

1

2,715,124

MANUFACTURE OF FREE-FLOWING WATER-SOLUBLE CARBOXYALKYL CELLULOSE ETHERS

Herbert C. Miller, Jr., Hopewell, Va., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the conversion of fibrous water-soluble carboxyalkyl cellulose ethers, particularly sodium carboxymethylcellulose, into free-flowing granular powder form.

Water-soluble salts of carboxyalkyl cellulose in fibrous form, particularly sodium carboxymethylcellulose, are easily prepared by an etherification reaction between cellulose fibers, sodium hydroxide and a carboxyalkylating agent in the presence of an amount of aqueous alcohol such that upon completion of the etherification reaction, the resulting cellulose ether product is obtained as a mass of loose moist fibers having a fiber form similar to that of the starting cellulose. Following the etherification reaction the crude product may either be neutralized and dried directly, or it may be neutralized and then washed free of by-product salts with a suitable aqueous alcohol and then dried. In either case the product retains substantially the fibrous form of the starting cellulose through the subsequent processing steps.

Although it is highly advantageous and desirable to carry out the etherification reaction while maintaining the product in the fibrous form, there are certain disadvantages in the fibrous form of the ether during subsequent processing, particularly purification and/or drying, and in a number of important uses for the cellulose ether. These difficulties stem largely from the fact that the fibrous form of the ether tends to cling together and form fiber aggregates. Such aggregates impede flow through the processing equipment and are quite bulky. Moreover, when the fibrous form of carboxyalkyl cellulose derivatives is added to water to prepare a solution of the product, there is a marked tendency for the fiber aggregates to cling together rather than disperse uniformly through the dissolving medium so that each individual fiber can be simultaneously swollen and dissolved by the water. These aggregates become gelled on the outside and persist as gel lumps in the solution, requiring inordinately long periods of very vigorous agitation to completely break up the gel lumps and obtain a homogeneous solution. Unfortunately, mechanical disintegration of the fibrous product does not destroy the fibrous structure although it reduces the length of the fibers, and the resulting comminuted fibrous material still exhibits the above-mentioned disadvantages of the fibrous form.

A number of methods are known for converting fibrous forms of water-soluble cellulose ethers, including carboxyalkyl cellulose derivatives such as sodium carboxymethylcellulose, into free-flowing granular powders after they have been purified and/or dried ready for use. It is also known to add limited amounts of water, insufficient to destroy the fibrous character of the ether, to sodium carboxymethylcellulose moist with aqueous al-

2

cohol of such composition that the cellulose ether would normally dry to a dry fluffy product, to change its original characteristics so that upon being subjected to mechanical comminution it is converted into a product of improved flowability with any desired particle size. While these methods have been fairly successful in overcoming the disadvantages of the fibrous form of these cellulose ethers in their ultimate uses, none of these methods, however, overcome the processing difficulties inherent in the fibrous form of these cellulose ethers during purification and/or drying.

Now in accordance with this invention fibrous forms of carboxyalkyl cellulose derivatives are converted into free-flowing substantially granular powder forms thereof by agitating a loose fibrous mass comprising a water-soluble carboxyalkyl cellulose derivative moist with an aqueous alcohol and containing water and alcohol in such proportions that the mass would normally dry to a loose fibrous product, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the carboxyalkyl cellulose derivative, said active solvent containing at least about 67.5% by weight of water, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxyalkyl cellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxyalkyl cellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

In a preferred embodiment of the invention the active solvent containing at least about 67.5% water by weight is displaced from the gels with aqueous alcohol containing less than about 40% water by weight prior to drying the gels. If desired, the dried gels can be mechanically comminuted and/or classified for particle size by screening.

In a specific embodiment of the invention fibrous forms of carboxymethylcellulose derivatives are converted into free-flowing substantially granular powder forms thereof by agitating a loose fibrous mass comprising a water-soluble carboxymethylcellulose derivative containing from about 0.5 to about 1.5 parts by weight, based on said carboxymethylcellulose derivative, of an aqueous alcohol containing not more than about 40% of water by weight, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to raise the water content of the aqueous alcohol present in the fibrous mass to at least about 67.5% by weight and sufficient to form with the aqueous alcohol present in the mass an active solvent for the carboxymethylcellulose derivative, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxymethylcellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxymethylcellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

It has been found that fibrous carboxyalkyl cellulose derivatives treated in accordance with this invention are converted substantially into gels which upon drying are granular in contrast to the original fibrous form. The discrete, separate gel particles flow freely in the processing vessels in contrast to the fibrous form of the cellulose ether which impedes flow during processing. Moreover, the gel particles thus formed are purified faster and more completely than the fibrous cellulose ether with aqueous alcohol washing fluids. Upon drying the gels a free-flowing granular powder product results, which can be readily comminuted to any particle size desired. The granular product formed in accordance with this invention exhibits improved dispersibility in water and an improved rate of solution in contrast to the fibrous form of the cellulose ether.

