United States Patent Office 2,839,526 Patented June 17, 1958

2,839,526

WATER-SOLUBLE CARBOXYALKYL CELLULOSE DERIVATIVE AND METHOD OF MANUFACTURE

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No Drawing. Application December 30, 1954 Serial No. 478,932

4 Claims. (Cl. 260—232)

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

It is known that 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. Additionally, the material in fibrous form has undesirable properties in that it is dusty in handling and tends to segregate badly in dry blends.

A number of methods are also 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 alcohol 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 overcome the processing difficulties inherent in the fibrous form of these cellulose ethers during purification and/or drying.

However, the processing difficulties referred to above have been overcome in accordance with the process set forth in my copending application Serial No. 364,960, filed June 29, 1953.

In accordance with my copending application, 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 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 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.

In a specific embodiment of my copending application 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 coa-

lesce into doughy masses, and drying the gels thus formed to obtain a free-flowing substantially granular powder.

It has been discovered that in order to obtain water-soluble carboxyalkyl cellulose derivatives possessing a combination of outstanding desirable characteristics such as freedom from dust, quick solution rate, freedom of segregation in dry blends, and freedom from lumping in making solutions, it is first necessary to convert fibrous carboxyalkyl cellulose derivative into gel particles which upon drying are granular in contrast to the original fibrous form and then classifying the gel particles or granular material within critical limits. More specifically, in accordance with this invention, in processes for converting water-soluble fibrous carboxyalkyl cellulose derivative into substantially free-flowing powder, there is provided the improvement which comprises converting the fibrous carboxyalkyl cellulose derivative into gel particles and classifying the gel particles to obtain in dry form 100% through a U. S. standard series sieve No. 12 with not more than about 20% through a U. S. standard series sieve No. 100, whereby the product so converted, dried and classified in addition to being a free-flowing substantially granular powder is quickly soluble in water and substantially dust-free. The preferred procedure for converting the fibrous carboxyalkyl cellulose derivative into gel particles is that of my copending application since the procedure has been found particularly efficacious when employed for the conversion step in the present invention.

The following examples are presented in illustration of this invention. It is to be understood, however, that the examples are purely illustrative and are not to be construed as a limitation of the invention.

EXAMPLE 1

A series of runs was made employing as starting material a commercial grade of sodium carboxymethylcellulose known as Hercules CMC–70–High. This material had a degree of substitution of 0.68–0.78 carboxymethyl radical per glucose anhydride unit, and a viscosity of 1300–2500 cps. in a 1% aqueous solution. This material was prepared and purified in accordance with the procedure set forth in U. S. Patent 2,517,577. The resulting product was a dry loose mass of fibers having substantially the same fibrous form as the starting cellulose. This fibrous material was then pulverized to pass substantially 100% through a U. S. standard series sieve No. 30 and approximately 50% through a sieve No. 100. The grinding did not change the fibrous nature of the material although the fiber length was shortened. The physical properties of this fibrous sodium carboxymethylcellulose (CMC) are given in Table I.

Table I

PHYSICAL PROPERTIES OF FIBROUS CMC

Run No.	Bulk Density, g./cc.	Flow No.[1] (6 mm.)[2]	Solution Time (Min.)	Dust Loss,[3] Percent
1	.40	72	5.3	6.1
2	.47	47	9.9	5.5
3	.43	79	11.2	3.5
4	.46	43	7.3	4.1
5	.45	65	8.6	4.0
6	.42	61	9.3	3.2
7	.38	79	8.5	6.9
8	.45	47	8.7	
9	.46	50	8.5	2.7
10	.45	36	10.3	2.4
11	.47	34	8.6	3.2
12	.43	54	9.5	4.7
13	.44	45	9.2	3.0
14	.42	52	11.6	4.6
15	.44	45	12.2	
16	.46	52	11.1	2.8
17	.47	59	12.7	2.5
18	.46	41	8.5	2.1
19	.48	38	7.3	2.1
20	.50	52	10.0	3.5
21	.45	54	11.6	5.0

[1] Flow number is the number of times required to assist the flow of 50 g. CMC through a funnel with a 4 mm. opening until the funnel is empty.

[2] A 6 mm. funnel was used for the fibrous CMC since flow numbers for all samples were over 100 using the 4 mm. funnel.

[3] Weight percent of CMC lost when funneling 50 g. CMC from one container to another.

NOTE.—The method for assisting flow of a sample of CMC through the funnels consisted in thrusting a stiff wire about 7 inches long and 0.07 inch diameter down through the sample in the funnel and then withdrawing it. One such thrust and withdrawal constituted one assist.

