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(54) Title: STABILIZED MICROFIBRILLAR CELLULOSE

(57) Abstract: A derivatized microfibrillar cellulose, derivatized to contain a substituent that provides cationic charge. A method for producing a derivatized microfibrillar cellulose to include a substituent that provides cationic charge, which may include derivatizing a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose, microfibrillizing a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose, or microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously. A method of modifying the rheological properties of a composition of matter using derivatized microfibrillar cellulose. Methods of improving coatings, paper manufacture, and the stability of emulsions, dispersions, and foams using a derivatized microfibrillar cellulose. Compositions that include derivatized microfibrillar cellulose, including paper compositions, comestible compositions, non-comestible spreadable compositions, and emulsions, dispersion, and foams.

DescriptionSTABILIZED MICROFIBRILLAR CELLULOSEFIELD OF THE INVENTION

5           The present invention relates to stabilized microfibrillar cellulose. More specifically, the present invention relates to microfibrillar cellulose that is electrostatically stabilized by cationic groups.

BACKGROUND OF THE INVENTION

10           Polysaccharides are often found in nature in forms having fibrous morphology. Polysaccharides which are not found in nature in fibrous form can often be transformed into fibrous morphologies using fiber-spinning techniques. Whether the fibrous morphology is of natural or artificial origin, the polysaccharide will often be present in such a form that the fibers can be reduced to fibrillar and microfibrillar sub-morphologies through the application of energy.

15           Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these materials have a tendency to poorly occupy volume, and to exhibit gross inhomogeneities in distribution.

20           Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby incorporated by reference thereto. These documents, in part, purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

25           Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by

reference. Nanofibrils are characterized as having diameters in the range of about 2 to about 10 nanometers.

EP 845495 discusses cationic cellulose particulate which is characterized as insoluble, positively charged, and used in water treatment, specifically to treat  
5 water in a paper manufacturing plant. In papermaking this cationic particulate is said to remove anionic trash from the water. The particles are obtained by milling, which is stated to reduce particle size uniformly such that particles are typically round as described by a length/diameter ratio of approximately 1. Particle size is stated to be 0.001 mm (i.e., 1  $\mu\text{m}$ ), and preferably 0.01 mm (10  
10  $\mu\text{m}$ ).

EP 859011 ("EP '011") is directed to a process for obtaining cationic cellulose microfibrils or their soluble derivatives. The process is described as including making a cationic cellulose derivative and processing the derivative through a high-pressure homogenizer to form transparent gels. The product can  
15 be dehydrated and rehydrated. Viscosity measurements are reported on the product at a concentration of 2% in water. EP '011 indicates that the degree of substitution ("DS") of the cellulose can range from 0.1 to 0.7, with a DS of between 0.2 and 0.7, 0.3 and 0.6, and 0.5 and 0.6 characterized as representing increasing orders of preference. The examples show cellulose with a DS ranging  
20 from a low of 0.24 up to 0.72. Gelling is reported to occur above a microfibril concentration of 10 g/L, or above 1%, in water. EP '011 defines gelling as occurring when  $G' > G''$ , where  $G'$  is the dynamic storage modulus and  $G''$  is the dynamic loss modulus.

Microfibrillated chitosan is reported to form uniplanar, oriented sheets upon  
25 drying by H. Yokata, J. Polymer Sci., Part C: Polymer Letters, 24:423-425 (1986). This article mentions that at a level of 4% chitosan in water, a gel is formed having a viscosity of 26,600 cps (Brookfield, 20° C, rotor #7, 10rpm). The microfibrillated chitosan is made by homogenization of commercial chitosan flakes in a Gaulin homogenizer. The commercial chitosan is deacetylated using  
30 sodium hydroxide.

JP 59 [1984]-84938 discusses a method for producing a chitosan suspension. Commercial chitosan separated and purified from crabs and lobsters is pulverized to pieces having maximum length of about 1-2 mm. The pieces are then suspended in water at up to 15% chitosan, and are run in multiple passes  
5 through a high-pressure homogenizer at between 3,000 and 8,000 psi.

It would be desirable to obtain microfibrillar cellulose capable of forming a gel at concentrations of 1% or less, thereby providing economy and ease of formulation, while still providing necessary rheological behavior and homogeneity of distribution.

10 In addition, there is a continuing need in industry to improve the stability of commercial emulsions, such as paper sizing emulsions. At present, one method for stabilizing such emulsions is the addition of charged materials, such as cationic starches, which may be added in amounts equal to 10-20% by weight of the size component. Interaction with anionic components, such as sulfonates, can  
15 also improve stability. However, emulsion failure still takes place in such emulsions, either through density-driven separation, also referred to as creaming, or through gellation. It would accordingly be desirable to develop a material that could be added to emulsions to provide long-term stability.

#### SUMMARY OF THE INVENTION

20 The present invention is directed to a derivatized microfibrillar cellulose which is derivatized to include a substituent that provides cationic charge and is capable of forming a gel in water at a concentration of less than 1%. The cellulose used to prepare the derivatized microfibrillar cellulose may be obtained from any suitable source, including but not limited to chemical pulps, mechanical  
25 pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits. Preferably the cellulose is obtained from purified, optionally bleached wood

pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; or vegetables.

The substituent which provides cationic charge to the derivatized microfibrillar cellulose may be, or include, an amine. A quaternary amine is particularly preferred.

The derivatized microfibrillar cellulose may form a gel in water throughout the concentration range of between about 0.01 % and about 100%, or throughout the concentration range of between about 0.01 % and about 50 %, in water. Moreover, the derivatized microfibrillar cellulose may form a gel at a concentration of less than about 1% in water, and preferably forms a gel at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

The derivatized microfibrillar cellulose of the present invention may include a solvent in which the derivatized microfibrillar cellulose is substantially insoluble. Suitable solvents include water, alcohol, or oil, with water being preferred.

The derivatized microfibrillar cellulose may have a degree of substitution of less than about 0.5, or of less than about 0.35, or of less than about 0.2, or of less than about 0.18, or of less than about 1.15. Preferably the degree of substitution is between about 0.02 and about 0.5, and more preferably between about 0.05 and about 0.2.

A particularly preferred embodiment of the present invention is microfibrillar 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose having a degree of substitution of less than about 2.0, preferably of less than about 0.35, more preferably of between about 0.02 and about 0.20, and most preferably between about 0.1 and about 0.2.

The derivatized microfibrillar cellulose may form part of a comestible composition of matter, including but not limited to a low fat, reduced fat, or fat-free mayonnaise, or a salad dressing. When it forms part of a comestible composition of matter, the derivatized microfibrillar cellulose may include a

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Description

STABILIZED MICROFIBRILLAR CELLULOSE

FIELD OF THE INVENTION

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BACKGROUND OF THE INVENTION

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15           Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these materials have a tendency to poorly occupy volume, and to exhibit gross inhomogeneities in distribution.

20           Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby incorporated by reference thereto. These documents, in part, purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

25           Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by

pharmaceutically active ingredient, and may at least partially provide for the controlled, sustained, or delayed release of the pharmaceutically active ingredient.

Alternatively, the derivatized microfibrillar cellulose may form part of a non-comestible composition of matter, such as, by way of non-limiting example, a wound care product. Suitable wound care products include, without limitation, wound dressings and ostomy rings. In another embodiment, the non-comestible composition of matter may be a skin care lotion or cream, a sunscreen lotion or cream, or an oral care composition, such as a toothpaste.

The non-comestible composition of matter may further be or include an agricultural composition, such as a fertilizer, herbicide, fungicide, or pesticide. The derivatized microfibrillar cellulose may provide at least partially for the controlled, sustained, or delayed release of the fertilizer, herbicide, or pesticide.

In an alternative embodiment, the non-comestible composition of matter may be a drilling fluid.

In another embodiment, the present invention is directed to a paper composition which contains the derivatized microfibrillar cellulose described herein.

The present invention further includes a method for producing the derivatized microfibrillar cellulose described herein, which involves at least one of the following steps:

- (a) a derivatizing step of treating a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose;
- (b) a microfibrillizing step of treating a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose; or,
- (c) microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously.

In the above method, the derivatized microfibrillar cellulose is derivatized to include a substituent that contains cationic charge, as for example by the

presence of amine groups. Preferably the derivatizing step involves derivatizing the cellulose with a quaternary amine reagent, such that the derivatized microfibrillar cellulose includes quaternary amine functionalized cellulose.

5 The derivatizing step of the above method may include contacting a non-microfibrillar cellulose with a swelling agent. This contact may occur under alkaline conditions, and the swelling agent may be an anionic reagent. Moreover, the alkaline conditions may include contacting the cellulose with the anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an  
10 alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof. The derivatizing step may further take place at high solids.

In a preferred method, the derivatized microfibrillar cellulose is obtained by:

- 15 (a) derivatizing cellulose with 3-chloro-2-hydroxypropyl trimethylammonium chloride under alkaline conditions to produce 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose;
- (b) suspending the 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose in water to form a suspension; and
- 20 (c) homogenizing the suspension to produce microfibrillated 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose.