Having now set forth the general nature of the invention, the following examples are presented in illustration thereof, but these are not to be construed as a limitation of the invention.

Example 1

A crude fibrous sodium carboxymethylcellulose having a carboxymethyl substitution of approximately 0.7 was prepared in accordance with the procedure set forth in U. S. Patent 2,517,577, employing purified fibrous wood pulp, 50% aqueous caustic soda, aqueous isopropanol containing approximately 87% isopropanol and 13% water, and anhydrous monochloroacetic acid to form the cellulose ether. The crude ether containing approximately 15% by weight of by-product salts such as sodium chloride and sodium glycolate, and suspended as a slurry of fibers in the 87% aqueous isopropanol, was centrifuged to produce a loose moist mass of fibers having substantially the same fibrous physical form as the starting cellulose, and containing approximately 60 parts by weight of 87% aqueous isopropanol for each 100 parts by weight of crude sodium carboxymethylcellulose on a dry-weight basis. A sample of this loose moist fibrous mass dried at 70° C. produced a dry loose mass of fibers having substantially the same fibrous form as the starting cellulose, and grinding did not change the fibrous nature of the product, although fiber length was shortened by grinding.

One hundred sixty parts by weight of the above loose moist mass of crude sodium carboxymethylcellulose fibers containing 100 parts of the crude ether and 60 parts of 87% aqueous isopropanol containing 51 parts isopropyl alcohol and 9 parts of water was charged to a mixer adapted to stir and tumble the mass. While the mass was being stirred and tumbled in the mixer, 100 parts of water was sprayed onto the tumbling mass as a fine mist or spray from pressure nozzle, requiring about 3 minutes, and agitation was continued until the fibrous structure of the mass was substantially destroyed and the sodium carboxymethylcellulose was substantially converted into separate, discrete, translucent gel particles, requiring about 5 minutes. Agitation was discontinued while the mass was still substantially in the form of separate, discrete gel particles and before the gels coalesced into doughy balls or lumps. Observation under a 15-power microscope showed substantially complete conversion of the fibers into translucent gel particles.

The gels were then discharged from the mixer into a large volume of 99% methanol, calculated to be sufficient to reduce the aqueous content of the total liquid from about 68.1% to about 25%. This caused the gels to dehydrate and shrink. After centrifuging, the gels were discharged to a drier and were dried at about 70° C. to a volatile content below about 5% to form a free-flowing granular powder. The dried powder was passed through a micropulverizer and was screened and classified to a particle size between 40 and 100 mesh.

The moist gels formed in the mixer flowed freely through the processing equipment, thus facilitating handling in emptying the mixer, slurrying in 99% alcohol, centrifuging and drying in contrast to the behavior of fibrous

sodium carboxymethylcellulose which aggregates together and impedes flow. The granular powder after drying dispersed readily and completely in water and dissolved much more rapidly without lumping than did fibrous sodium carboxymethylcellulose of similar substitution, viscosity, and by-product salt content. The bulk density of the crude sodium carboxymethylcellulose was increased from an original value of 0.72 g./cc. for the fibrous form of the cellulose ether to 0.96 g./cc. for the granular product.

In this example the total liquid to crude sodium carboxymethylcellulose during the conversion was 160:100 or 1.6:1. The ratio of isopropanol on an anhydrous basis to total water was 51:109. This corresponds to an aqueous alcohol containing approximately 68.1% water and 31.9% alcohol by weight.

Example 2

A crude fibrous sodium carboxymethylcellulose prepared substantially as set forth in Example 1, after centrifuging was found to contain 120 parts of 87% aqueous isopropanol for each 100 parts of crude fibrous sodium carboxymethylcellulose. Following the procedure set forth in Example 1, this material was converted into a mass of separate, discrete gel particles by spraying the agitated fibrous mass in the mixer with 240 parts of water for each 220 parts of aqueous isopropanol-moist fibers with substantially the same results. After slurrying in 99% methanol as set forth in Example 1 and centrifuging, the sodium carboxymethylcellulose gels were purified by washing with fresh 75% aqueous methanol, centrifuged, and dried to a volatile content below about 5% by weight to form a free-flowing granular powder. The dried powder was passed through a micropulverizer and was screened and classified to a particle size between 40 and 100 mesh. Substantially the same processing benefits were realized as in Example 1, and the final granular powder exhibited substantially the same desirable properties as the product from Example 1.

