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(54) **CELLULOSE ETHER HAVING ENHANCED GEL STRENGTH AND COMPOSITIONS CONTAINING IT**

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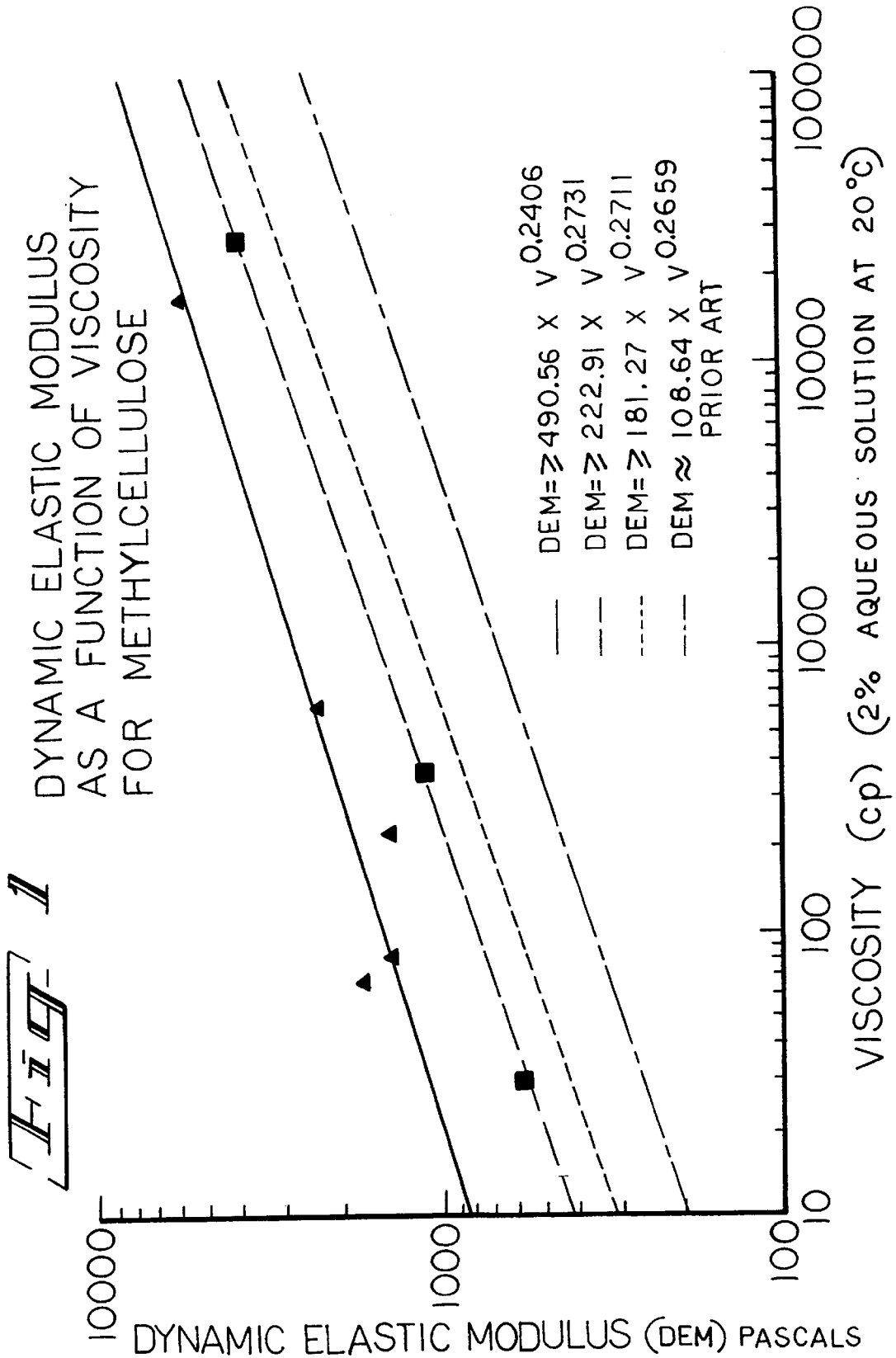
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(57) **ABSTRACT**

According to the present invention, there is a methylcellulose having a methoxy substitution of about 21 to about 42 percent based upon the weight of the cellulose ether and elastic modulus (EM) of $EM \geq 181.3 \times (v^{0.2711})$ wherein "v" is viscosity of a two percent solution of the cellulose ether at 20° C. Further described is a process for making the cellulose ether, a food composition containing it, and a pharmaceutical capsule containing it.

