	0
Gabrosa DM-3000	0	0	0	0	0	0	0	0	0	0	11.4	17.1	0	0
HV CELLEX	0	0	0	0	0	0	0	0	0	0	0	0	11.4	17.1

Properties After Stirring 20 Minutes, and Rolling at 23.5°C for 16 Hours

Apparent Viscosity, cp.	15	27	13.5	19	8	18	10	27	7.5	16	7	18.5	12	38
Plastic Viscosity, cp.	10	14	10	13	7	17	9	20	6	12	6	15	11	29
Yield Point, Kg/m^2	0.49	1.27	0.34	0.59	0.05	0.1	0.1	0.68	0.15	0.39	0.1	0.34	0.1	0.88
pH	7.2	8.3	6.6	7.3	7.5	7.6	7.7	7.7	7.7	7.6	8.0	8.0	7.6	8.0
Drilling Fluid Yield, ml/g	156		189		41		45		106		56		72	

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The rheological characteristics of the CMC from Example 1A were compared with those of DRISPAC, a purified premium grade CMC, by mixing these CMC products in aqueous solutions containing various concentrations of calcium chloride. The data, given in Table 4 below, indicate the superior viscosification properties of the CMC of this invention at all concentrations of calcium chloride. As the data in Table 4 also indicate, the aqueous solutions containing from 10 to 35% by weight CaCl_2 , preferably from 12 to 32% by weight, exhibit higher viscosities than the other CaCl_2 solutions containing the CMC of this invention. Indeed, the data indicate that aqueous solutions containing between 20 and 30% by weight CaCl_2 possess superior thermal stability.

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Table 4
Effect of Calcium Chloride Concentration

<u>11.4 g/l CMC in Various CaCl_2 Solutions</u>							
<u>Apparent Viscosity, cp.</u>							
	<u>CaCl_2 (% by weight)</u>	<u>Example 1A</u>			<u>DRISPAC</u>		
		<u>Initial</u>	<u>65.5°C</u>	<u>Final</u>	<u>Initial</u>	<u>65.5°C</u>	<u>Final</u>
20	0	78.5	47.5	77	121	62.5	108
	2	58	4.5	48	5.5	1	4
	4	47	5	40	3	1.5	2.5
	5	45.5	6.5	40	3	1	2.5
	6	46.5	8	41	3	1.5	3
25	8	52	15.5	48	3.5	1.5	3
	10	55.5	21.5	52.5	4.5	2	4
	15	74.5	42.5	73.5	11.5	3.5	9.5
	20	85	55	86	26	7.5	2.4
	30	63	81.5	70	4	27.5	16
30	37	32	88	44.5	4.5	11.5	9.5

The aqueous calcium chloride solutions containing the CMC samples indicated in Table 4 were admixed with 142.65 g/l of Glen Rose shale, rolled for 16 hours at 65.5°C, cooled to room temperature, and evaluated for API RP 13B fluid loss. The data obtained, given in Table 5, indicate the superior fluid loss control characteristics of the CMC of this invention in calcium chloride solutions.

Table 5
Effect of CaCl₂ Concentration After Shale Contamination

	<u>11.4 g/l CMC</u>	<u>% by weight CaCl₂</u>	<u>pH</u>	<u>API Filtrate ml</u>
10	Example 1A	0	8.2	6.0
		2	7.2	11.6
		4	7.0	12.0
15		8	6.8	10.2
		10	6.6	9.6
		15	6.4	8.6
		20	6.2	15.2
		30	5.7	7.5
20		37	5.3	2.8
	DRISPAC	0	8.4	7.3
		2	7.2	166
		4	7.0	272
		8	6.8	268
25		10	6.6	286
		15	6.4	228
		20	6.3	120
		30	5.6	70
		37	5.5	136

The effect of pH on the rheological characteristics of the CMC of this invention was investigated by adjusting the initial pH of a 4% by weight CaCl_2 solution with NaOH and mixing 11.4 g/l CMC therewith. DRISPAC, a commercial CMC, was similarly evaluated. The data obtained, given in Table 6, indicate that the pH of the calcium chloride solution must be less than 11.0, preferably less than 10.0, to obtain the superior rheological characteristics of the CMC produced by the process of the present invention.