The microfibrillizing step of the above method may include applying energy to the cellulose under conditions sufficient to produce microfibrillar cellulose, and the cellulose may be treated with enzyme prior to microfibrillizing.

25 Any suitable approach may be used to apply sufficient energy to the cellulose to obtain microfibrillar cellulose, including, without limitation, one or more of homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and milling. Use of a homogenizer is preferred, and preferred homogenization  
30 conditions include passing the non-microfibrillar cellulose through a pressure



differential of at least about 3,000 psi, and more preferably passing the non-microfibrillar cellulose through the homogenizer at least three times.

Preferably, the derivatized microfibrillar cellulose obtained by the above methods forms a gel throughout a concentration range of from about 0.01 % to about 100% in water, and more preferably throughout a concentration range of  
5 between about 0.01 % and about 50 % in water. Alternatively, the derivatized microfibrillar cellulose should form a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water. In a particularly preferred embodiment, the derivatized microfibrillar cellulose forms a gel at a  
10 concentration of about 0.9% in water.

The present invention extends to derivatized microfibrillar cellulose produced by the above-described method, including it's the described variations of the method.

In yet another embodiment, the present invention includes a method of  
15 modifying the rheological properties of a composition of matter by incorporating the derivatized microfibrillar cellulose into the composition of matter, which may be a liquid, such as water. The derivatized microfibrillar cellulose may be used in an amount which is effective to provide scale control and/or corrosion control. Alternatively, the derivatized microfibrillar cellulose may be used to modify one  
20 or more of the viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention of the composition of matter. Compositions whose rheological properties may be modified in this manner include foods, pharmaceuticals, nutraceuticals, personal care products, fibers, papers, paints, coatings, and construction compositions. More  
25 specifically, possible compositions include oral care products; creams or lotions for epidermal application, including moisturizing, night, anti-age, or sunscreen creams or lotions; food spreads, including reduced fat, low fat, or fat free food spreads (for example, mayonnaise); and drilling fluids.

Alternatively, the derivatized microfibrillar cellulose may be incorporated  
30 into a coating composition in order to improve its physical and/or mechanical

properties. Those properties may include one or more of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

The derivatized microfibrillar cellulose may further be incorporated into the manufacture of paper and paper products in order to improve at least one of  
5 sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, absorbency, film formation, membrane formation, and polyelectrolyte complexation during manufacture. Microfibrillated quaternary amine functionalized cellulose is particularly preferred for use in this method.

In one embodiment of this method, the microfibrillated quaternary amine  
10 functionalized cellulose may be used to increase the rate of drainage and/or dewatering during paper manufacture. In another embodiment, the microfibrillated quaternary amine functionalized cellulose may be used for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture. Representative dispersed particles which may be retained  
15 in this manner include pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof. In a yet further embodiment, the microfibrillated quaternary amine functionalized cellulose may be used in a papermaking machine to improve the uniformity of formation of a sheet of paper  
20 during its manufacture. Additionally, the microfibrillated quaternary amine functionalized cellulose may be used in a papermaking machine to improve the strength of a sheet of paper produced on a paper machine.

In each of the embodiments described in the above paragraph, the microfibrillated quaternary amine functionalized cellulose may be used in the  
25 presence of one or more of the following: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and  
30 combinations thereof.

The derivatized microfibrillar cellulose may further be used in a method for improving the stability of an emulsion, dispersion, or foam system, by including the derivatized microfibrillar cellulose in the system. Where the system being treated is an emulsion, the emulsion may be produced by processing of an emulsion formulation, in which case the derivatized microfibrillar cellulose may be added to the emulsion formulation prior to completion of processing of the emulsion formulation. In one variation, a non-microfibrillated derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is then processed under conditions sufficient to microfibrillate the non-microfibrillated derivatized cellulose. In another variation, a microfibrillated non-derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is then processed under conditions sufficient to derivatize the microfibrillated non-derivatized cellulose. In yet a third variation, a non-microfibrillated, non-derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is further processed under conditions sufficient to both microfibrillate and derivatize the non-microfibrillated, non-derivatized cellulose.

Emulsion systems which may be treated in this manner include water-in-oil and oil-in-water emulsions. The present invention includes the system produced by the above method.

In a yet further embodiment, the present invention extends to a system comprising an emulsion, dispersion, or foam containing a the derivatized microfibrillar cellulose.

In another embodiment, the present invention includes a polyelectrolyte complex containing the derivatized microfibrillar cellulose.

The derivatized microfibrillar cellulose of the present invention may also be used in a method for treating wastewater, which includes the step of adding, to the wastewater, a amount of the derivatized microfibrillar cellulose sufficient to treat the wastewater. Materials being treated by this method in the wastewater

may include, by way of non-limiting example only, anionic contaminants and color bodies.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the dynamic mechanical spectra of Sample 1 from Table 4.

5 Fig. 2 shows the dynamic mechanical spectra of Sample 2 from Table 4.

Fig. 3 shows the dynamic mechanical spectra of Sample 3 from Table 4.

Fig. 4 shows the dynamic mechanical spectra of Sample 4 from Table 4.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises stabilized microfibrillar cellulose. Sources  
10 of cellulose for use in this invention include the following: (a) wood fibers, such  
as from chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-  
thermal mechanical pulps, recycled fibers, newsprint; (b) seed fibers, such as  
from cotton; (c) seed hull fiber, such as from soybean hulls, pea hulls, corn hulls;  
(d) bast fibers, such as from flax, hemp, jute, ramie, kenaf; (e) leaf fibers, such as  
15 from manila hemp, sisal hemp; (f) stalk or straw fibers, such as from bagasse,  
corn, wheat; (g) grass fibers, such as from bamboo; (h) cellulose fibers from  
algae, such as velonia; (i) bacteria or fungi; and (j) parenchymal cells, such as  
from vegetables and fruits, and in particular sugar beets, and citrus fruits such as  
lemons, limes, oranges, grapefruits. Microcrystalline forms of these cellulose  
20 materials may also be used. The cellulose may be used as is, or spinning may be  
used to generate or improve fibrous structure. Preferred cellulose sources are (1)  
purified, optionally bleached, wood pulps produced from sulfite, kraft (sulfate),  
or prehydrolyzed kraft pulping processes; (2) purified cotton linters; and, (3)  
fruits and vegetables, in particular sugar beets and citrus fruits. The source of the  
25 cellulose is not limiting, and any source may be used, including synthetic  
cellulose or cellulose analogs.

Cellulose is found in nature in several hierarchical levels of organization  
and orientation. Cellulose fibers comprise a layered secondary wall structure  
within which microfibrils are arranged. Microfibrils comprise multiple  
30 microfibrils which further comprise cellulose molecules arranged in crystalline

and amorphous regions. Cellulose microfibrils range in diameter from about 5 to about 100 nanometers for different species of plant, and are most typically in the range of from about 25 to about 35 nanometers in diameter. The microfibrils are present in bundles which run in parallel within a matrix of amorphous

5 hemicelluloses (specifically xyloglucans), pectinic polysaccharides, lignins, and hydroxyproline rich glycoproteins (includes extensin). Microfibrils are spaced approximately 3-4 nm apart with the space occupied by the matrix compounds listed above. The specific arrangement and location of the matrix materials and how they interact with the cellulose microfibrils is not yet fully known. Further

10 background on the structure, functions, and biogenesis of native cellulose may be found in Haigler, C.H., Cellular Chemistry and Its Applications, Nevell, pp. 30-83 (1985), the entirety of which is hereby incorporated by reference.

For purposes of the present invention microfibrils refer to small diameter, high length-to-diameter ratio substructures which are comparable in dimensions

15 to those of cellulose microfibrils occurring in nature. By way of non-limiting example, cellulose microfibrils may have diameters in the range of about 5 to about 100 nanometers, combined with lengths providing high aspect ratios, such as in excess of 100, in excess of 500, or in excess of 1,000. While the present specification and claims refer to microfibrils and microfibrillation, the scope of

20 the present invention also includes nanofibrils, and the rheology modification, stabilization, and other properties that may be obtained with microfibrils by practicing the present invention may also be obtained using nanofibrils, either alone or in combination with microfibrils.

The derivatized microfibrillar cellulose of the present invention is

25 characterized by being in microfibrillar form, and by the presence of cationic substituents that provide electrostatic functionality. The amount of substituent present may be quantified by the degree of substitution, or DS. The degree of substitution, which will vary with the molecular weight of the cellulose, is the average number of substituted hydroxyl groups per anhydroglucose unit, while

30 the molar substitution is the average number of substituent groups added per

anhydroglucose unit. The DS determines the solubility of the derivatized cellulose, and may be readily adjusted to obtain a derivatized cellulose that is substantially insoluble in the environment of use, whether aqueous or non-aqueous. While the environment of use will frequently be aqueous, the  
5 derivatized microfibrillar cellulose of the present invention has utility in applications having other solvents or liquid carriers, such as paints, coating, lacquers, oil-rich foods, inks (including but not limited to ink-jet inks), and water-in-oil emulsions.