25 Claims, 1 Drawing Sheet



CELLULOSE ETHER HAVING ENHANCED GEL STRENGTH AND COMPOSITIONS CONTAINING IT

FIELD OF THE INVENTION

The present invention relates to a cellulose ether having enhanced gel strength and a process for making.

BACKGROUND OF THE INVENTION

Cellulose ethers have been employed as additives to food compositions and processes to provide physical properties such as thickening, freeze/thaw stability, lubricity, moisture retention and release, film formation, texture, consistency, shape retention, emulsification, binding, suspension, and gelation.

A physical property important in some food compositions is gel strength or elastic modulus. This property relates to the strength with which a cellulose ether binds or holds food particles together. Efforts to significantly increase gel strength for conventional cellulose ethers beyond levels observed for given viscosity grades have been largely unsuccessful.

Having a cellulose ether which exhibits enhanced gel strength for given viscosity grades would enable food compositions with superior binding, consistency, and shape retention to be developed. Also, viscosity contribution and cellulose ether concentrations could be reduced in food compositions while maintaining desired gel functionality.

It would be desirable to have a cellulose ether which exhibits elevated gel strength for a given molecular weight or viscosity grade. It would also be desirable to have a process for making the cellulose ether.

SUMMARY OF THE INVENTION

According to the present invention, there is a methylcellulose having a methoxy substitution of about 25 to about 42 percent based upon the weight of the cellulose ether and a viscosity (v) to elastic modulus (EM) relationship of $EM \geq 181.3 \times (v^{0.2711})$. " \geq " means "greater than or equal to." Viscosity is for a 2 percent aqueous solution at 20° C. EM corresponds to gel strength.

Further according to the present invention, there is a process for making a cellulose ether. The process comprises the following: a) contacting a cellulose pulp with a first amount of aqueous alkaline hydroxide at reaction conditions sufficient to alkalinize it to a first level of alkalization which is about 20 percent or more of a total level of alkalization; b) contacting the cellulose pulp of first level of alkalization with a first amount of a methylating agent at reaction conditions sufficient to form a cellulose ether having a first level of methoxy substitution which is about 20 percent or more of a total level of methoxy substitution; c) contacting the cellulose ether of first level of etherification with a second amount of aqueous alkaline hydroxide at reaction conditions sufficient to alkalinize it to a second level of alkalization which is about 40 percent or more of the total level of alkalization; and d) continuously or incrementally contacting the cellulose ether of second level of alkalization with a second amount of a methylating agent over a period of time at reaction conditions sufficient to form a cellulose ether of the second level of methoxy substitution which is about 40 percent or more of the total level of methoxy substitution, the second amount of the methylating agent provides about 20 percent or more of the total level of methoxy substitution; the second amount of the methylating

agent is contacted with the cellulose ether of second level of alkalization at about 65° C. to about 110° C. for 15 minutes or more.

Further according to the present invention, there is a food composition comprising a foodstuff and the present cellulose ether.

Further according to the present invention, there is a pharmaceutical capsule comprising the present cellulose ether.

DESCRIPTION OF THE DRAWING

The FIGURE is a graphical representation depicting the elastic modulus of cellulose ethers of the present invention and those of the prior art.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides novel cellulose ethers having elevated gel strength for a given viscosity grade and substitution type and level compared to that of conventional cellulose ethers. The cellulose ethers are useful in conventional cellulose ether applications, particularly in food compositions and pharmaceutical capsules.

For purposes of the present invention, a cellulose ether is a cellulose ether with a methoxy substitution of about 21 to about 42 weight percent based upon the weight of the cellulose ether. More preferred cellulose ethers have a methoxy substitution of about 21 to about 35 weight percent and most preferred cellulose ethers have a methoxy substitution of about 25 to about 35 weight percent. Methoxy substitution is determined according to ASTM D2363-72.

