Title: WATER-SOLUBLE, LOW SUBSTITUTION HYDROXYETHYLCELLULOSE, DERIVATIVES THEREOF, PROCESS OF MAKING, AND USES THEREOF

Abstract: This invention relates to water-soluble hydroxyethylcelluloses (HECs) and derivatives thereof having a hydroxyethyl molar substitution (HE-MS) from about 0.7 to 1.3. These HECs are more efficient in thickening aqueous systems than prior art HEC products and show unique rheology in low water activity systems. These HECs can be distinguished from prior art and commercial HEC products by having an unsubstituted anhydroglucose trimer ratio (U3R) less than 0.21 and a water solubility greater than 90 wt %. This invention also relates to a unique continuous caustic reduction hydroxyethylolation process for making the water-soluble, slowly substituted HECs and uses thereof in functional systems.
WATER-SOLUBLE, LOW SUBSTITUTION HYDROXYETHYLCYLULOSE, DERIVATIVES THEREOF, PROCESS OF MAKING, AND USES THEREOF

[0001] This application claims the benefit of U.S. Provisional Application No. 60/657,963, filed March 2, 2005.

FIELD OF INVENTION

[0002] The present invention relates to cellulose ether compositions, derivatives thereof, a process for making the composition, and uses thereof in functional systems. More specifically, this invention relates to water-soluble hydroxyethylcelluloses (HECs) having a hydroxyethyl molar substitution (HE-MS) from 0.7 to 1.3, and derivatives thereof. This invention also relates to a continuous caustic reduction hydroxyethylation process for making the watersoluble, lowy substituted HECs and uses thereof in functional systems.

BACKGROUND OF THE INVENTION

[0003] Hydroxyethylcellulose (HEC) is cellulose ether usually made by reacting alkali cellulose with ethylene oxide (EO). In general, the molar ratio of EO to the anhydroglucose units of cellulose is higher than 1.5 to provide adequate water-solubility to the cellulose backbone. HEC is a water-soluble/water-swellable polymer that generally is used to viscosify aqueous media of functional systems such as personal care and household products, paints, construction material products, paper coatings, oilfield media, emulsions, latex components, etc. Furthermore, high molecular weight HEC is used in the pharmaceutical industry as an excipient to provide a swellable diffusion barrier in controlled release applications.

[0004] In commercial HECs that are made by a single-stage ethoxylation of cellulose, the hydroxyethylene substituents are nearly randomly distributed among the anhydroglucose segments of the polymer. Examples of prior art that disclose the preparation of HEC are US Patents 2,572,039, 2,682,535,
Another commercial HEC product is a more highly substituted HEC in which the ethylene oxide is reacted in two-steps thereby reducing the amount of unsubstituted anhydroglucose units. This results in the formation of a cellulose derivative that is less susceptible to enzymatic degradation, i.e. enhanced resistance to biodegradation. Examples of prior art that disclose the preparation of this type of HEC are US Patent 3,131,176, Canadian Patent 1014289, and US Patent Application US 2005/0139130 A1. The solution viscosities of HECs with these types of EO substitution patterns usually depend on the molecular weight of the cellulose backbone.

U.S. Patent Application Serial No. 11/353,621, entitled "Water-Soluble, Low Substitution Hydroxyethylcellulose, Derivatives Thereof, Process Of Making, And Uses Thereof," filed February 14, 2006 discloses non-uniformly substituted ("blocky") hydroxyethylcelluloses (HECs) and derivatives thereof that show associative thickening properties that are unknown in commercial HEC products. These blocky HEC products are characterized by a novel parameter called the unsubstituted trimer ratio (U3R) which is defined as the ratio of the molar fraction of unsubstituted trimers to the molar fraction of the most abundant class of (hydroxyethyl-substituted) trimers. The U3R of blocky products is greater than 0.21 for the HE-MS range of 1.3 and 5.0.