Any suitable method may be used to obtain the derivatized microfibrillar  
10 cellulose. In particular, the steps of microfibrillation and derivatization to impart electrostatic functionality to the cellulose may be carried out separately or combined to arrive at the end result. Therefore, a non-microfibrillar cellulose starting material may be derivatized with cationic groups and then microfibrillated, or may first be microfibrillated and then derivatized.

15 Alternatively, if the starting material is microfibrillar cellulose, only the derivatizing step would be necessary, whereas if the starting material is a cellulose that has already been properly derivatized with cationic groups, only the microfibrillation step is required.

The degree of substitution of the cellulose should be sufficiently low so that  
20 the derivatized microfibrillar cellulose will be substantially insoluble in the solvent or carrier that is present in the intended environment of use. In many applications the solvent or carrier will be water, and in such applications the degree of substitution should be such that the derivatized microfibrillar cellulose is substantially insoluble in water. However, in other applications a polar solvent  
25 or carrier (such as an alcohol) may be used having different solubility characteristics, or a non-polar solvent or carrier (such as an oil) may be used, and in such cases the degree of substitution should be adjusted to obtain a derivatized microfibrillar cellulose that is substantially insoluble in the solvent or carrier used in the application of interest, which, for purposes of convenience, will  
30 hereafter be referred to as the "solvent of use". Functionally, the derivatized

microfibrillar cellulose should be sufficiently insoluble in the environment of use to provide the desired properties in the intended application.

The presence of substantially insoluble material may be confirmed by observation of a 1-5% suspension of the material in question in the solvent or carrier of use under a light microscope at sufficient magnification to see insoluble material. A size determination may be made by preparing a suspension of the material under consideration at approximately 0.1-0.01% in a liquid non-solvent which is effective in dispersing microfibrils. This suspension is then dried on a transmission electron microscope (TEM) grid; the sample is coated to protect it from electron beam damage, and examined at sufficient magnification and focus to observe structure in the 1-1000 nanometer range. If microfibrillar elements are present they can be detected under these conditions, and the combination of insolubility under the light microscope and microfibrillar structure under the TEM will indicate the presence of substantially insoluble microfibrillar material.

For purposes of simplicity, unless specifically indicated otherwise the term "substituents" shall be used herein to mean chemical species that provide electrostatic functionality to the cellulose through cationic charge. In addition, "electrostatic" means cationic charge. "Derivatization" refers not only to chemical reactions resulting in covalent bonds, but to any process whereby the substituents become sufficiently associated with the cellulose to provide the rheological and other benefits of the present invention, and may include, for example, adsorption. However, "derivatized" does not include the naturally-occurring, de minimis presence of groups that would only provide the electrostatic functionality required by the present invention at concentrations higher than those found in nature.

The sequence of steps used to arrive at the derivatized microfibrillar cellulose of the present invention is not critical. Therefore, the starting material used to make the derivatized microfibrillar cellulose may be in microfibrillar or non-microfibrillar form. Similarly, the starting material may already be derivatized with electrostatic substituents, or not. If the starting material is non-

microfibrillar, substituents may be placed on the cellulose followed by microfibrillation, or the microfibrillation may be carried out first, followed by the placement of the substituents onto the resulting microfibrils. It is also acceptable to process cellulose into fibrils, place the substituents on the fibrils, and then  
5 further process the fibrils into microfibrils. Similarly, any non-microfibrillar form of cellulose which already contains such substituents may be processed into microfibrillar form. Moreover, derivatization and microfibrillation may be carried out simultaneously.

It will be understood that most, if not all, cellulose will contain some  
10 quantity of both microfibrillar and non-microfibrillar structure both before and after processing, and that the ratio between the two structures may range from cellulose that is substantially completely microfibrillar, to cellulose that is substantially completely non-microfibrillar. As used herein, the terms "microfibrillar", "microfibrillated", and the like include celluloses that are  
15 substantially completely microfibrillated, and those which may be substantially microfibrillated while containing minor but significant amounts of non-microfibrillar structure, provided the cellulose is sufficiently microfibrillated to confer the benefits afforded by the present invention.

Processes which minimize the energy needed to produce microfibrils from  
20 non-microfibrillar starting material, and/or which reduce the amount of water extracted during the process or at its end, are preferred. In this regard, it should be noted that while the derivatized microfibrillar cellulose of the present invention can be made by derivatizing a microfibrillated cellulose, the microfibrillation process generally requires less energy, and/or is more efficient,  
25 if the cellulose has already been derivatized. Without being bound by theory, this may be because the presence of electrostatic functionalities on the cellulose 'loosens' the structure of fibril bundles.

The ability to use less energy not only offers cost savings, but results in less breakage of the cellulose microfibrils. Therefore, microfibrillating a cellulose  
30 that has already been derivatized may result in a derivatized microfibrillar



cellulose with relatively longer microfibrils as compared to effecting derivatization after microfibrillation. This is particularly significant because the energy required for microfibrillation can be significantly reduced by amounts of derivatization which are below the level that would render the resulting

5 derivatized microfibrillar cellulose freely soluble in water. For example, derivatization of cellulose resulting in a DS on the order of 0.1 or 0.2 will 'loosen' the fibril bundles enough to permit microfibrillation using conventional shearing devices such as a homogenizer, impingement mixer, or ultrasonicator. These low DS cellulose microfibrils have diameters on the order of 50 nanometers

10 combined with lengths of up to 500 microns, resulting in aspect ratios in excess of 1,000. While the low DS allows microfibrillation, it is too low to allow the resulting material to be fully soluble in the solvent or carrier of use at the concentrations of interest. Without being bound by theory, the presence of insoluble regions in the fibers may explain the data showing maximum gel

15 formation at low DS's. These gels may be strengthened by weak association of the more hydrophobic unsubstituted regions.

The stabilization or derivatization is accomplished by the generation or placement of substituents onto the fibril and/or microfibril. It appears that the substituents become associated predominantly with the surface regions of the

20 fibrils or microfibrils. Regardless of the precise mechanism, in functional terms microfibril-microfibril contact is inhibited by electrostatic mechanisms or forces. The presence of the substituents also causes the microfibrils to occupy more volume than when they are not derivatized, possibly due to inhibition of contact along at least part of the length of the microfibrils. Rheological performance of

25 the resulting derivatized microfibrillar cellulose is enhanced at low concentration since volume is better occupied and the materials are distributed more homogeneously.

Without being bound by theory, the surfaces of the derivatized microfibrils appear to have some areas free of the substituents such that some limited

30 interaction between microfibrils still takes place. Limited interaction may even

be necessary to facilitate network formation, and may be a cause of the rheological attributes of interest such as yield stress, shear reversible gelation, and insensitivity of the modulus to temperature. It also appears that the length/diameter ratio, or aspect ratio, of the fibrils and microfibrils also  
5 contributes to the performance of the materials of the present invention.

Any suitable process may be used to generate or place the substituents on the cellulose. For convenience, the possible processes will generally be referred to collectively as "derivatization" herein; however, within the context of this invention, derivatization is used to mean any process which results in a cellulose  
10 (including fibrillar and microfibrillar cellulose ) having the substituents sufficiently associated with the cellulose to provide the desired benefit(s), and includes not only chemical reactions resulting in covalent bonding, but also physical adsorption. In addition, the present application will refer both to "derivatization" and to "stabilization". Chemically, both terms refer to the same  
15 type of process, namely, the placement or generation of substituents on the cellulosic substrate. Functionally, "derivatization" is generally the broader term, as "stabilization" implies a functionality which is usually observed primarily or exclusively when the cellulose is in microfibrillar form.

Possible derivatization processes include any synthetic method(s) which  
20 may be used to associate the substituents with the cellulose. More generally, the stabilization or derivatization step may use any process or combination of processes which promote or cause the placement or generation of the substituents. For example, the conditions for treating non-microfibrillar cellulose should generally include both alkalinity and swelling of the cellulose, in order to  
25 make the surface of the fibrils more accessible to the placement or generation of the substituents. Alkalinity and swelling may be provided by separate agents, or the same agent may both provide alkalinity and cause swelling of the cellulose. In particular, alkaline agents often serve multiple purposes, in that they may catalyze the reaction between the cellulose and the substituent, optionally de-

protonate the derivative, and swell open the cellulose structure to allow access of the reagents to carry out the derivatization.

Specific chemical methods which may be used to achieve the present invention include but are not limited to generation of cationic groups, such as quaternary amine and/or amine, on or near the surface of the particulate cellulose. Alkaline conditions are preferably obtained by using sodium hydroxide. Any material that functions as a swelling agent for the cellulose may be used, and alternative alkaline agents include alkali metal or alkaline earth metal oxides or hydroxides; alkali silicates; alkali aluminates; alkali carbonates; amines, including aliphatic hydrocarbon amines, especially tertiary amines; ammonium hydroxide; tetramethyl ammonium hydroxide; lithium chloride; N-methyl morpholine N-oxide; and the like. In addition to catalytic amounts of alkaline agent, swelling agents may be added to increase access for derivatization. Interfibrillar and intercrystalline swelling agents are preferred, particularly swelling agents used at levels which give interfibrillar swelling, such as sodium hydroxide at an appropriately low concentration.