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Table 6

Effect of pH on the Viscosity of CMC in 4% by weight CaCl_2

11.4 g/l CMC in 4% by weight CaCl_2 Solution

		Initial pH	Apparent Viscosity cp.	Plastic Viscosity cp.	Yield Point Kg/m ²	Final pH
(15	CMC					
	Example 1A	7.0	57	22	3.42	7.2
		8.5	54	20	3.27	7.4
		10.5	52	21	2.98	8.2
		10.7	39	17	2.10	9.7
20		11.0	5.5	2	0.34	10.2
		11.5	2.5	2.5	0	11.0
	DRISPAC	7.0	3.5	3	0.05	7.1
		8.5	3.5	3	0.05	7.3
		10.5	3	2	0.1	8.4
		11.5	2	1.5	0.05	10.9

CLAIMS:

1. A process for preparing an alkali metal salt of carboxymethyl cellulose having a yield of at least 130 ml. of 15 centipoise fluid containing 4% calcium chloride, per g. of said alkali metal salt, which comprises reacting cellulose with an alkali metal hydroxide in the absence of air at a temperature less than 35°C in an aqueous solution containing from 84.9% to 88.9% by weight of isopropanol, and at an isopropanol-water solution: cellulose weight ratio from 2:1 to 7.5:1, and reacting the resulting alkali metal cellulose with monochloroacetic acid containing less than 2% by weight of dichloroacetic acid, wherein the amount of alkali metal hydroxide is such that the alkali metal hydroxide to monochloroacetic acid molar ratio during the subsequent carboxymethylation of the cellulose is greater than 2.00 to 1.

2. A process as claimed in Claim 1 wherein the aqueous solution contains from 85% to 88% isopropanol, the isopropanol-water solution: cellulose weight ratio is from 3:1 to 6:1, the alkali metal hydroxide to monochloroacetic acid molar ratio is from 2.03:1 to 2.1:1, the alkali metal hydroxide is sodium hydroxide, and the molar ratio of dry cellulose: sodium hydroxide: monochloroacetic acid is in the range from 1:1.725-2.415:0.85-1.15.

3. A process as claimed in Claim 1 which comprises:

(a) forming a slurry of swollen cellulose by intensively shearing and agitating a mixture of high molecular weight cellulose, isopropanol and water;



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(b) removing oxygen from the reaction vessel;
(c) pressurizing the reaction vessel with an inert gas;

(d) adding alkali metal hydroxide, while
5 maintaining the temperature of the aqueous isopropanol solution less than 35°C;

(e) forming alkali metal cellulose by reacting the alkali metal hydroxide with the cellulose while maintaining the temperature of the aqueous
10 isopropanol solution at less than 35°C;

(f) forming an alkali metal salt of carboxymethyl cellulose by adding monochloroacetic acid and carboxymethylating the cellulose at a temperature of from 55 to 90°C;

(g) removing isopropanol from the vessel by azeotropic distillation; and

(h) drying and pulverizing the alkali metal salt of carboxymethyl cellulose;
wherein the concentration of isopropanol in the
20 aqueous isopropanol solution in step (e) is from 84.9% to 88.9% by weight, the aqueous isopropanol solution to cellulose weight ratio in step (f) is from 2:1 to 7.5:1, the amount of alkali metal hydroxide in step (d) is such that the alkali
25 metal hydroxide to monochloroacetic acid molar ratio in step (f) is greater than 2.00 to 1, the monochloroacetic acid contains less than 2% by weight of dichloroacetic acid, and the molar ratio of dry cellulose: alkali metal hydroxide: monochloroacetic acid in step (f) is from 1:1.725-
30 2.415:0.85-1.15.

4. A process as claimed in Claim 3 wherein the alkali metal hydroxide is sodium hydroxide.

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5. A process as claimed in Claim 3 or 4 wherein the aqueous isopropanol solution of



step (a) contains more than 90% by weight of isopropanol and water is added in step (d) to form an aqueous isopropanol solution in step (e) having the required concentration of isopropanol.

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6. A process as claimed in Claim 4 wherein the concentration of isopropanol in the aqueous isopropanol solution in step (e) is from 85 to 88% by weight, and the molar ratio of sodium hydroxide to monochloroacetic acid in step (f) is from 2.03:1 to 2.1:1.

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7. A process as claimed in any preceding Claim, wherein the concentration of isopropanol in the aqueous isopropanol solution is substantially 86.9% by weight.

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8. A process as claimed in Claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 8.

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9. An alkali metal salt of carboxymethyl cellulose produced by a process as claimed in any of the preceding Claims.

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