EXAMPLE 2

A series of runs was made employing as starting material sodium carboxymethylcellulose reacted in the same manner as that employed in Example 1. However, in this series of runs the fibrous material was converted to a granular form in accordance with my copending application as hereinbefore described, purified, and then classified after drying. The moist gels formed by the conversion flowed freely through the processing equipment and were easily purified. The physical properties of the granular classified sodium carboxymethylcellulose (CMC) thus produced are given in Table II.

Table II

PHYSICAL PROPERTIES OF GRANULAR, CLASSIFIED CMC

Run No.	Bulk Density, g./cc.	Flow[1] No. (4 mm.)	Solution Time (min.)	Dust[2] Loss, Percent	Sieve Classification, Percent Retained on—					
					20	30	40	80	100	Pan
1	0.53	3	2.1	0.26	0.3	13.5	28.8	45.2	3.7	8.8
2	0.63	0	4.1	0.02	0.4	4.4	26.6	63.5	2.5	2.6
3	0.58	0	4.1	0.26	0	15.6	31.9	38.6	2.3	11.6
4	0.51	4	4.1	0.12	0	27.3	40.2	30.1	0.8	1.6
5	0.62	1	3.6	0.12	0.1	7.4	23.3	54.4	4.4	10.4
6	0.55	0	2.8	0.10	0	18.6	34.2	42.0	1.7	3.5
7	0.40		4.5	0.02	0.2	33.5	40.4	23.1	0.7	2.1
8	0.58	0	1.7		0	0	24.4	55.2	3.6	16.8
9	0.66	0	3.2	0.06	0	0.4	27.4	57.3	3.5	11.4
10	0.59	0	2.3	0.16	0	0	30.2	57.5	3.2	9.1
11	0.62	0	1.6		0	0.3	44.1	50.5	1.8	3.3
12	0.41	0	1.3	0.20	0	0.1	56.8	39.4	0.8	2.9
13	0.62	0	2.9	0.24	0	0	27.5	58.6	3.3	10.6
14	0.59	0	2.7	0.20	0	0.2	30.8	52.5	3.5	13.0

[1] Flow number is the number of times required to assist the flow of 50 g. CMC through a funnel with a 4 mm. opening until the funnel is empty.

[2] Weight percent of CMC lost when funneling 50 g. CMC from one container to another.

EXAMPLE 3

A series of tests was made to demonstrate the relative segregation of fibrous and granular, classified, sodium carboxymethylcellulose (CMC). For this test, the fibrous product of Example 1 was compared to the granular, classified product of Example 2 by thoroughly blending equal parts of the products with sugar and placing in 8 ounce cylindrical glass jars. The blends were then

subjected to gentle agitation for 90 minutes and were then separated into equal portions from the top and bottom of the containers. The results of these tests are given in Table III.

Table III

RELATIVE SEGREGATION OF FIBROUS AND GRANULAR, CLASSIFIED CMC

Test No.	Type	Viscosity (cps.) 1% Solution		
		Top	Bottom	Difference
1	Fibrous	545	295	250
2	do	79	388	309
3	do	136	185	49
4	do	53	1,168	1,115
5	Granular	292	292	0
	Classified			
6	Granular	272	264	8
	Classified			
7	Granular	187	203	16
	Classified			
8	Granular	237	256	19
	Classified			
9	Granular	234	232	2
	Classified			
10	Granular	110	135	25
	Classified			

With reference to the above examples and tables, it is evident that the improvement in processing in acordance with this invention is quite outstanding in yielding granular, classified products having significant commercial advantage over those heretofore available to the art. For example, the improvement in free-flowing characteristics is of value in a number of handling operations, such as pouring from containers, unloading from bins, and dry blending with other materials. The improvement in solution time is quite important. The fibrous products of Example 1 had an average solution time value of 9.5 minutes while the granular, classified products of Example 2 had an average value of only 2.9 minutes. Moreover, the data presented relative to solution time were obtained by a controlled laboratory test where only a small quantity of material was used. This test was conducted as follows:

Measure 300 ml. of water into a 600 ml. beaker. Heat to 65° C. and agitate slowly, so as to form a vortex of about ½ inch. Weigh 1.5 g. of the carboxyalkylcellulose product to be tested and pour into vortex in 1 to 2 seconds. Start stop watch simultaneously with addition of said product to water. Continue agitation until complete solution of said product. Complete solution may be determined more readily by placing a polaroid glass and a light behind the solution. Stop the watch as soon as said product is completely in solution, and record the elapsed time as solution time.

In commercial practice, where large quantities of material are dissolved in water the lumping tendency of fibrous material is still more pronounced and solution times are increased proportionately. The granular, classified material made in accordance with this invention, however, disperses readily and therefore dissolves in several minutes under conditions which in some instances require several hours for fibrous or finely pulverized material. The relative freedom from dusting is quite important in economy of use and handling where it will be observed that the dust lost for the fibrous material averaged 3.8% while that of the granular, classified material made in accordance with this invention averaged only 0.15%.