Furthermore, HECs can be modified with additional substituents to improve functionality. For example, US Patent No. 4,228,277 discloses the use of long chain alkyl modifiers having 10 to 24 carbon atoms. Another example of a modified HEC is disclosed in US Patent No. 4,826,970 that describes a carboxymethyl hydrophobically modified hydroxyethyl cellulose ether derivative (CMHMHEC) that is used as thickeners and protective colloids in water based protective coating compositions. US Patent No 4,904,772 discloses a water-soluble HEC derivative that has a mixed hydrophobe having two or more hydrophobic radicals having 6 to 20 carbons whereby one of the hydrophobic radicals has a carbon chain length that is at least two carbon atoms longer than that of the other hydrophobic radical. US Patent 4,663,159 discloses a water-soluble, cationic hydroxyethyl cellulose.
[0007] Commercial HEC products are the thickeners of choice in many industries because they provide the desired rheology and thickening efficiency. Notwithstanding, a need always exists for an HEC-based rheology modifier that would be more efficient in thickening aqueous systems and interact more strongly with components in the system and/or with itself so that additional desired rheological properties can be achieved.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to a new class of lowly substituted HECs in which the EO is distributed extremely uniformly along the backbone of the cellulose in order to render it water-soluble. This unique class of HEC is water-soluble unlike other classes of HEC in the prior art with similar hydroxyethyl molar substitution (HE-MS) and cellulose molecular weight. These lowly substituted HECs can be further modified with hydrophobic, cationic, or anionic reagents.

[0009] An advantage of this product is that it provides a much higher solution viscosity than regular commercial HEC at similar concentrations and molecular weight. Consequently, a lesser amount of the HEC of the present invention can produce comparable or better viscosity relative to analogous commercial HECs of similar molecular weight. Furthermore, it has been surprisingly found that HECs and derivatives thereof of the present invention are efficient thickeners and suspending agents in low-water activity solutions such as those that contain high concentrations of salt or those that contain a fraction of a miscible organic solvent. There is a need for universal thickeners that function in the broad spectrum of aqueous systems as cellulosics, natural gums, and synthetic carboxomers often do not dissolve or function in solutions that have only a low level of free water available.

[0010] The present invention is directed to water-soluble HECs that have hydroxyethyl groups that are uniformly distributed on the cellulose backbone, wherein the ratio of unsubstituted anhydroglucose trimers to the most frequently occurring substituted anhydroglucose trimers (U3R) is less than
0.21 and the hydroxyethyl molar substitution is greater than about 0.7 and less than about 1.3.

[00011] The present invention is further directed to a slurry process for making the above mentioned HEC composition comprising
A) mixing and reacting cellulose, water and alkali in an organic solvent for a sufficient time and at a sufficient temperature in order to form an alkali cellulose mixture, wherein the water to anhydroglucose (AGU) molar ratio is in the range of about 5 to 35 and the alkali to AGU molar ratio is greater than about 1.6,
B) adding a sufficient amount of ethylene oxide to produce the desired hydroxyethyl molar substitution (HE-MS)
C) adding a sufficient amount of acid continuously in order to reduce the alkali to AGU molar ratio to less than about 0.4 and greater than about 0.04, while reacting the ethylene oxide with the alkali cellulose at a sufficient temperature and for a sufficient time to form a water soluble HEC product with a HE-MS of greater than about 0.7 and less than about 1.3.

[00012] The HEC product prepared by the above mentioned process can optionally be further reacted with at least one other derivatizing reagent to form a modified HEC product.

[00013] Likewise, the HEC or modified HEC product, optionally, can further be reacted with a viscosity reducing agent.

[00014] The present invention is also related to a functional system composition including the water-soluble, low HE-MS HEC composition or derivatives thereof.

**BRIEF DESCRIPTION OF THE DRAWING**

[00015] Figure 1 shows a bar graph of the ethylene oxide distribution profile of a HEC polymer.
DETAILED DESCRIPTION OF THE INVENTION

[00016] It has been surprisingly found that low HE-MS, water-soluble HECs can produce unique rheology that has not been noted prior to this invention and can be prepared using a continuous caustic reduction during the hydroxyethylolation manufacturing process.

[00017] The present invention is directed to water-soluble, low HE-MS HECs and modified HECs (nonionic, anionic, and cationic) in which a large fraction of the anhydroglucose units (AGU) in the molecule are substituted with ethylene oxide (EO). The features that differentiate these HECs from prior art are high water solubility at a HE-MS that is greater than about 0.7 and less than about 1.3; and a structural parameter, the unsubstituted trimer ratio (U3R) that is less than 0.21. This unique class of soluble HECs while nearly uniformly hydroxyethylated shows surprising associative behavior through hydrogen bonding due to the very low HE-MS. As a result, these HECs exhibit significantly higher solution viscosities as compared to other classes of HECs with similar HE-MS (hydroxyethyl molar substitution) and cellulose molecular weight. Furthermore, they show excellent viscosifying power in salt-containing solutions and lean solvents, whereas commercial HECs have difficulty hydrating.