Cellulose ethers having viscosities of up to about 1,000,000 centipoise (cP) in a two percent aqueous solution at 20° C. can be prepared in the present invention. Preferred cellulose ethers may have viscosities of about 1 to about 600,000 cP (two percent solution). Most preferred cellulose ethers may have viscosities of about 1 to about 100,000 cP (two percent solution). Viscosities of aqueous solutions are determined by Ubbelohde tube according to ASTM D1347-72 and D2363-79.

A useful embodiment of the present cellulose ether is a methylcellulose. The methylcellulose has a non-methoxy substitution content or level of about 1 percent or less by weight based upon the total weight of the methylcellulose and is most preferably substantially free of non-methoxy substitution content. Non-methoxy substitution includes but is not limited to hydroxyethyl, hydroxypropyl, and hydroxybutyl substitution.

The present methylcellulose can exhibit an elastic modulus (EM) in a 1.5 weight percent aqueous solution according to the following: $EM \geq 181.3 \times (v^{0.2711})$; preferably $EM \geq 222.9 \times (v^{0.2731})$; and most preferably $EM \geq 490.6 \times (v^{0.2406})$ wherein " v " is viscosity of a 2 weight percent aqueous solution at 20° C. EM corresponds to gel strength. The above relationships are depicted graphically in the FIGURE along with an analogous relationship for conventional methylcellulose. The relationship for conventional methylcellulose is representational and deemed to be an approximate average since actual viscosity to EM relationships for various conventional methylcellulose specimens will vary to some degree in a range above and below the indicated approximate average. DEM in the FIGURE corresponds to EM.

EM is determined by measuring the storage modulus of a 1.5 weight percent aqueous solution of the cellulose ether in

a dynamic rheometer. Techniques for measuring elastic modulus (storage modulus) are described in *Kinetics of Thermal Gelation of Methylcellulose and Hydroxypropylmethylcellulose in Aqueous Solutions*, Carbohydrate Polymers, volume 26, no. 3, pp. 195–203, which is incorporated herein by reference.

Cellulose ethers which can be made by the process of the present invention include but are not limited to methylcellulose (MC), hydroxypropylmethylcellulose (HPMC), hydroxyethylmethylcellulose (HEMC), and methylethylcellulose (MEC).

Another useful embodiment of the present cellulose ether is a hydroxypropylmethylcellulose (HPMC). Hydroxypropyl substitution is preferably about 32 weight percent or less, more preferably about 1 to about 14 weight percent and most preferably about 3 to about 12 weight percent based upon the total weight of the cellulose ether.

Although not bound by any theory, the enhanced physical properties of the present cellulose ethers may come from a greater degree of “blocking” or periodicity in methoxy substitution distribution in its polymeric structure than in the structure of conventional cellulose ethers. The disclosed process may induce the formation of such blocking.

The present cellulose ethers can be soluble in any of water, polar organic solvents, and mixtures thereof depending upon the type and degree of substitution of the cellulose ethers.

In addition to enhanced gel strength, preferred cellulose ethers may exhibit lower gelation temperatures than conventional cellulose ethers of equivalent viscosity and substitution. Lower gelation temperature is a desired and preferred but non-essential feature of the present invention. Reduced gelation temperature is useful in food manufacturing and processing. Food compositions can be gelled at lower temperatures saving energy and processing time during heating/cooling cycles. Further, food compositions can retain form at broader temperature ranges during processing. Gelation temperature is determined by heating a 1.5 percent by weight percent aqueous solution of the cellulose ether and observing the narrow temperature range at which gelation takes place.

Preferred cellulose ethers may also exhibit longer meltback times than conventional cellulose ethers of equivalent viscosity and substitution. Meltback time generally refers to the length of time required for a gel of a cellulose ether to melt while cooling to an ambient temperature. Preferred cellulose ether may even be stable (no meltback) at ambient temperature (72° F. (22° C.)). Longer meltback time or stability to meltback are desired and preferred but non-essential features of the present invention. Longer meltback time or stability to meltback at ambient temperature is useful in food processing and manufacturing. Gelation can be maintained over a wider temperature range and longer and better retention of texture during food processing and consumption are possible. Meltback time is determined according to the following: provide 15 grams of a 1.5 weight percent of an aqueous solution of the cellulose ether in a 20 milliliter beaker; heat the solution for 8 minutes in boiling water—the solution will gel in the beaker; invert the beaker onto a flat surface in an ambient temperature environment; allow the gel to cool and subsequently melt to form a puddle on the surface. Meltback time is measured from the time cooling begins (removal from the boiling water) to when a clear puddle forms. A gel is said to be stable to meltback if it cools to ambient temperature and resists melting for 8 hours or more.