These derivatization reactions, if carried out on the original fibrous cellulose structure, may require specific conditions to maximize the efficiency of location of the derivatization onto the surface of the cellulose. For example, in the case of cellulose from wood pulp the concentration of the swelling agent used appears to have an effect on the performance of the final cellulose. In particular, in using sodium hydroxide it has been determined that the level of the sodium hydroxide can have a significant effect on the rheological performance.

It is preferred that derivatization of these fibrous celluloses be performed in a manner which limits the formation of microfibrils which are soluble in the intended end use composition, as these may not contribute significantly to the desired rheological performance. This typically limits the degree of derivatization which can be made where derivatization at higher levels would make the cellulose soluble in the end use composition. Specific limits may be readily determined based on the application in question, but as a matter of

general guidance it is preferred that the degree of substitution (DS) be below about 0.5, or below about 0.35, or below about 0.2, or below about 0.18, or below about 0.15.

5 The derivatization may be carried out in any suitable manner, including but not limited to suspension in water; in organic solvent, either alone or in mixtures with water; in solution; and in high solids, either with water alone or with water and a minor amount of organic solvent. (For purposes of the present disclosure, "high solids" refers to a polysaccharide content of greater than about 25%.

10 Optional derivatizations or functionalities which may also be placed on the cellulose include but are not limited to short chain aliphatic and other hydrophobic-type substitutions; oligomeric and polymeric substitutions; uncharged substitutions, as for example short chain ethylene and propylene glycols; other associative-type functionality; surfactant-like functionality; methyl; ethyl; propyl; and combinations of these. These substitutions are  
15 optional in that they may not be intended for stabilization of the cellulose, and will instead provide additional functionality such as surface activity, emulsification power, adsorption characteristics, and the like.

The method for processing a non-microfibrillar form of cellulose into the microfibrillar form may be carried out before, during, or after the derivatization  
20 reaction. The preferred method involves the use of a homogenizer on a dilute suspension of the non-microfibrillar cellulose in an aqueous medium. The aqueous medium optionally may have additives such as swelling agents, in particular interfibrillar and/or intercrystalline swelling agents, for example sodium hydroxide, to aid in improving the ease of microfibril generation. A  
25 more preferred method of microfibrillation involves the use of mechanical energy on an aqueous suspension of derivatized cellulose which has not been dried. Other microfibrillation processes include, by way of non-limiting example, use of an impingement mixer; heat; steam explosion; pressurization-depressurization cycle; freeze-thaw cycle; impact; grinding (such as a disc grinder); pumping;  
30 mixing; ultrasound; microwave explosion; and milling. Combinations of these

may also be used, such as milling followed by homogenization. Essentially any method of reducing particle size may be used, but methods for reducing particle size while preserving a high aspect ratio in the cellulose are preferred. As described previously, the degree of substitution of the cellulose also affects the ease of processing the cellulose to microfibrillar form.

The process to generate the particulate may either be run by the consumer in the final application such that the particulate is generated in situ, or be run as described above in aqueous media, the material dehydrated, and the resulting particulate dried. The dried particulate of this invention, hereafter referred to as the ready-to-gel or RTG form, can be rehydrated readily in polar solvents to obtain the desired rheological attributes. Dehydration can be accomplished by displacing water with less polar solvents and drying.

In terms of general properties, applications where the derivatized microfibrillar celluloses of the present invention have particular utility include those where the desired rheological attributes include at least one of yield stress, shear reversible gelation, and a modulus which is insensitive to temperature. The ability to provide the rheological attributes described herein also makes it possible to provide stabilization of mixtures of liquids and solids having different densities; gel-like properties; pumpable gels; stabilization at elevated temperatures; and, control of hydration and diffusion.

In terms of more specific applications or fields of use, the utility of the present derivatized microfibrillar cellulose includes, without limitation, foods, personal care products, household products, pharmaceuticals, nutraceuticals, paper manufacture and treatment, coating compositions, water and wastewater treatment, drilling fluids, agriculture, construction, and spill control and/or recovery. Use in food applications is also possible, subject to satisfactory resolution of any concern regarding introduction of cationic materials into substances intended for consumption.

In food applications, the derivatized microfibrillar celluloses of the present invention may be useful as rheology modifiers; as stabilizers, such as by

inhibiting creaming or settling in suspensions; and as non-digestible dietary fiber.

They may also be used to control ice crystal growth during, for example, ice cream manufacture and storage.

In personal care products, the derivatized microfibrillar cellulose may be  
5 used to stabilize emulsions, dispersions, suspensions, and foams, and may find  
use in creams, lotions, gels, and pastes, including those intended for epidermal  
application (it should be noted that the derivatized microfibrillar cellulose of the  
present invention has substantivity to biological surfaces, including but not  
limited to skin, hair, and nails). Representative but not exhaustive examples  
10 include sunscreens; moisturizing or anti-aging creams and lotions; cleaning soaps  
or gels; antiperspirants and deodorants, including those in stick, pump spray,  
aerosol, and roll-on form; fragrance releasing gels; lipsticks, lip glosses, and  
liquid makeup products; oral care products, including toothpastes, tooth polishing  
and whitening agents, and denture care products such as cleaners and adhesives,  
15 and further including use in sorbitol, sorbitol-water mixtures, and glycerol-water  
mixtures; products where controlled, sustained, or delayed release of an  
ingredient would be desirable; wound care products, such as ointments (including  
anesthetic, antiseptic, and antibiotic ointments), dressings, and products such as  
ostomy rings where good liquid retention is desirable; and absorbent products,  
20 such as diapers. The present invention may have particular utility, not only in  
personal care products but in other applications, with products dispersed by a  
pumping action. The shear-reversible gelation exhibited by the derivatized  
microfibrillar cellulose is well suited for pump dispensing, and may be  
advantageously combined with its ability to stabilize emulsions, dispersions, and  
25 foams to improve the uniform delivery of product.

In the area of household products, the rheological properties of the present  
derivatized microfibrillar celluloses, and their ability to stabilize emulsions,  
dispersions, and foams, provide utility in areas such as detergents, shampoos,  
cleaners, and air fresheners. Specific examples include, without limitation,  
30 laundry products (including detergents, pre-spotting cleaners, and fabric

treatment compositions, such as softeners); rug and upholstery shampoos; toilet bowl cleaners (particularly those dispensed in liquid or gel form); air fresheners; and general purpose cleaning agents, including liquids, gels, pastes, and foams used in cleaning and/or disinfecting household surfaces.

5           In pharmaceutical applications, the derivatized microfibrillar cellulose may have utility in controlled, sustained, or delayed release formulations (including epidermal patches used for slow and/or prolonged release of one or more active ingredients); as disintegrants; as dietary fiber; in wound care, particularly in applications (such as ostomy rings) where liquid-holding ability is important; and  
10 as rheology modifiers.

          In the area of paper manufacture and treatment, the derivatized microfibrillar cellulose of the present invention has utility in emulsion modification and/or stabilization; sizing; retention; clarification; absorbence; drainage; formation (such as by functioning as a flocculation aid); deposit or  
15 scale control (by inhibiting the formation and/or growth of inorganic deposits); water and wastewater treatment; dewatering; film and membrane formation; polyelectrolyte cross-linking; removal of detrimental organic and/or inorganic materials; in paper coatings; and in improving properties such as stiffness, wet strength, absorbancy, softness, toughness, tear resistance, and fold resistance.

20           In the context of paper manufacture, scale control refers to the prevention of calcium carbonate and calcium oxalate deposits forming during the pulping process. Scale control can be achieved by dispersion of salt crystals in the medium to prevent growth and deposition, inhibition of nucleation, or modification of the crystal growth mechanism to prevent the formation of crystal  
25 forms that will lead to deposits. The use of derivatized microfibrillar cellulose having micron and smaller particle size, stabilized with appropriate functional groups, would serve to control scale deposit because such microcarriers inhibit the crystal growth which leads to deposition. Moreover, cellulosic materials would be easier to recover from the pulping process due to their organic nature.  
30 Preferred functional groups would include amines. Alternative functional groups

and appropriate use levels may be readily determined by those of ordinary skill in the art, based on the particular environment of use.

The derivatized microfibrillar cellulose may also be used in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; to retain organic and/or inorganic dispersed particles (such as pulp fines, fillers, sizing agents, pigments, and/or clays); to retain detrimental organic and inorganic particulate materials; to improve the uniformity of formation of a sheet of paper; and to improve the strength of a sheet of paper. With particular regard to drainage, drainage aids are additives that increase the rate at which water is removed from a paper slurry on a paper machine. These additives increase machine capacity, and hence profitability, by allowing faster sheet formation. Charged microfibrillar cellulosic derivatives are capable of greatly increasing drainage, either alone or in combination with other charged polymers.