[00018] In accordance with the present invention, the water-soluble low HE-MS HEC composition can be further modified with one or more nonionic, anionic, and cationic substituents or mixtures thereof. The substituents are attached to the HEC backbone via an ether, ester, or urethane linkage.

[00019] When the substituents have nonionic chemical functionality, the substituents have the formula:

\(-R, \text{ or } -A-R, \text{ wherein } A \text{ is} \)
\(\text{CH}_2-\text{CH(OH)},\)
\(\text{CH}_2-\text{CH(OH)}-\text{CH}_2,\)
\((\text{CH}_2-\text{CH}_2-\text{O})_n \text{ where } n = 1 - 100,\)
\(\text{CH}_2-\text{CH(OH)}-\text{CH}_2-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_n \text{ where } n = 1 - 100,\)
\(\text{CH}(R)-\text{C}(O)-\text{CH}_2, \text{ and} \)
R is selected from one of the following groups:

i) an acyclic or cyclic, saturated or unsaturated, branched or linear hydrocarbon moiety having 1 to 30 carbon atoms,

ii) an acyclic or cyclic, saturated or unsaturated, branched or linear heterohydrocarbon moiety having 1 to 30 carbon atoms and one of more oxygen, nitrogen, or silicone atoms,

iii) an acyclic or cyclic, saturated or unsaturated, branched or linear hydrocarbon moiety having 1 to 30 carbon atoms and one or more aromatic hydrocarbon groups,

iv) an acyclic or cyclic, saturated or unsaturated, branched or linear heterohydrocarbon moiety having 1 to 30 carbon atoms and one or more oxygen, nitrogen, or silicone atoms and one or more aromatic groups, and

v) an acyclic or cyclic, saturated or unsaturated, branched or linear, heterohydrocarbon moiety having 1 to 30 carbon atoms and one or more oxygen, nitrogen, or silicone atoms and one or more heteroaromatic groups containing one or more oxygen, nitrogen, or silicone groups.

[00020] Based on the formula R above, the substituents may be selected from alkyl, alkenyl, alkynyl, aryl, alkyl aryl, aryl alkyl, alkenyl aryl, aryl alkenyl, or mixtures thereof, having when possible, from 1 to 30 carbon atoms.

[00021] When the substituents have anionic chemical functionality, the anionic chemical functionality can be carboxylate, sulfaté, sulfonate, phosphate, phosphonate or mixtures thereof. More specific examples of this functionality are carboxymethyl, sulfoethyl, phosphonomethyl, and mixtures thereof.

[00022] When the substituents have cationic chemical functionality, the substituents have the formula \( R^1R^2R^3R^4N^+(A^-) \), where \( R^1 \) is \( \text{CH}_2\text{CHOH-CH}_2^- \) or \( \text{CH}_2\text{CH}_2\text{CH}_2^- \), and \( R^2, R^3, R^4 \) are each independently selected from an alkyl or aryl alkyl group having 1 to 20 carbon atoms, and \( A^- \) is a halide, sulfate, phosphate, or tetrafluoroborate ion.
More specifically, the cationic substituents can be selected from 2-hydroxypropyltrimethylammonium chloride, 2-hydroxypropyldodecyltrimethylammonium chloride, 2-hydroxypropylcocoalkyldimethylammonium chloride, 2-hydroxypropyloctadecyltrimethylammonium chloride and mixtures thereof.

Another important cationic group that can be used in this invention is the group derived from the grafting reaction of diallyldimethylammonium chloride with HEC or its derivatives.