An important aspect of the present invention is the process by which the cellulose ether is made. This process differs from that conventionally employed to make cellulose ethers. In conventional processes, cellulose pulp is completely alkalinized with sodium hydroxide and etherified with methyl chloride. In the present process, cellulose pulp is partially alkalinized and partially etherified with alkaline hydroxide and methyl chloride in a first stage or step and further alkalinized and further etherified with additional alkaline hydroxide and methyl chloride to the desired level of completion in a later stage or stages. Methyl chloride is continuously or incrementally introduced over a period of time at certain reaction conditions in a second or later stage.

The raw material used to make the present cellulose ether is cellulose. Cellulose pulp is typically obtained from wood pulp or cotton. The pulp is preferably provided in a powder or chip form. Wood pulp is preferred.

The alkalinization and etherification of the cellulose pulp is carried out in a stepwise manner in stages. A “stage” refers to a two-step reaction sequence in which an alkalinization reaction and a methylation reaction take place. A stage effectively advances or increases the level of methoxy substitution of the cellulose pulp or a partially etherified cellulose ether. Optionally, other types of etherification such as hydroxypropyl substitution can be effected along with or in addition to methoxy substitution.

The cellulose pulp is alkalinized in two or more stages in one or more reactors with an alkaline hydroxide, preferably sodium hydroxide. The pulp is partially alkalinized in the first stage and alkalinized to a desired, total level of completion in a second stage or a later stage. The pulp may be alkalinized with alkaline hydroxide by any means known in the art such as steeping in a bath or stirred tank containing aqueous hydroxide or spraying aqueous hydroxide directly on dry pulp. Reaction time varies according to hydroxide concentration, temperature, and retention time. The aqueous hydroxide is preferably used at an alkaline hydroxide content of about 30 to about 70 percent by weight based upon the weight of the water. The temperature of alkylation preferably ranges from about 30° C. to about 110° C. and most preferably about 30° C. to about 90° C. Uniform swelling and alkali distribution in the pulp may be controlled by mixing and agitation. The rate of addition of aqueous alkaline hydroxide may be governed by the ability to cool the reactor during the exothermic alkalinization reaction. The rate of addition of hydroxide is not critical to the present invention. If desired, an organic solvent such as dimethyl ether may be added to the reactor as a diluent and a coolant. If desired, the headspace of the reactor or reactors may be evacuated or purged with an inert gas such as nitrogen to control oxygen-catalyzed depolymerization of the cellulose ether product.

The alkylated cellulose pulp is etherified (methylated) in two or more stages in one or more reactors to form a cellulose ether. Reaction time for etherification will depend on concentration, pressure, temperature, and retention time. The primary etherifying agent is a methylating agent such as methyl chloride or dimethyl sulfate. Methyl chloride is preferred. The methylating agent may be added in a batch load at one time or continuously or incrementally over a period of time in one or more stages but must be added continuously or incrementally over a period of time in at least one stage after the first stage, preferably in the second stage. “Batch load addition” means addition substantially without pause over a relatively short period of time. “Continuous addition” means addition substantially without pause over a longer period of time. “Incremental addition”

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means periodic addition of smaller, discrete amounts over a longer period of time. The alkaline hydroxide and the methylating agent may be added to the reactor at the same time but are preferably added sequentially with the alkaline hydroxide being added first and the methylating agent second.