In this example the total liquid to crude sodium carboxymethylcellulose during conversion was 360:100 or 3.6:1. The ratio of isopropanol on an anhydrous basis to total water was 102:258, which corresponds to an aqueous alcohol containing approximately 71.6% water and 28.4% alcohol.

Example 3

Fibrous sodium carboxymethylcellulose having a carboxy methyl substitution of approximately 0.7 was prepared substantially as set forth in Example 1, and was purified by washing with aqueous methanol containing 85% methyl alcohol and 15% water by weight. Upon centrifuging from the purification alcohol the fibrous product contained 64.2% by weight of purified sodium carboxymethylcellulose and 35.8% of 85% aqueous methanol by weight. Portions of this loose moist mass of sodium carboxymethylcellulose fibers were treated, respectively, with 1 part, 1.5 parts, 2 parts, and 3 parts of water for each part of sodium carboxymethylcellulose on the dry basis substantially as set forth in Example 1 to convert the fibers of the starting material into free-flowing gel particles. After the conversion treatment with water, each sample was reslurried in methanol, centrifuged, dried, ground, and screened and classified as set forth in Example 1. Substantially the same processing benefits were realized from each sample as were realized in Example 1, that is, the gels flowed freely in the various pieces of processing equipment, thus facilitating handling in unloading the mixer, in reslurrying in methanol, in centrifuging, and in the drier. The final granular powder in each case exhibited substantially the same desirable properties as the product from Example 1. The following table sets forth the composition of the starting loose moist fibrous mass, the amount of water added to each sample to effect conversion, the total liquid to sodium carboxymethylcellulose during conversion, the ratio of water to alcohol present in the liquid during conversion,

and the per cent of water in the liquid during conversion. In every case substantial conversion of the fibers to gels was accomplished.

may be in the form of the crude product still containing by-product salts such as sodium chloride and sodium glycolate, partially purified, or purified when processed

	Composition of Starting Mass (Parts by wt.)	Water Added For Conversion (Parts by wt.)	Total Liquid to Cellulose Ether During Conversion (Parts by wt.)	Total Water to Alcohol During Conversion (Parts by wt.)	Percent Water in Alcoholic Liquid During Conversion
Sodium carboxymethylcellulose.....	82.2	82.5	128.3:82.2	89.4:38.9	69.7
Methanol.....	38.9				
Water.....	6.9				
Sodium carboxymethylcellulose.....	82.2	123.5	169.3:82.2	130.4:38.9	77
Methanol.....	38.9				
Water.....	6.9				
Sodium carboxymethylcellulose.....	82.2	164.5	210.3:82.2	171.4:38.9	81.5
Methanol.....	38.9				
Water.....	6.9				
Sodium carboxymethylcellulose.....	82.2	247.0	292.8:82.2	253.9:38.9	86.7
Methanol.....	38.9				
Water.....	6.9				

Example 4

A crude fibrous sodium carboxymethylcellulose prepared substantially as set forth in Example 1, after centrifuging was found to contain 47% by weight of 85% aqueous isopropyl alcohol. Following the procedure set forth in Example 1, this material was converted into a mass of separate, discrete gel particles by spraying the agitated fibrous mass in the mixer with 110 parts by weight of 10% aqueous isopropanol containing 11 parts isopropyl alcohol and 99 parts water for each 100 parts by weight of the original loose moist mass of fibers with substantially the same results. The resulting gels were then dried to a volatile content below about 5% by weight to form a free-flowing granular powder which was then comminuted by grinding. Substantially similar processing benefits were realized as in Example 1, and the final granular powder exhibited substantially the same desirable properties as the product from Example 1.

In this example the total liquid to crude sodium carboxymethylcellulose during conversion was 296:100 or approximately 3:1. The ratio of isopropanol on an anhydrous basis to total water was 96:200 which corresponds to an aqueous alcohol containing approximately 67.5% water and 32.5% alcohol.