In accordance with the present invention, more specific modified hydroxyethylcellulose are methyl hydroxyethylcellulose, ethyl hydroxyethylcellulose, octyl hydroxyethylcellulose, cetyl hydroxyethylcellulose, cetoxy-2-hydroxypropyl hydroxyethylcellulose, butoxy-2-hydroxypropyl hydroxyethylcellulose, butoxy-2-hydroxypropyl cetyl hydroxyethylcellulose, butoxy-2-hydroxypropyl cetoxy-2-hydroxyethylcellulose, carboxymethyl hydroxyethylcellulose, carboxymethyl ethyl hydroxyethylcellulose, carboxymethyl octyl hydroxyethylcellulose, carboxymethyl cetyl hydroxyethylcellulose, carboxymethyl cetoxy-2-hydroxypropylcellulose, carboxymethyl butoxy-2-hydroxyethylcellulose, sulfoethyl hydroxyethylcellulose, sulfoethyl ethyl hydroxyethylcellulose, sulfoethyl cetyl hydroxyethylcellulose, sulfoethyl cetoxy-2-hydroxypropylcellulose, 2-hydroxypropyltrimethylammonium chloride hydroxyethylcellulose, 2-hydroxypropyltrimethylammonium chloride ethyl hydroxyethylcellulose, 2-hydroxypropyltrimethylammonium chloride butoxy-2-hydroxypropyl hydroxyethylcellulose, 2-hydroxypropyltrimethylammonium chloride octyl hydroxyethylcellulose, 2-hydroxypropyltrimethylammonium chloride cetyl hydroxyethylcellulose, 2-hydroxypropyltrimethylammonium chloride cetoxy-2-hydroxypropyl hydroxyethylcellulose, 2-hydroxypropylauryldimethylammonium chloride hydroxyethylcellulose, 2-hydroxypropyltrimethylammonium chloride 2-hydroxypropylauryldimethylammonium chloride hydroxyethylcellulose,
diallyldimethylammonium chloride grafted hydroxyethylcellulose, 
diallyldimethylammonium chloride grafted cetyl hydroxyethylcellulose.

[00026] The lowly hydroxyethylated water soluble HECs can be prepared by 
completely opening up the cellulose fiber with high initial caustic level (AC1) 
and then "quenching" continuously to a low caustic level (AC2) during the 
hydroxyethylation reaction. This process drives a more uniform substitution 
so as to render high water solubility at low HE-MS. In accordance with 
the present invention, the process requires mixing and reacting cellulose with 
water and alkali in an organic solvent wherein the molar ratio of alkali to 
anhydroglucose (AGU) is greater than about 1.6 and the molar ratio of water 
to AGU is 5 – 35. After about 1 hour at 20° C, a high base content alkali 
cellulose is formed. Subsequently, EO is added to the reaction mixture so 
that upon reacting, the HE-MS of the final HEC product will be about 0.7 to 
1.3. Next, the high base content alkali cellulose is continuously neutralized 
with a sufficient amount of an acid to reduce the alkali content to an alkali to 
AGU molar ratio between about 0.4 and 0.04 while simultaneously reacting 
the ethylene oxide with the alkali cellulose at about 60° C to form a water-
soluble hydroxyethylcellulose product. The acid can be added over about 30 
to 90 minutes during the hydroxyethylation. Upon completion of the 
hydroxyethylation, the product can be further modified with nonionic, anionic 
or cationic reagents. In addition, the product can be viscosity reduced, 
purified, dried, and ground as known to those skilled in the art.

[00027] In the slurry process of the present invention, organic solvent used 
in this process is selected from ethanol, isopropanol, tert-butanol, acetone, 
methyl ethyl ketone, dimethoxyethane, or mixtures thereof. This slurry 
process uses alkalis that are selected from lithium hydroxide, sodium 
hydroxide, potassium hydroxide, and mixtures thereof. The raw cellulose 
starting material used in the process for making the low HE-MS, water soluble 
HECs can be cotton linters, wood pulps, or mixtures thereof.

[00028] The water-soluble HEC compositions mentioned above can be 
optionally further reacted with at least another derivatizing reagent to form a
modified hydroxyethylcellulose composition. The derivatizing reagent used to make this modified hydroxyethylcellulose composition can be nonionic, cationic, or anionic organic compounds or mixtures thereof. These organic compounds capable of reacting with the hydroxyl groups of the HEC can be halides, epoxides, glycidyl ethers, carboxylic acids, isocyanates, or mixtures thereof.

[00029] The HEC or derivatives thereof of the invention made by the slurry processes mentioned above can be further reacted with a viscosity reducing agent, such as peroxide, persulfate, peracid, salt of halide oxo acids, oxygen, or ozone. This enables a person using this process to modify the final product to the desired viscosity or other properties for the desired end use.