The derivatized microfibrillar cellulose of the present invention may also be used in coated papers, where cellulose derivatives may be used to control the rheology of the color coating and to provide water retention, thereby controlling the amount of liquid that permeates into the base sheet.

In coating compositions, such as paints and inks, the derivatized microfibrillar cellulose can provide rheology modification, improving properties such as spatter, leveling, sag resistance, flooding, and floating, and may have particular utility in gel paints. It may also improve pigment dispersion and/or stabilization, and function as charge control or flow control agents, including in inks, such as ink jet inks.

In the area of water treatment, the derivatized microfibrillar cellulose of the present invention can provide scale control, that is, inhibiting the formation and/or growth of inorganic deposits in aqueous systems; clarification; flocculation; sedimentation; coagulation; charge delivery; and softening.



In drilling fluids, the present derivatized microfibrillar cellulose can provide rheology modification, reduce or prevent fluid loss, and improve secondary oil recovery.

5 In agricultural applications, the derivatized microfibrillar cellulose of the present invention can be used in soil treatment, and may provide moisture retention, erosion resistance, frost resistance, and controlled, sustained, or delayed release of agricultural materials such as fertilizers, pesticides, fungicides, and herbicides. It may also be used for crop protection, such as to minimize or prevent frost damage.

10 In construction, derivatized microfibrillar cellulose can be used in dry wall muds, caulks, water-soluble adhesives, and board manufacture.

In other areas, derivatized microfibrillar cellulose can be used for control and cleanup of liquid spills; as absorbents for oil; as stabilizers for emulsions, dispersions, and foams (including but not limited to oil-in-water and water-in-oil emulsions); and for emulsification. Stability of commercial emulsions, such as paper size emulsions, is a recurring issue in industry. Current commercial emulsions include those which generally consist of an oil, waxy, or rosin phase dispersed in water. These dispersions are generally stabilized by the addition of charged materials such as cationic starches, sodium lignin sulfonate, and aluminum sulfate. Such materials are generally added in amounts equal to about 10-20% by weight of the size component. The resulting dispersions are typically 0.2 to 2 micron particles, thought to be stabilized by charge repulsion, for example, with the positively charged starches on particle surfaces repelling each other.

25 One cause of emulsion failure is density-driven separation. This can be limited by increasing viscosity, or internal structure within the fluid. For example, an emulsion which maintains a viscosity of less than about 20 centipoise throughout a standard aging test might have its viscosity increased initially by as much as 100 centipoise through addition of a viscosifier to the

formulation, and still be within acceptable commercial viscosity, provided that the viscosity did not then increase over time to exceed acceptable limits.

One method to accomplish this result would be to use a viscosifying agent that does not cause a substantial increase in viscosity when first added to an emulsion formulation, but which does provide an increase in viscosity during normal processing of the emulsion formulation to produce the emulsion. This can be accomplished by including, as an additive to the emulsion formulation, cellulose that has been derivatized as described herein but not yet microfibrillated. When the emulsion formulation is then subjected to energy, typically high shear, during the processing used to turn the emulsion formulation into an emulsion, the shear will also microfibrillate the derivatized cellulose, resulting in the derivatized microfibrillar cellulose of the present invention, which will be present as part of the emulsion. The gel produced by the derivatized microfibrillar cellulose will then thin under shear stress but re-form when shear stops. Moreover, the insolubility of such low DS cellulose may cause it to concentrate at the oil/water interface of oil-and-water emulsions, rather than the aqueous bulk phase, which may be desirable.

Effectively the same result may be achieved by adding the derivatized microfibrillar cellulose of the present invention to an emulsion formulation, or to the final emulsion, or at any point during production of the emulsion. Further variations would include introducing derivatized cellulose that is only partially microfibrillated into the emulsion-making process at a point where subsequent processing would provide sufficient energy to complete the microfibrillation. It may also be possible to accomplish some or all of the derivatization as part of the emulsion production process; for example, the emulsion formulation may include a charged species that will adsorb onto the cellulose microfibrils, or such a species may be added during processing of the emulsion formulation, separately or in combination with the cellulose. Therefore, the derivatized microfibrillar cellulose of the present invention may serve as a stabilizing additive to

emulsions, with several process routes being available to accomplish this end result.

While the choice of method may cause some variation in the properties of the resulting emulsion, the basic benefit of improved emulsion stability should be achieved by any procedure which has, as its final result, the presence of the derivatized microfibrillar cellulose of the present invention in the final emulsion.

Commercially, it may be desirable to supply customers with derivatized, non-microfibrillated cellulose as a powder which, when added to a formulation and subjected to high shear or other appropriate forms of energy, will microfibrillate and yield the derivatized microfibrillar cellulose of the present invention.

This improved emulsion stability may enable use of emulsion formulations which would not perform satisfactorily in the absence of the derivatized microfibrillar cellulose. Other benefits may include improved retention in paper, improved drainage of water from paper systems due to association of fillers and pulp fines with the retained microfibrils, and resistance to emulsion breakage in the presence of high salt concentrations.

The subject electrostatically derivatized materials of this invention have also been discovered to provide rheology to aqueous systems over a wide range of pH and ionic strength. This insensitivity to pH and ionic strength facilitates use in areas where low pH and high salt conditions exist, such as in personal care creams and lotions, food products, and the like.

In addition to the above, the derivatized microfibrillar cellulose of the present invention represent a vehicle for providing cationic charge to a given environment. This may include utility in water and wastewater treatment, where charged particles may be used to remove color bodies and to flocculate particulates and other contaminants. Thus, by way of non-limiting example, a suitable amount of the derivatized microfibrillar cellulose may be added to water (or to an aqueous system) that is contaminated with anionic material and/or color bodies; allowed to bind or complex with the contaminants, optionally with mixing and/or heating; and physical, chemical, and/or other conventional

separation techniques may then be used to separate the bound or complexed cellulose/contaminant combination from the water. While any amount of derivatized microfibrillar cellulose would facilitate removal of some amount of contaminant from the water, in order to have the most effect the amount of derivatized microfibrillar cellulose should preferably be at least equal to the stoichiometric equivalent necessary to bind or complex with the measured or estimated concentration of the contaminant whose separation or removal is desired.

The following examples indicate various possible methods for making and using the derivatized microfibrillar cellulose of the present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications. Throughout this description, "gelling" is defined to occur when  $G' > G''$ , where  $G'$  is the dynamic storage modulus and  $G''$  is the dynamic loss modulus. This is the functional definition used in EP '011; for general background, see Ferry, J.D., Viscoelastic Properties of Polymers, John E. Wiley & Sons, NY, 1980.

The following examples indicate various possible methods for making and using the derivatized microfibrillar cellulose of present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications.

### Example 1

#### Preparation Of A Quaternary Amine Functionalized Cellulose (QAC).

Isopropanol (IPA) and deionized (DI) water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. Bleached sulfate wood pulp (approximately 400  $\mu\text{m}$  length, 5.2% moisture)(Wayerhauser Company) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which

the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15°C.

The reactor was then inerted, and aqueous NaOH (50% NaOH) was slowly added to the reactor while maintaining the mixture slurry's temperature at or below 15°C. The slurry was agitated for 1 hour after completion of caustic addition. Dow Quat 188 (3-chloro-2-hydroxypropyl trimethylammonium chloride, Dow Chemical Company, Midland, MI) (65% in water) was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at 15° C. After Dow Quat addition, the reaction slurry was heated to 70° C and held for 1 hour. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times.

The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was broken into small particles using a rubber spatula and then dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen.

25 Table 1: QAC Recipes  
(all weights in grams)

Quaternary Amine Functionalized Cellulose							
Sample #	Cellulose Length	Wt. Cellulose (dry wt. Basis)	Wt. IPA	Wt. H <sub>2</sub> O	Wt. 50% NaOH (aq)	Wt. Dow Quat 188 (65% aq. Soln)	DS
1	~400 μm	65	750	110	18.46	58.02	0.02

Quaternary Amine Functionalized Cellulose							
Sample #	Cellulose Length	Wt. Cellulose (dry wt. Basis)	Wt. IPA	Wt. H <sub>2</sub> O	Wt. 50% NaOH (aq)	Wt. Dow Quat 188 (65% aq. Soln)	DS
2	~400 μm	65	750	110	13.84	43.52	0.03
3	~400 μm	65	750	110	23.07	72.53	0.03
4	~200 μm	65	750	110	18.46	58.02	0.07
5	~200 μm	65	750	110	18.46	58.02	0.08
6	~200 μm	65	750	110	23.07	72.53	0.11
7	~400 μm	65	750	110	23.07	72.53	0.11
8	~400 μm	65	750	110	23.07	72.53	0.11
9	~400 μm	65	750	110	23.07	72.53	0.12
10	~400 μm	65	750	110	23.07	72.53	0.13
11	~200 μm	65	750	110	23.07	72.53	0.14
12	~400 μm	65	750	110	N/A	N/A	0.25

**Slurry preparation:** An 800 g 1% slurry was made from each Sample in Table 1 using the following materials:

		<u>Weight</u>	<u>Weight%</u>
5	QAC	8.00 grams	1.0 ±
	0.06%		
	Germaben® II biocide (Sutton Laboratories, New Jersey)	4.00 grams	0.5%
	<u>Deionized water</u>	<u>788.00 grams</u>	<u>98.5 ±</u>
10	<u>0.06%</u>		
	Total	800.00 grams	

The container was closed and shaken to wet and disperse the QAC solids. The solids will settle if left standing, so the container was shaken just prior to pouring the slurry into the homogenizer.