Example 5

A purified fibrous sodium carboxymethyl hydroxyethyl cellulose having a carboxymethyl substitution of 0.33 and a hydroxyethyl substitution of 0.8, prepared in accordance with U. S. Patent 2,618,632, containing 33% by weight of an aqueous methanol composed of 85% methanol and 15% water was converted into a mass of separate, discrete gel particles, in accordance with the procedure set forth in Example 1, by spraying the agitated fibrous mass in the mixer with 53 parts of water for each 100 parts by weight of the original loose moist mass of fibers with substantially the same results. The resulting gels were then dried to a volatile content below 5% by weight to form a free-flowing granular powder which was then comminuted by grinding. Substantially similar processing benefits were realized as in Example 1, and the final granular powder exhibited substantially the same desirable properties as the product from Example 1.

In this example the total liquid to purified sodium carboxymethyl hydroxyethyl cellulose during conversion was 129:100 or approximately 1.3:1. The ratio of isopropanol on an anhydrous basis to total water was 42:87 which corresponds to an aqueous alcohol containing approximately 67.5% water and 32.5% alcohol.

The process of this invention is suitable for converting any fibrous water-soluble carboxyalkyl cellulose derivative into free-flowing substantially granular powder form, including, by way of example, any of the alkali-metal or ammonium salts of carboxymethyl-, carboxyethyl-, carboxypropyl-, carboxymethyl hydroxyethyl-, carboxyethyl hydroxyethyl-celluloses, and the like. The cellulose ether

in accordance with this invention. In order to reap the greatest benefits it is preferred to apply the process of this invention to the crude carboxyalkyl cellulose derivative containing by-product salts, for after drying and pulverizing, if desired, the product is in the desired physical form for use without further treatment. On the other hand, if a purified product is required, the initially formed fibrous product is thus converted into gels which offer distinct handling advantages of the product during purification and drying.

Several interrelated and important factors must be taken into consideration in practicing this invention. To begin with, the fibrous carboxyalkyl cellulose derivative must initially be moist with an aqueous solution of an alcohol containing water and alcohol in such proportions that the mass would normally dry to a loose fibrous product, and the composition of the aqueous alcohol to satisfy this condition will depend somewhat upon the alcohol employed and the degree of substitution and viscosity of the cellulose ether. For example, a higher portion of methyl alcohol to water is required than for ethyl alcohol, which in turn is higher than for isopropyl alcohol. Also, a higher proportion of alcohol to water is required the higher the degree of substitution and the lower the viscosity of the cellulose ether. In general, however, this condition is satisfied with aqueous alcohol containing about 60% or more of alcohol and about 40% or less of water. For practical reasons the amount of such aqueous alcohol should be within the range between about 0.5 and about 1.5 parts for each part by weight of dry carboxyalkyl cellulose derivative present, and preferably between about 0.75 and about 1.25 parts. Any water-miscible alcohol is suitable for this purpose, and includes, by way of example, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, tertiary butyl alcohol, and the like.

In order to substantially destroy the initial fibrous structure of the mass and convert the carboxyalkyl cellulose derivative into separate, discrete gel particles, an aqueous fluid is introduced into the aqueous alcohol-moist fibrous mass until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the carboxyalkyl cellulose derivative, and sufficient to raise the water content of the aqueous alcohol present in the fibrous mass to at least about 67.5% by weight. Aqueous alcohols containing about 67.5% or more of water are sufficiently good solvents for water-soluble carboxyalkyl cellulose derivatives so that if used in large quantities they would dissolve the cellulose ether and form a solution. However, by maintaining the total liquid content of the mass below about 4 parts by weight, conversion of the fibrous cellulose ether into gels is accomplished and formation of a solution is avoided. The fibrous structure of the mass is destroyed by the active aqueous alcoholic solvent and the carboxyalkyl cellulose derivative is converted into a mass

of separate, discrete, translucent gel particles. These gels, although soft, are remarkably firm, and unless subjected to kneading pressure can be agitated and tumbled and still remain as a mass of separate, discrete gels. Excessive agitation, or application of kneading pressure, however, tends to cause the individual gels to coalesce into larger gels or pills, and eventually to form doughy masses which are undesirable. Aqueous alcohols containing less than about 67.5% water by weight, although capable of causing incipient gelation at the surface of the individual fibers and causing the individual fibers to swell to a certain extent, are not sufficiently active in solvent strength to cause destruction of the fibrous structure of the mass and cause conversion into gels.