[00030] The process and process conditions determine how the EO is distributed along the cellulose backbone. Products of the invention are characterized and can be differentiated from HECs made by prior art by reducing the low HE-MS polymer down to monomers and oligomers and measuring the degree of unsubstituted oligomers, more specifically unsubstituted trimers. A parameter called the unsubstituted trimer ratio (U3R) can be defined as the ratio of the molar fraction of unsubstituted trimers to the molar fraction of the most abundant class of (hydroxyethyl-substituted) trimers, with $0 \leq \text{U3R} \leq 1.0$. U3R is measured by a mass spectrometric technique that is described below. The U3Rs of the HECs of the present invention are equal to or less than about 0.21, preferably less than 0.18 while the HE-MS is in the range of 0.7 to 1.3.

[00031] Trimers, oligomers with a degree of polymerization (DP) of 3 anhydroglucose units, and other compounds of structure 1 are made by partial methanolysis of permethylated HEC derivatives. It is assumed that the cleavage of the permethylated HEC-backbone is a random process and that the formed oligomers of structure 1 have an EO-distribution that is representative for the EO-distribution of the whole sample.

Unsubstituted Trimer Ratio (U3R) Determination

[00033] More specifically, in the present invention, the investigated HEC polymers are dissolved or swollen in dimethyl sulphoxide (DMSO). The hydroxyl groups in the polymer are deprotonated using a lithium methylsulphinyl carbanion solution in DMSO and they are converted to methoxyl groups by the reaction with methyl iodide.

[00034] The obtained permethylated HEC polymer is purified. More specifically, the permethylated HEC polymer is extracted in three extraction steps with chloroform from an aqueous DMSO layer that is acidified to pH < 2 with hydrochloric acid. The pooled chloroform extracts are washed four times with water. Some methanol is added after the last wash step and all solvents are evaporated.

[00035] The permethylated polymer is partially degraded by methanolysis. More specifically, the permethylated polymer is dissolved / swollen in
methanol. Sufficient hydrochloric acid in methanol is added to get a hydrochloric acid concentration of about 0.50 molar. The sample is dissolved completely at 50°C for 15 minutes. Partial methanolysis is done at 70°C for 2.5 hours. The reaction is quenched by the addition of 2-methyl-2-propanol and all solvents are evaporated, yielding a residue that is composed of a mixture of oligomers of structure 1.

[00036] The residue is dissolved in methanol and a fraction of this sample is mixed with 2,5-dihydroxybenzoic acid solution that is spiked with sodium iodide. Mass spectra of the oligomer mixture are recorded with a Bruker Reflex II MALDI-TOF-MS (matrix assisted laser desorption ionization – time of flight – mass spectrometer), which instrument is equipped with a microchannel plate detector. The compounds of structure 1 are measured as their sodium ion adducts. The mass numbers of the monoisotopic mass peaks of the trimers are m/z 667.32, 711.34, 755.35, 799.39, etc. It is assumed that all trimers are measured with equal probability, independent of their molar HE-substitution, chain length of the substituents and their positions in the anhydroglucose residues.

[00037] Trimer fractions are derived by two data processing steps from the measured peak intensities of their monoisotopic mass peaks. First the background signal of the MALDI spectrum is subtracted from the measured peak intensities. Secondly, mainly due to 13C-isotopes that are incorporated in structure 1 the monoisotopic mass peaks make up only 70.6, 68.9, 67.2, 65.6 %, etc of all isotopes of trimers having 0, 1, 2, 3, etc attached EO-units, respectively. Unfortunately, the peak intensities of 13C-isotopes can not be measured accurately by MALDI-TOF-MS because of the recovery time that is needed for the microchannel plate detector after an intense mass peak has been recorded. In order to compensate the signal for the missing contribution of 13C-isotope peaks, the background corrected monoisotopic mass peak intensities are multiplied by a correction factor that is calculated from the theoretical isotope composition of the trimers. This factor increases with increasing number of C-atoms in structure 1, and values have been used of
1.417, 1.452, 1.488, 1.525, etc for trimers having 0, 1, 2, 3, etc attached EO-units, respectively.

[00038] Figure 1 shows an example of the EO-distribution profile of trimers that are derived from a HEC polymer. The fraction of unsubstituted trimers is indicated in gray. The most abundant class of trimers in this example is that of trimers with 7 attached EO-units. This class is indicated in white. The unsubstituted trimer ratio, i.e. the gray fraction divided by the white fraction, is calculated to be 0.121 for this example. It should be noted that the number of EO-units in the most abundant class of trimers varies, depending on factors as the molar substitution of the HEC and the process type by which the HEC was made, for example.