A two-stage process is the preferred process for making the present cellulose ether. In stage one, the aqueous alkaline hydroxide and the methylating agent are reacted in sequence with a cellulose pulp to form a partially etherified cellulose ether of a first level of methoxy substitution. Each of the alkaline hydroxide and the methylating agent may be added in stage one in a batch load at one time or continuously or incrementally over a period of time. The rate of addition is not critical. The reaction temperature in the first stage is preferably controlled so that generally uniform contact and reaction can occur between the alkaline hydroxide/methylating agent and the cellulose pulp. In the second stage, additional amounts of the aqueous alkaline hydroxide and the methylating agent are reacted with the partially etherified cellulose ether to form a cellulose ether with a second level or desired, total level of methoxy substitution. The alkaline hydroxide may be added in the second stage in a batch load at one time or continuously or incrementally over a period of time. The rate of addition of hydroxide in the second stage is not critical. The methylating agent must, however, be added continuously or incrementally over a period of time in the second stage to form the present cellulose ether. The methylating agent is added in the second stage at about 65° C. to about 120° C. (temperature of contents within reactor) at 15 minutes or more; preferably at about 75° C. to about 100° C. at 20 minutes or more; and most preferably at about 80° C. to about 90° C. at 25 minutes

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carry it out at about 65° C. to about 120° C. and more preferably from about 80° C. to about 90° C. Temperature within the reactor can be determined by means such as a thermocouple which protrudes into the contents (cellulose pulp/cellulose ether mass) of the reactor. In a preferred two-stage process, both stages are carried out in the same reactor. Preferably, about 20 to about 80 percent of the total methoxy substitution is carried out in the first stage and about 80 to about 20 percent in the second stage. More preferably, about 40 to about 60 percent of the total methoxy substitution is carried out in the first stage and about 60 to about 40 percent in the second stage. Some embodiments of two-stage processes are described in Table 1.

A three-stage process is also useful for making the present cellulose ether. The first stage is carried out in a manner similar to that of the first stage in the two-stage process described above. Either or both of the second and third stages are carried out in the same manner as the second stage in the two-stage process described above (the methylating agent is added continuously or incrementally over a period of time). In a preferred three-stage process, about 20 to about 60 percent of the total methoxy substitution is carried out in each of the first and second stages and about 5 to about 30 percent in the third stage. Some embodiments of three-stage processes are described in Table 1.

It is also possible to have processes with four or more stages. The first stage of such a process would be carried out in the same manner as the first stage in the two-stage process described above. One or more of the subsequent stages would be carried out in the same manner as the second stage in the two-stage process described above (the methylating agent is added continuously or incrementally over a period of time).

TABLE 1

Some Useful Embodiments of the Process of the Present Invention

Features	Embodiments							
	#1	#2	#3	#4	#5	#6	#7	#8
partial alkalization in first stage; addition of alkaline hydroxide	X	X	X	X	X	X	X	X
partial etherification in first stage; batch load addition of methylating agent	X	X			X	X		
partial etherification in first stage; continuous/incremental addition of methylating agent			X	X			X	X
partial alkalization in second stage; addition of alkaline hydroxide	X	X	X	X	X	X		
partial etherification in second stage; continuous/incremental addition of methylating agent	X	X	X	X	X	X		
partial etherification in second stage; batch load or continuous/incremental addition of methylating agent								X X
partial alkalization in third stage; addition of alkaline hydroxide					X	X	X	X
partial etherification in third stage; continuous/incremental addition of methylating agent							X	X
partial etherification in third stage; batch load or continuous/incremental addition of methylating agent					X	X		
single reactor for all stages	X		X		X		X	
separate reactor for each stage		X		X		X		X

or more. Although the methylating agent can be added continuously or incrementally over any extended period of time in the second stage, it is preferred for reasons of time economy to carry out the addition in about 120 minutes or less, more preferably in about 60 minutes or less, and most preferably in about 25 to about 45 minutes. After addition of the methylating agent in the second stage, etherification can be carried out at any temperature at which the reaction can proceed, but it is preferred for reason of time economy to

Cellulose ethers such as hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, methylethylcellulose and hydroxyethylmethylcellulose can be prepared by reacting the cellulose pulp or partially etherified cellulose ether with another etherifying agent in addition to the methylating agent (also an etherifying agent). Useful etherifying agents include ethyl chloride, ethylene oxide, propylene oxide, and butylene oxide. The other etherifying agent can be reacted in any stage before, during, or after reaction by the methylating

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