The aqueous fluids in accordance with this invention can be liquid water, steam, aqueous salt solutions, or aqueous alcohol solutions containing 15% or less of water-miscible alcohol. In order to insure uniform treatment of the whole mass, it is desirable to add the aqueous fluid while the mass is being agitated and tumbled. When steam is employed, it may be introduced through an open pipe. However, when liquid water, salt solution, or aqueous alcohol is employed, it is preferred to introduce it through pressure nozzles which break up the aqueous stream into a fine spray or mist. If desired, however, such aqueous liquids may be introduced through conventional sprinkling heads under the force of gravity alone.

Agitation is continued until the fibrous structure of the mass is substantially destroyed and the carboxyalkyl cellulose derivative is converted into separate, discrete gel particles. The progress of this conversion can be readily followed by simple visual observation of samples taken periodically from the agitated mass. The object is to obtain as nearly complete conversion as possible. However, even under the most favorable operating conditions a few particles may still remain in the fibrous state. It is considered that the purposes of this invention are accomplished by conversion of 70% or more of the fibrous particles into gel particles, for the small proportion of fibrous particles still remaining does not interfere in any marked degree to impair the free-flowing characteristics of the gelled particles during purification and/or drying. Moreover, any small proportion of fibrous particles still remaining after the conversion treatment is readily converted into granular powder form by subsequently subjecting the product to a pulverizing or grinding operation after drying.

It was previously pointed out that excessive agitation tends to cause the individual gels to coalesce into larger gels or pills and eventually to form large doughy masses. Hence, agitation is discontinued while the mass is still substantially in the form of separate, discrete gel particles and before the gels coalesce into doughy masses. Ordinarily the period of agitation after addition of the aqueous fluid will be between about 3 minutes and about 20 minutes depending upon the aqueous strength of the alcoholic fluid in the mass, the viscosity and substitution of the water-soluble carboxyalkyl cellulose derivative, and the total amount of liquid in the mass. Generally, the higher the content of water in the alcoholic medium, the lower the viscosity of the cellulose ether, the higher the degree of substitution, and the higher the total amount of liquid in the mass, the shorter will be the permissible period of agitation within the limits set forth above. Under any circumstances agitation is discontinued with indication that the individual gels are beginning to coalesce into larger gels or pills.

Suitable agitation is obtained with any conventional paddle stirrer, ribbon mixer, tumbling barrels, and the like. However, mixers such as Werner-Pfleiderer dough mixers which exert a kneading action are unsuitable for the purposes of this invention.

In a preferred embodiment of the invention the active solvent containing at least about 67.5% water by weight

is displaced from the gels after the conversion treatment with aqueous alcohol containing not more than 40% water by weight prior to drying the gels. The purpose of this step is to harden and shrink the gels. This is readily accomplished by immersing or slurring the mass of gels, following conversion, in a water-miscible alcoholic fluid sufficiently low in water content to reduce the aqueous content of the total liquid in the mass below about 40% by weight.

Drying of the gels follows conventional practice with respect to drying times, temperatures, drying equipment, and the like. Ordinarily it is preferred to dry the product at a temperature of about 70° C. under vacuum to a volatile content below about 5% by weight. Since the dried product is in the form of a free-flowing granular powder, it can be used directly without any further treatment. Ordinarily, however, it is preferred to comminute or pulverize the product to meet specified particle size requirements for certain uses. The dry granular product from the drier is readily comminuted or pulverized to any desired particle size with conventional comminuting means such as hammer mills, knife mills, ball mills, and the like. The comminuted product is then classified, if desired, by passing it through screens with graded openings to obtain particles within specified size limitations, such as, for example, between 8-40 mesh, or between 40-100 mesh, or between 100-200 mesh, and the like.

Visually the dried product has the appearance of being completely granular. However, microscopic examination at 60 magnifications indicates the presence of some fibrous particles, usually less than 10% of the total mass, and also indicates that some gel particles appear to have a fiber core. Such fibrous particles and gels with fiber cores do not, however, interfere to impair the desirable free-flowing characteristics of the substantially granular product derived from the conversion treatment of this invention.

What I claim and desire to protect by Letters Patent is:

1. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble carboxyalkyl cellulose derivative moist with an aqueous alcohol and containing water and alcohol in such proportions that the mass would normally dry to a loose fibrous product, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the carboxyalkyl cellulose derivative, said active solvent containing at least about 67.5% by weight of water, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxyalkyl cellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxyalkyl cellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

2. A process in accordance with claim 1 in which the aqueous fluid is water.

3. A process in accordance with claim 1 in which the aqueous fluid is an aqueous salt solution.

4. A process in accordance with claim 1 in which the aqueous fluid is an aqueous alcohol solution containing not more than 15% water-miscible alcohol.

5. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble carboxyalkyl cellulose derivative moist with an aqueous alcohol and containing water and alcohol in such proportions that the mass would nor-

mally dry to a loose fibrous product, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the carboxyalkyl cellulose derivative, said active solvent containing at least about 67.5% by weight of water, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxyalkyl cellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxyalkyl cellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, displacing the active solvent containing at least about 67.5% water from the gels with aqueous alcohol containing less than 40% water by weight, and drying the gels to obtain a free-flowing substantially granular powder.

6. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble carboxyalkyl cellulose derivative moist with an aqueous alcohol and containing water and alcohol in such proportions that the mass would normally dry to a loose fibrous product, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the carboxyalkyl cellulose derivative, said active solvent containing at least about 67.5% by weight of water, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxyalkyl cellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxyalkyl cellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, displacing the active solvent containing at least about 67.5% water from the gels with aqueous alcohol containing less than 40% water by weight, washing the gels with aqueous alcohol containing more than 60% by weight of alcohol, and drying the gels to obtain a free-flowing substantially granular powder.

7. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble carboxymethylcellulose derivative containing from about 0.5 to about 1.5 parts by weight, based on said carboxymethylcellulose derivative, of an aqueous alcohol containing not more than about 40% water by weight, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to raise the water content of the aqueous alcohol present in the fibrous mass to at least about 67.5% by weight and sufficient to form with the aqueous alcohol in the fibrous mass and active solvent for the carboxymethylcellulose derivative, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxymethylcellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxymethylcellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

8. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble carboxymethylcellulose de-

5 rivative containing from about 0.5 to about 1.5 parts by weight, based on said carboxymethylcellulose derivative, of an aqueous alcohol containing not more than about 40% water by weight, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to raise the water content of the aqueous alcohol present in the fibrous mass to at least about 67.5% by weight and sufficient to form with the aqueous alcohol in the fibrous mass an active solvent for the carboxymethylcellulose derivative, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxymethylcellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxymethylcellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, displacing the active solvent containing at least about 67.5% water from the gels with an aqueous alcohol containing less than 40% water by weight, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

9. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble carboxymethylcellulose derivative containing from about 0.5 to about 1.5 parts by weight, based on said carboxymethylcellulose derivative, of an aqueous alcohol containing not more than about 40% water by weight, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to raise the water content of the aqueous alcohol present in the fibrous mass to at least about 67.5% by weight and sufficient to form with the aqueous alcohol in the fibrous mass an active solvent for the carboxymethylcellulose derivative, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the carboxymethylcellulose derivative, continuing agitation until the fibrous structure of the mass is substantially destroyed and the carboxymethylcellulose derivative is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, displacing the active solvent containing at least about 67.5% water from the gels with an aqueous alcohol containing less than 40% water by weight, washing the gels with aqueous alcohol containing more than 60% by weight of alcohol, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

10. A process for converting fibrous carboxyalkyl cellulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble sodium salt of carboxymethylcellulose moist with an aqueous alcohol and containing water and alcohol in such proportions that the mass would normally dry to a loose fibrous product, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the sodium salt of carboxymethylcellulose, said active solvent containing at least about 67.5% by weight of water, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the sodium salt of carboxymethylcellulose, continuing agitation until the fibrous structure of the mass is substantially destroyed and the sodium salt of carboxymethylcellulose is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

11. A process for converting fibrous carboxyalkyl cel-

11

lulose derivatives into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising a water-soluble sodium salt of carboxymethyl hydroxyethyl cellulose moist with an aqueous alcohol and containing water and alcohol in such proportions that the mass would normally dry to a loose fibrous product, simultaneously introducing thereto a dispersed stream of aqueous fluid until the amount of water introduced is sufficient to form with the aqueous alcohol present in the mass an active solvent for the sodium salt of carboxymethyl hydroxyethyl cellulose, said active solvent containing at least about 67.5% by weight of water, maintaining the total liquid content in the mass below about 4 parts by weight based on the dry weight of the sodium salt of carboxymethyl hydroxyethyl cellulose, continuing

12

agitation until the fibrous structure of the mass is substantially destroyed and the sodium salt of carboxymethyl hydroxyethyl cellulose is converted into a mass of separate, discrete gel particles, discontinuing agitation while the mass is still substantially in the form of separate, discrete gel particles and before said gels coalesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

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