[00039] HEC derivatives that contain secondary substituents such as nonionic, cationic and anionic substituents and mixtures thereof are analyzed similarly as non-modified HECs. In the case of modification levels smaller than 3.5 substituents per 100 monomer units, such as associative hydrophobic reagents for example, less than 10% of the trimers are modified and consequently the fraction of modified trimers can be neglected.

[00040] The fraction of unmodified trimers decreases with increasing degree of substitution (DS) of the modifying agent. If the secondary substituent distribution is random along the cellulose backbone, than only half of the trimers would remain unmodified at a DS level of 0.21. The carboxymethyl (CM)-modified HEC listed in Table 2 has a CM-DS value in this order of magnitude and it is concluded for this sample that the fraction of CM-modified trimers cannot be neglected.

[00041] Furthermore, CM-groups that are attached to the HEC-backbone are converted into their methylesters by the derivatization procedure. The sodium ion adduct of dimers with two attached EO-units and two attached CM-groups has $m/z$ 667.28. The mass resolution of MALDI-TOF-MS is insufficient to separate this mass peak from $m/z$ 667.32, i.e. the mass peak of
unsubstituted trimers, so that an accurate measurement of the U3R for carboxymethylated HEC-derivatives is not applicable (N/A).

**Water Solubility Determination:**

[00042] A 0.25 or 0.50 wt % HEC solution in water is prepared and mixed for at least 2 hours until the polymer is dissolved. The solution is filtered through a 10 - 15 micron fritted filter. The filtrate is dried in a vacuum oven at 102° C for at least 24 hours or until there is no weight change over two hours. The percent soluble is determined by gravimetry as:

\[
\left(1 - \frac{\text{Weight polymer recovered from filtered solution}}{\text{Weight polymer in unfiltered solution}}\right) \times 100
\]

**APPLICATIONS:**

[00043] Many of these HEC samples exhibit novel and highly desirable rheology and performance properties in end use systems. In accordance with the present invention, the viscosity builds up not only by means conventional to HEC, but also is boosted significantly by molecular association. The association becomes stronger in low water activity systems and leads to network formation manifesting as gel-like properties in lean solvents and aqueous based functional systems. The HECs and derivatives of the present invention have been shown to lower the HEC use-level needed and to provide rheology attributes that are unique as compared to other prior art HECs.

[00044] Furthermore, these HECs and derivatives thereof may be used in applications where there is a need for a specific rheology characteristic, e.g., viscosity, thixotropy, yield stress, elasticity, or solid state characteristics such as thermoplasticity and film flexibility. Examples of functional systems include aqueous based coatings (e.g., latex paints), building and construction materials (e.g., cements, plasters), personal care products (e.g., skin care, hair care, oral care, nail care, and personal hygiene products), household care products (e.g., industrial cleaning liquids, pet care products), pharmaceuticals (e.g., excipients for tablets, capsules, and granules), oilfield
applications (e.g., drilling fluids, completion fluids, and fracturing fluids), civil engineering, printing inks, adhesives, paper coating formulations, and retention and drainage aids in paper making.

[00045] In accordance with the present invention, the functional system can either be prepared in a continuous or batch process and either in a stepwise addition of the ingredients or a simple mixing of all of the ingredients at once. The order of addition of the ingredients can also vary over a wide range of additions. For example, the functional ingredients can be individually added one at a time to the formulation or all at once or the low HE-MS, water soluble HEC products can be added directly to the formulated ingredients in a single step. Hence, the process of thickening an aqueous based functional system (e.g., personal care products, household care products, oil field servicing fluids, civil engineering servicing fluids, paper coating products, paper making compositions, building and construction fluids, ceramic glazes, mineral processing products, and water based protective coatings such as architectural and industrial coatings), includes adding and mixing a sufficient amount of the low HE-MS, water soluble HEC polymer of the present invention that is compatible with the aqueous based functional system to thicken the functional system. The resulting functional system has comparable or better rheology and viscosity properties as compared to when using similar thickening agents including commercial HECs.

PERSONAL CARE

[00046] In accordance with the present invention, when the composition is a personal care composition, it includes (a) from about 0.1 % to about 99.0 % by weight of the vehicle component and (b) at least one active personal care ingredient.