With reference to the foregoing, it is evident that there are several factors which will influence conditions for most satisfactory operation of the invention in which the actual requirements are determined by the processing sequence and finished products desired. In general, the conversion of the fibrous material to the granular form should be substantially complete with not more than 10% of fibrous particles present in the total converted mass. Since conversion of the fibrous material to the granular form ordinarily involves a densification step, the granular classified product normally has a somewhat higher bulk density than the fibrous product. This will be seen with reference to Tables I and II where the average bulk density of the fibrous and granular products was 0.45 g./cc. and 0.56 g./cc., respectively. Bulk density is relatively unimportant in determining product quality with the exception that coarse grains of very high bulk density tend to hydrate and dissolve much less rapidly than less dense grains of the same size. It has been found that a bulk density range of from about 0.30 to about 1.0 g./cc. gives very satisfactory results.

The range of operability in respect to classification of the converted product is substantially 100% through a U. S. standard series sieve No. 12 with not more than about 20% through a U. S. standard series sieve No. 100. The optimum range from a product standpoint appears to be 100% through a sieve No. 40 with 100% retained on a sieve No. 100. However, such narrow particle size distribution is not feasible in commercial production and products of 100% through a sieve No. 20 with 90% retained on a sieve No. 100 have been found satisfactory.

It will be appreciated that this invention is suitable for processing any fibrous water-soluble carboxyalkylcellulose derivative 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 derivative 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. In order to obtain the greatest benefit in end product, it is preferred to apply the process of this invention to purified water-soluble carboxyalkyl cellulose derivatives. Purified derivatives do not contain any substantial amount of by-product salts which to some extent contribute to improved water solubility.

Drying of the gels after conversion as herein set forth follows conventional practice with respect to drying times, temperatures, drying equipment, and the like. Although the moist or wet gels may be classified by suitable wet screening equipment to give the end product classification desired, it is preferred to dry the product to a volatile content below about 5% by weight and then classify. Since the dried product is in the form of a free-flowing granular powder, it may be classified directly without further treatment.

The water-soluble products produced in accordance with this invention are readily and rapidly dissolved in water and find a wide application of improved use where other water-soluble gums have heretofore been employed. The products of this invention are especially efficacious in compounding stabilizers for various frozen comestibles, particularly in compounding stabilizers for ice cream.

This application is a continuation-in-part of my copending application Serial No. 364,960, filed June 29, 1953, now U. S. Patent 2,715,124 which issued August 9, 1955.

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

1. In 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 substan-

tially 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: the improvement which comprises classifying the gel particles to obtain in dry form substantially 100% through a U. S. standard series sieve No. 12 with not more than about 20% through a U. S. standard series sieve No. 100, whereby the product so converted, dried and classified in addition to being a free-flowing substantially granular powder is quickly soluble in water and substantially dust-free.

2. In 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: the improvement which comprises classifying the powder to obtain substantially 100% through a U. S. standard series sieve No. 12 with not more than about 20% through a U. S. standard series sieve No. 100, whereby the product so converted, dried and classified in addition to being a free-flowing substantially granular powder is quickly soluble in water and substantially dust-free.

3. In a process for converting fibrous carboxymethylcellulose into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising water-soluble 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 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 carboxymethylcellulose, continuing agitation until the fibrous structure of the mass is substantially destroyed and the 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: the improvement which comprises classifying the gel particles to obtain in dry form substantially 100% through a U. S. standard series sieve No. 12 with not more than about 20% through a U. S. standard series sieve No. 100, whereby the product so converted, dried and classified in addition to being a free-flowing substantially granular powder is quickly soluble in water and substantially dust-free.

4. In a process for converting fibrous carboxymethylcellulose into free-flowing substantially granular powder which comprises agitating a loose fibrous mass comprising water-soluble 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 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 carboxymethylcellulose, continuing agitation until the fibrous structure of the mass is substantially destroyed and the 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: the improvement which comprises classifying the powder to obtain substantially 100% through a U. S. standard series sieve No. 12 with not more than about 20% through a U. S. standard series sieve No. 100, whereby the product so converted, dried and classified in addition to being a free-flowing substantially granular powder is quickly soluble in water and substantially dust-free.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,839,526 June 17, 1958

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 3, for "It has been" read -- It has now been --; column 4, Table II, under the heading "Sieve Classification, Percent Retained on--", under the subheading "20", first line thereof, for "0.3" read -- 0 --.

Signed and sealed this 26th day of August 1958.

(SEAL)

Attest:
KARL H. AXLINE

Attesting Officer

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Commissioner of Patents