- 15 **Homogenization of QAC slurries:** The suspension was processed in the homogenizer equipped with an agitated feed pot as follows: the homogenizer was turned on before the slurry was loaded. An 800-gram slurry was processed for about 20 minutes at about 3000 psi by recycling the discharged stream from the homogenizer to the feed pot. Pressure was monitored and appropriate

adjustments made to the primary stage handwheel to keep the total pressure at about 3000 psi. After the processing was completed, the discharge tube was redirected so that the sample was collected and stored in a capped jar.

**Rheological testing of microfibrillated QAC:** each microfibrillated QAC sample prepared in Example 1 was then tested for rheological properties. Data was collected on a Bohlin CS Rheometer (Bohlin Instruments, Cranbury, New Jersey). Dynamic mechanical properties were measured including the dynamic storage modulus, the dynamic loss modulus, complex viscosity, and yield stress.

Rheometer Test Conditions

10 Temperature Sweep: Measuring System: PP 40; 25° C - 65° C; Shear Stress: automatic; Frequency: 1 Hz; Temperature Ramp Rate: 5° C/60 seconds; Measurement Interval: 20 seconds; Gap: 1 mm.

Yield Stress Test: Measuring System: CP 4/40; Stress: 6.0E-02 - 1.0E+02; Sweep Time: 60.0 seconds; Number of Steps: 30; Temperature: Manual (25° C); No of measurements: 1; Measurement Interval: 5 seconds.

15 Stress Sweep Test: Measuring System: PP 40; Temperature: Manual (25 °C); Number of Measurements: 1; Gap: 1 mm; Measurement Interval: 5 seconds; Frequency: 1 Hz.

Table 2: Rheology of Microfibrillated QAC

Sample #	Cellulose Length	DS of Quat-Cellulose	YIELD STRESS(Pa)	G' @ 5.75 Pa(Pa)	G' @25° C/50° C(Pa)	Homogenizer Processing Time(minutes)
1	~400 $\mu$ m	0.02	NONE			20
2	~400 $\mu$ m	0.03	NONE			20
3	~400 $\mu$ m	0.03	NONE			20
4	~200 $\mu$ m	0.07	38.0	572	619/633	25
5	~200 $\mu$ m	0.08	44.7	489	468/450	30
6	~200 $\mu$ m	0.11	51.4	480	505/530	25
7	~400 $\mu$ m	0.11	38.0	622	621/646	15
8	~400 $\mu$ m	0.11	34.7	482		20
9	~400 $\mu$ m	0.12	68.0	500	488/487	20
10	~400 $\mu$ m	0.13	18.1	420		20
11	~200 $\mu$ m	0.14	21.4	497	577/592	15
12	~400 $\mu$ m	0.25	51.4	106	119/131	30

### Example 2

#### Ready-To-Gel(RTG) Process For Quaternary Amine Cellulose

5 Gels are made as described in the "Slurry preparation" and "Homogenization of QAC Slurries" steps in Example 1. The gels are then processed as follows:

The following description pertains to Sample #1 in the data table. A similar procedure was used for all of the other samples.

10 Approximately 2800 ml of IPA was added to a grounded 12-quart stainless steel (SS) beaker. The IPA was stirred at the top speed of an overhead stirrer driven by house air. A SS cowls blade on an SS shaft was used to stir the IPA. Next, approximately 1400 grams of 1% QAC gel was slowly added to the stirring IPA. The material ratio is 2 ml IPA/1 gram gel. The beaker was covered with  
15 Saran Wrap and the slurry was stirred for ten minutes.

When ten minutes had passed, the slurry was filtered through a synthetic straining cloth. The slurry was filtered using gravity. The slurry was covered with Saran Wrap during the filtration to reduce IPA evaporation. Occasionally the gel on the cloth was stirred with a plastic spatula to help speed filtration. When it



appeared that the filtration had gone about as far as it could, the wet cake was transferred back to the 12 quart SS beaker.

A fresh amount of approximately 2800 ml IPA was added to the beaker and the slurry was again stirred for ten more minutes with the cowls blade/air stirrer.

5 The slurry was then filtered on a 20 cm Buchner funnel with #415 VWR filter paper. The wet cake was transferred to a glass crystallization dish. The dish containing the wet cake was placed into an 80° C oven under vacuum overnight for drying. The sample was dried to constant weight, and the solids were ground in a Waring Blender.

10 The dehydrated gels were examined by rehydration as follows: a premix of deionized water and Germaben II was prepared.

	<u>Weight</u>	<u>Weight%</u>
Deionized water	788.00 grams	99.49%
Germaben II biocide	4.00 grams	0.51%

15 The water/Germaben II solution was then weighed into a small Waring blender cup along with the ready-to-gel dry QAC.

	<u>Weight</u>	<u>Weight%</u>
water/Germaben	29.70 grams	99.0%
Ready-to-gel QAC	0.30 grams	1.0%

20 The blender cup was covered and the sample was mixed until it appeared to be homogeneous. The resulting gel was transferred to a glass jar. It was then shaken on a vortex mixer.

**Rheological testing:** Same as described in example 1.

25 Table 3: Rheology of RTG QAC

Sample #	DS of QAC	YIELD STRESS (Pa)	G' @ 5.75 Pa (Pa)
1	0.09	61.4	385

**Rheological properties as a function of concentration:** a series of gels were prepared from a 1% QAC (DS 0.09) by diluting with DI water.

Table 4: Rheology of RTG QAC by Concentration

Sample #	QAC Concentration (wt%)	G' @ 5.75 Pa (Pa)
1	1	246
2	0.5	35.6
3	0.25	0.475
4	0.1	0.136

G' > G'' in all samples (1 - 4); see Figures 1 to 4, respectively.

**Stable water/oil emulsions containing QAC:** cetyl trimethyl ammonium

- 5 bromide was mixed with deionized water. The CTAB solution was added to 1% quaternary amine (DS=0.15) functionalized microfibrillated cellulose gel prepared as in Example 1. The mixture was stirred in a Waring Blender for 3 minutes on high speed. The sample remained a gel. This gel was processed through a Gaulin homogenizer, 1 pass at 4000 psi. Ten percent (10%) miglyol emulsions were prepared from the gels by adding miglyol and deionized water to  
10 the gel and mixing with a rotary mixer for 4 minutes. The resulting emulsions were aged in a 50° C oven.

Table 5: Stability of Water/Oil Emulsions

10% Miglyol Emulsion	Stability at 50° C
0.45% QAC/0.008% CTAB	> 3 weeks
0.90% QAC/0.016% CTAB	> 3 weeks

- 15 **Use in paper sizing compositions:** the following examples relate to use of QAC as made in example 1 having a DS of about 0.10 in connection with compositions used in paper sizing.

### Example 3

- 20 A 600 ml beaker was used to combine 66.0 grams of Precis® 787 ketene dimer (available from Hercules Incorporated, Wilmington, Delaware; Precis is a registered trademark of Hercules Incorporated), 1.5g of QAC, and 232.5 grams of deionized (DI) water. The mixture was stirred, and then passed through a

Microfluidics Corporation Model M110 Series impingement mixer (Microfluidics Corp.) with its pressure set at 5000 PSI. The emulsion was collected, and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, the jar was capped, and then cooled in a 5 to 15° C water bath.

#### Example 4

Three grams of QAC were dispersed in 465g of DI water for 5 minutes using a Tekmar Ultra-turax SD45 rotor-stator high shear mixer (Tekmar Company, Cincinnati, Ohio) at a power setting of 50. The resulting materials was then given three passes through the impingement mixer at 5000 psi. As in Example 3, 66.0 g of Precis were combined with 234.0 g of QAC in DI water gel, stirred using the high shear mixer at a power setting of 50, then given two passes through the impingement mixer at 5000 psi and cooled in a 5 to 15° C water bath.

#### Example 5.

Four (4.0) grams of QAC was dispersed in 400g of DI water for 5 minutes using the high shear mixer at a power setting of 50, then given three passes through the impingement mixer at 5000 psi to create a gel. A 44% emulsion of Precis ketene dimer was made by combining 176.0 grams of Precis 787 ketene dimer with 224.0 grams of DI water in a wide mouth jar; the pre-mix was sheared in a high shear mixer for 5 minutes at a power setting of 50, the resulting material was quickly poured into the feed chamber of the impingement mixer, and, with mechanical stirring set at about 250 RPM, the premix was passed twice through the impingement mixer set at 5000 psi. Next, 150.0 g of the QAC gel was combined with 150.0 g of the Precis ketene dimer 44% emulsion and stirred for 5 minutes using the high shear mixer at a power setting of 50.