[00047] In accordance with the present invention, the personal care active ingredient must provide some benefit to the user’s body. Personal care products include hair care, skin care, oral care, nail care, and personal
hygiene products. Examples of substances that may suitably be included in the personal care products as active ingredients according to the present invention are as follows:

1) Perfumes, which give rise to an olfactory response in the form of a fragrance and deodorant perfumes which in addition to providing a fragrance response can also reduce body malodor;

2) Skin coolants, such as menthol, methyl acetate, methyl pyrrolidone carboxylate N-ethyl-p-menthane-3-carboxamide and other derivatives of menthol, which give rise to a tactile response in the form of a cooling sensation on the skin;

3) Emollients, such as isopropyl myristate, silicone oils, mineral oils and vegetable oils which give rise to a tactile response in the form of an increase in skin lubricity;

4) Deodorants other than perfumes, whose function is to reduce the level of or eliminate micro flora at the skin surface, especially those responsible for the development of body malodor. Precursors of deodorants other than perfume can also be used;

5) Antiperspirant actives, whose function is to reduce or eliminate the appearance of perspiration at the skin surface;

6) Moisturizing agents that keep the skin moist by either adding moisture or preventing moisture from evaporating from the skin;

7) Cleansing agents that remove dirt and oil from the skin;

8) Sunscreen active ingredients that protect the skin and hair from UV and other harmful light rays from the sun. In accordance with this invention a therapeutically effective amount will normally be from 0.01 to 10% by weight, preferably 0.1 to 5% by weight of the composition;

9) Hair treatment agents that condition the hair, cleans the hair, detangles hair, act as styling agents, volumizing and gloss agents, anti-dandruff agent, hair growth promoters, hair dyes and pigments, hair perfumes, hair relaxer, hair bleaching agent, hair moisturizer, hair oil treatment agent, and anti-frizzing agent;
10) Shaving products, such as creams, gels and lotions and razor blade lubricating strips;
11) Tissue paper products, such as moisturizing or cleansing tissues;
12) Beauty aids, such as foundation powders, lipsticks, and eye care; and
13) Textile products, such as moisturizing or cleansing wipes.

[00048] In personal care compositions, the rheology modifiers of the present invention can be used either alone or may also be used in combination with other known rheology modifiers including, but not limited to, polysaccharides (e.g., carrageenan, pectin, alginate), cellulose ethers, biopolymers (e.g., xanthan gum), synthetic polymers, and abrasive/thickening silicas.

HOUSEHOLD CARE

[00049] In accordance with the present invention, when the composition is a household care composition, it includes (a) from about 0.1 % to about 99.0 % by weight of the vehicle component and (b) at least one active household care ingredient.

[00050] In accordance with the present invention, the household care active ingredient must provide some benefit to the user. Household care products include fabric care, laundry detergent, hard surface cleaner, industrial institutional liquid soaps, and dish detergents. Examples of active ingredients or substances that may suitably be included according to the present invention are as follows:

1) Perfumes, that give rise to an olfactory response in the form of a fragrance and deodorant perfumes that in addition to providing a fragrance response can also reduce odor;
2) Insect repellent agent whose function is to keep insects from a particular area or attacking skin;
3) Bubble generating agent, such as surfactants which generates foam or lather;
4) Pet deodorizer such as pyrethrins that reduce pet odor;
5) Pet shampoo agents and actives, whose function is to remove dirt, foreign material and germs from the skin and hair surfaces;
6) Industrial grade bar, shower gel, and liquid soap actives that remove germs, dirt, grease and oil from skin, sanitize skin, and condition the skin;
7) All purpose cleaning agents that remove dirt, oil, grease, and germs from the surfaces in areas such as kitchens, bathroom, and public facilities;
8) Disinfecting ingredients that kill or prevent growth of germs in a house or public facility;
9) Rug and Upholstery cleaning actives that lift and remove dirt and foreign particles from the surfaces and also deliver softening and perfumes;
10) Laundry softener actives that reduce static and makes fabric feel softer;
11) Laundry detergent ingredients that remove dirt, oil, grease, and stains and kill germs;
12) Dishwashing detergents that remove stains, food, germs;
13) Toilet bowl cleaning agents that remove stains, kill germs, and deodorize;
14) Laundry prespotter actives that help in removing stains from clothes;
15) Fabric sizing agents that enhance appearance of the fabric;
16) Vehicle cleaning actives that remove dirt, grease, etc. from vehicles and equipment;
17) Lubricating agents that reduce friction between parts; and
18) Textile products, such as dusting or disinfecting wipes.