The following table provides testing results for the sample emulsions using TAPPI standard Method T560:

Table 6: Surface Sizing of Example 3 through Example 5 Size Emulsions  
(formulation weight in grams)

			(Pre-shear)
Designation		( MF gel)	( MF gel)
Example	3	4	5
Precis 787	66.00	66.00	66.00
QAC	1.50	1.50	1.50
DI Water	232.50	232.50	232.50
Total	300.0	300.0	300.0
Tekmar Shearing cond.	2 min.@ 50	2 min.@ 50	2 min.@ 50
Microfluidizer shearing	2X @ 5kpsi	2X @ 5kpsi	
Tekmar Gel Shearing		5 min.@ 50	5 min.@ 50
Microfluidizer Gel Shear		3X @ 5kpsi	3X @ 5kpsi
Calc. % Actives	22.00	22.00	22.00
IRAQ % Actives	NA	14.9	NA
pH	2.42	2.60	2.75
@temp	20.7	21.0	26.80
Particle size	0.75	0.97	Failed
Particle size Sonicated	0.70	0.63	Failed
Zeta Potential	-58.3	-57.9	Failed
Brookfield Visc.	Failed	119.3	Failed
	"Failed" means emulsion broke prior to testing.		

**Drainage Aids in Paper Manufacture:** the following examples

- 5 demonstrate the effectiveness of derivatized microfibrillar cellulose as a drainage-improvement aid.

Drainage measurements were performed on a Canadian Standard Freeness (CSF) tester, using a bleached kraft pulp consisting of 70% hardwood and 30% softwood. All freeness testing was performed in hard water having a pH of 7.95-  
10 8.05, alkalinity of 50 ppm (as calcium carbonate), and hardness of 100 ppm (as calcium carbonate) using TAPPI method T 227 om-92. A pulp consistency of 0.3% was used. Higher CSF values indicate better (faster) drainage.

The following results were obtained using microfibrillated quaternary amine cellulose (MFQAC), alone and in combination with microfibrillar

carboxymethyl cellulose (MFCMC). The preparation of MFCMC is described in U.S. patent application serial number 09/248,246, filed February 10, 1999, the disclosure of which is hereby incorporated in its entirety by reference thereto. The MFQAC had a degree of substitution of about 0.09, while the MFCMC had a  
 5 degree of substitution of about 0.17 charge group per anhydroglucose unit. All loadings are calculated as percent of additive (dry basis) relative to pulp.

### Example 6

MFQAC alone.

10	<u>% MFQAC</u>	<u>CSF</u>
	0.00	211
	0.05	264
	<u>% MFQAC</u>	<u>CSF</u>
	0.10	315
15	0.20	388
	0.30	451
	0.40	491
	0.50	509

20

### Example 7

MFQAC (0.2% loading) with Hercules Reten®1523H anionic polyacrylamide resin:

	<u>% Reten®1523H</u>	<u>CSF</u>
	0.000	464
	0.003	464
25	0.006	503
	0.009	513
	0.012	526

**Example 8**

MFQAC with MFCMC

	% MFQAC (based on pulp)	CSF VALUES	
		0% MFCMC	0.05% MFCMC
5	0.00	211	N/A
	0.10	315	432
	0.20	388	518
	0.40	491	612

10

In addition to the examples provided above, QAC may be produced with a range of alternative cellulose sources, including Avicel® pH-101NF (-90); Solka® Flocc (grade 300 FCC), which may be obtained from Fiber Sales & Development Corp., Urbana, Ohio; and Bleached CTMP (Chemical  
 15 Thermomechanical Pulp) Fluff, which may be obtained from SCA Graphic Sundsvall AB, Timra, Sweden.

The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was merely illustrative, and in no way constitutes any limitation on the  
 20 scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing from the scope of the present invention.

**WHAT I/WE CLAIM IS:**

1. A derivatized microfibrillar cellulose, derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized  
5 microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.
2. The derivatized microfibrillar cellulose of claim 1, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers,  
10 newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.
3. The derivatized microfibrillar cellulose of claim 2, wherein said cellulose is obtained from at least one of purified, optionally bleached wood  
15 pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.
4. The derivatized microfibrillar cellulose of claim 1, wherein said substituent comprises an amine.
5. The derivatized microfibrillar cellulose of claim 4, wherein said  
20 substituent comprises a quaternary amine.
6. The derivatized microfibrillar cellulose of claim 1, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 100% in water.
7. The derivatized microfibrillar cellulose of claim 6, wherein said  
25 derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 50 % in water.
8. The derivatized microfibrillar cellulose of claim 1, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of less than about 1% in water.

9. The derivatized microfibrillar cellulose of claim 8, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.
10. The derivatized microfibrillar cellulose of claim 1, further comprising a solvent, wherein said derivatized microfibrillar cellulose is substantially insoluble in said solvent.
11. The derivatized microfibrillar cellulose of claim 10, wherein said solvent is water, alcohol, or oil.
12. The derivatized microfibrillar cellulose of claim 11, wherein said solvent is water.
13. The derivatized microfibrillar cellulose of claim 1, having a degree of substitution of less than about 0.5.
14. The derivatized microfibrillar cellulose of claim 13, wherein said degree of substitution is less than about 0.35.
15. The derivatized microfibrillar cellulose of claim 14, wherein said degree of substitution is less than about 0.2.
16. The derivatized microfibrillar cellulose of claim 15, wherein said degree of substitution is less than about 0.18.
17. The derivatized microfibrillar cellulose of claim 16, wherein said degree of substitution is less than about 1.15.
18. The derivatized microfibrillar cellulose of claim 13, wherein said degree of substitution is between about 0.02 and about 0.5.
19. The derivatized microfibrillar cellulose of claim 18, wherein said degree of substitution is between about 0.05 and about 0.2.
20. Microfibrillar 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose having a degree of substitution of between about 0.10 and about 0.20.
21. A comestible composition of matter comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides



cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

22. The comestible composition of matter of claim 21, in the form of a low fat, reduced fat, or fat-free mayonnaise.

5 23. The comestible composition of matter of claim 22, in the form of a salad dressing.

24. The comestible composition of matter of claim 21, further comprising a pharmaceutically active ingredient.

10 25. The comestible composition of claim 24, wherein said derivatized microfibrillar cellulose at least partially provides controlled, sustained, or delayed release of said pharmaceutically active ingredient.

15 26. A non-comestible composition of matter comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

27. The non-comestible composition of matter of claim 26, in the form of a wound care product.

28. The non-comestible composition of matter of claim 27, wherein said wound care product is a wound dressing.

20 29. The non-comestible composition of matter of claim 27, wherein said wound care product is an ostomy ring.

30. The non-comestible composition of matter of claim 26, in the form of a skin care lotion or cream.

25 31. The non-comestible composition of matter of claim 26, in the form of a sunscreen lotion or cream.

32. The non-comestible composition of matter of claim 26, in the form of an oral care composition.

33. The non-comestible composition of matter of claim 32, wherein said oral care product is a toothpaste.

34. The non-comestible composition of matter of claim 26, in the form of a hair care composition.

35. The non-comestible composition of matter of claim 26, further comprising a fertilizer, herbicide, fungicide, or pesticide.

5 36. The non-comestible composition of matter of claim 35, wherein said derivatized microfibrillar cellulose at least partially provides controlled, sustained, or delayed release of said fertilizer, herbicide, or pesticide.

37. The non-comestible composition of matter of claim 26, in the form of a drilling fluid.

10 38. A paper composition comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 39. The paper composition of claim 38, wherein said derivatized microfibrillar cellulose is microfibrillar 2-hydroxy-3-(trimethylammonium chloride) – propylcellulose.

40. A method for producing derivatized microfibrillar cellulose, said method comprising at least one of the following:

20 a) a derivatizing step of treating a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose;

b) a microfibrillizing step of treating a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose; or,

c) a step of microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously,

25 wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

30 41. The method of claim 40, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps,

chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

5           42.     The method of claim 41, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

          43.     The method of claim 40, comprising the steps of:

10           a)     derivatizing cellulose with 3-chloro-2-hydroxypropyl trimethylammonium chloride under alkaline conditions to produce 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose;

          b)     suspending the 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose in water to form a suspension; and

15           c)     homogenizing said suspension to produce microfibrillated 2-hydroxy-3-(trimethylammonium chloride) – propylcellulose.

          44.     The method of claim 40, wherein said derivatizing step comprises contacting a non-microfibrillar cellulose with a swelling agent.

20           45.     The method of claim 44, further wherein said contacting takes place under alkaline conditions.

          46.     The method of claim 44, wherein said swelling agent is an anionic reagent.

25           47.     The method of claim 46, further wherein said alkaline conditions comprise contacting the cellulose with said anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof.

30           48.     The method of claim 40, wherein said derivatizing step takes place at high solids.

49. The method of claim 40, wherein said cationic charge comprises the presence of amine groups.

50. The method of claim 40, wherein said derivatizing step comprises derivatizing the cellulose with a quaternary amine reagent.

5 51. The method of claim 40, wherein said derivatized microfibrillar cellulose comprises quaternary amine cellulose.

52. The method of claim 40, wherein said microfibrillizing step comprises applying energy to said cellulose under conditions sufficient to produce microfibrillar cellulose.

10 53. The method of claim 52, further comprising enzyme-treating said non-microfibrillar cellulose prior to said microfibrillizing step

54. The method of claim 52, comprising applying at least one of homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and  
15 milling to said non-microfibrillar cellulose.

55. The method of claim 54, comprising passing said non-microfibrillar cellulose through a homogenizer under conditions sufficient to produce microfibrillar cellulose.

56. The method of claim 55, wherein said conditions comprise passing  
20 said non-microfibrillar cellulose through a pressure differential of at least about 3,000 psi.

57. The method of claim 56, further comprising passing said non-microfibrillar cellulose through said homogenizer at least three times.

58. The method of claim 40, wherein said derivatized microfibrillar  
25 cellulose forms a gel throughout a concentration range of from about 0.01 % to about 100% in water.

59. The method of claim 58, wherein said derivatized microfibrillar cellulose forms a gel throughout a concentration range of between about 0.01 % and about 50 % in water.

60. The method of claim 40, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water.

61. The method of claim 60, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of about 0.9% in water.

62. The method of claim 40, wherein said derivatized microfibrillar cellulose is substantially insoluble in the solvent of use.

63. The method of claim 62, wherein the solvent of use is water.

64. The method of claim 63, wherein said derivatized microfibrillar cellulose is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

65. The method of claim 64, wherein said degree of substitution is less than about 0.35.

66. The method of claim 65, wherein said degree of substitution is less than about 0.2.

67. The method of claim 66, wherein said degree of substitution is less than about 0.18.

68. The method of claim 67, wherein said degree of substitution is less than about 1.15.

69. The method of claim 64, wherein said derivatized microfibrillar cellulose has a degree of substitution of between about 0.02 and about 0.5.

70. The method of claim 69, wherein said degree of substitution is between about 0.05 and about 0.2.

71. The method of claim 43, wherein said 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose has a degree of substitution of less than about 2.0.

72. The method of claim 71, wherein said degree of substitution is less than about 0.35.

73. The method of claim 72, wherein said degree of substitution is between about 0.02 and about 2.0.

74. The method of claim 73, wherein said degree of substitution is between about 0.1 and about 0.2.

75. Derivatized microfibrillar cellulose produced by the method of claim 40.

5 76. Derivatized microfibrillar cellulose produced by the method of claim 43.

77. The derivatized microfibrillar cellulose of claim 40, wherein said cationic charge comprises the presence of amine groups.

10 78. A method of modifying the rheological properties of a composition of matter, said method comprising the step of incorporating, into said composition of matter, derivatized microfibrillar cellulose that is derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 79. The method of claim 78, wherein said composition comprises a liquid.

80. The method of claim 79, wherein said liquid is water.

20 81. The method of claim 80, comprising using said derivatized microfibrillar cellulose in an amount effective to provide scale control and/or corrosion control.

82. The method of claim 78, wherein said rheological properties are at least one of viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

25 83. The method of claim 78, wherein said composition of matter is a food, pharmaceutical, nutraceutical, personal care, fiber, paper, paint, coating, or construction composition.

84. The method of claim 83, wherein said composition of matter is an oral care product.

30 85. The method of claim 83, wherein said composition of matter is a cream or lotion for epidermal application.

86. The method of claim 85, wherein said composition of matter is moisturizing, night, anti-age, or sunscreen cream or lotion.

87. The method of claim 83, wherein said composition of matter is a food spread.

5 88. The method of claim 87, wherein said food spread is a reduced fat, low fat, or fat free food spread.

89. The method of claim 88, wherein said food spread is a reduced fat, low fat, or fat free mayonnaise.

10 90. The method of claim 83, wherein said composition of matter is a drilling fluid.

91. A method of improving the physical and/or mechanical properties of a coating composition by incorporating, into said coating composition, an effective amount of a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized  
15 microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

92. The method of claim 91, wherein said physical and/or mechanical properties include at least one of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

20 93. The method of claim 92, wherein said derivatized microfibrillar cellulose complexes, adsorbs, precipitates, or otherwise renders inactive dissolved detrimental substances.

94. A method of improving at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency,  
25 film formation, membrane formation, and polyelectrolyte complexation during paper manufacture, said method comprising the step of using a derivatized microfibrillar cellulose during said manufacture, wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is  
30 capable of forming a gel in water at a concentration of less than 1%.

95. The method of claim 94, wherein said derivatized microfibrillar cellulose is used as a drainage aid and/or as a component of a sizing agent.

96. The method of claim 94, wherein said derivatized microfibrillar cellulose is microfibrillated quaternary amine functionalized cellulose.

5 97. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture.

98. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one  
10 of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

15 99. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

20 100. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

25 101. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture

30 102. The method of claim 101, wherein said dispersed particles comprise at least one of pulp fines, fillers, sizing agents, pigments, clays,



detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof.

103. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one  
5 of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

104. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one  
10 of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

105. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one  
15 polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

106. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to improve  
20 the uniformity of formation of a sheet of paper during its manufacture.

107. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one  
25 of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic  
30 acid functionality; and combinations thereof.

108. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

109. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

110. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to improve the strength of a sheet of paper produced on a paper machine.

111. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

112. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

113. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

114. A method for improving the stability of an emulsion, dispersion, or foam system, said method comprising the step of including, in the system, a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

115. The method of claim 114, wherein said system comprises an emulsion, further wherein said emulsion is produced by processing of an emulsion formulation.

116. The method of claim 115, further wherein said derivatized microfibrillar cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation.

117. The method of claim 115, wherein a non-microfibrillated derivatized cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation and said emulsion formulation is processed under conditions sufficient to microfibrillate said non-microfibrillated derivatized cellulose, whereby said derivatized microfibrillar cellulose is produced.

118. The method of claim 115, wherein a microfibrillated non-derivatized cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation, and said emulsion formulation is further processed under conditions sufficient to derivatize said microfibrillated non-derivatized cellulose.

119. The method of claim 115, wherein a non-microfibrillated, non-derivatized cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation, and said emulsion formulation is further processed under conditions sufficient to microfibrillate and derivatize said non-microfibrillated, non-derivatized cellulose.

120. The method of claim 114, wherein said system is a water-in-oil or oil-in-water emulsion.

121. The system produced by the method of claim 114.

122. A system comprising an emulsion, dispersion, or foam containing a derivatized microfibrillar cellulose, wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming  
5 a gel in water at a concentration of less than 1%.

123. A polyelectrolyte complex comprising a derivatized microfibrillar cellulose comprising a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

10 124. A method for treating wastewater comprising the step of adding, to the wastewater, a sufficient amount of a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 125. The method of claim 124, wherein said wastewater contains at least one of anionic contaminants and color bodies.

# INTERNATIONAL SEARCH REPORT

Int. l. Application No  
PCT/US 01/03458

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C08B11/20 C08B11/145		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 588 861 A (SHIGERU YAMANAKA ET AL.) 24 September 1996 (1996-09-24) column 3, line 28 - line 32 column 5, line 9 - line 62 example 2; tables 2,3 ---	1-125
X	EP 0 859 011 A (AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS) 19 August 1998 (1998-08-19) cited in the application page 5, line 1 - line 4 example 29 ---	1-125
X	US 4 676 904 A (JOBST SCHRÖDER) 30 June 1987 (1987-06-30) column 1, line 55 - line 66 ---	1-20
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents :		
*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family	
Date of the actual completion of the international search  <p style="text-align: center;">17 May 2001</p>	Date of mailing of the international search report  <p style="text-align: center;">28/05/2001</p>	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <p style="text-align: center;">Lensen, H</p>	

INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/03458

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PATENT ABSTRACTS OF JAPAN vol. 1998, no. 11, 30 September 1998 (1998-09-30) &amp; JP 10 165823 A (NISSHINBO IND INC), 23 June 1998 (1998-06-23) abstract &amp; DATABASE WPI Week 199835 Derwent Publications Ltd., London, GB; AN 1998-406688 abstract</p> <p style="text-align: center;">---</p>	1-20
P, X	<p>WO 00 47628 A (HERCULES INCORPORATED) 17 August 2000 (2000-08-17) page 16, line 11 - line 24</p> <p style="text-align: center;">-----</p>	1-125

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Information on patent family members

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US 5588861 A	31-12-1996	US 5597318 A EP 0771479 A JP 10508143 T WO 9602960 A	28-01-1997 07-05-1997 04-08-1998 01-02-1996
EP 859011 A	19-08-1998	FR 2759376 A	14-08-1998
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