[00051] In household care compositions, the rheology modifiers of the present invention can be used either alone or may also be used in combination with other known rheology modifiers including, but not limited to, polysaccharides (e.g., carrageenan, pectin, alginate), cellulose ethers,
biopolymers (e.g., xanthan gum), synthetic polymers, and abrasive/thickening silicas.

[00052] The above are only limited examples of personal care and household active ingredients and are not a complete list of active ingredients that can be used. Other ingredients that are used in these types of products are well known in the industry. In addition to the above ingredients conventionally used, the composition according to the present invention can optionally also include ingredients such as colorants, preservatives, antioxidants, nutritional supplements, activity enhancers, emulsifiers, viscosifying agents (such as salts, e.g., sodium chloride, ammonium chloride and potassium chloride), water-soluble polymers (e.g., HEC, modified HEC, carboxymethylcellulose), and fatty alcohols (e.g., cetyl alcohol), alcohols having 1-6 carbons, and fats and oils.

PROTECTIVE COATINGS

[00053] Water-based protective coating compositions (commonly referred to as paints) in which cellulose ether derivatives are commonly used include latex paints or dispersion paints, of which the principal ingredient is the film-forming binders that include latices such as styrene-butadiene copolymers, vinyl acetate homopolymers and copolymers, and acrylic homopolymers and copolymers. Other binders that are typically used in paints include alkyd resins, and epoxy resins. Typically, they also contain opacifying pigments, dispersing agents and water-soluble protective colloids, the proportions being, by weight of the total composition, about 10 parts to about 50 parts of a latex, about 10 parts to about 50 parts of an opacifying pigment, about 0.1 part to about 2 parts of a dispersing agent, and about 0.1 part to about 2 parts of a water-soluble protective colloid.

[00054] These protective coatings can be either aqueous based architectural or industrial coating compositions. Architectural coatings are intended for on-site application to interior or exterior surfaces of residential, commercial, institutional or industrial buildings. Industrial coatings are applied
to factory-made articles before or after fabrication, usually with the aid of special techniques for application and drying.

[00055] Water-soluble polymers conventionally used in the manufacture of latex paints include casein, methyl cellulose, hydroxyethylcellulose (HEC), sodium carboxymethyl cellulose (CMC), polyvinyl alcohol, starch, and sodium polyacrylate. The HECs of the present invention can be used as rheology modifiers for water-based protective coating compositions.

PAPER COATINGS AND PAPER MAKING

[00056] Paper coating is a process in which the surface structure of paper or board is improved by applying a mineral coating that is subsequently dried. Coating process is the application of a water-borne pigment slurry, which is bound at the surface by one of several binders. Other coating components can be added to obtain a suitable rheology, and to impart properties such as brightness or water resistance.

[00057] A coating process can generally be divided into three different phases: (1) preparation of the coating formulation (known as called coating color), (2) coating and (3) drying. The general principles of formulating paper coating are mostly well known. Moreover, each paper maker has his own tailor-made recipes for his specific requirements. Therefore, it would not be possible to give a “recipe” for a specific coating process, coating type or printing process. However, a generic coating formulation recipe contains 75 - 90 % pigment (such as clay, satin white, calcium carbonate, titanium dioxide, talc, aluminum hydroxide, calcium sulfate, barium sulfate, synthetics, etc.), 0.10 - 0.50 % dispersant, 0.05 - 0.30 % alkali, 5 - 20 % binders (such as styrene-butadiene latices, acrylics, polyvinyl acetate, starch and starch derivatives, proteins such as casein, soya) and 0 - 2 % co-binder (cellulose ethers, polyvinyl alcohol and solution or polyacrylates emulsion). Other functional additives such as lubricants, optical brightening agents and defoamers are often added to the coating formulation. All amounts of ingredients are based on weight of pigment. The HECs of the present
Invention can be used as rheology modifiers for water-borne paper coating compositions.

[00058] In addition to paper coating, the HECs of the present invention can be used in papermaking process and for surface sizing. In papermaking process, the low HE-MS, water soluble HEC can be used as an additive in the stock as a refining agent, wet-strength agent, dry strength agent, internal bonding agent, water retention agent and improving the sheet formation. For surface sizing, the low HE-MS, water soluble HEC can be used as a binding agent and aiding in film formation.

OILFIELD SERVICING FLUIDS

[00059] Drilling an oil or gas well is a complex operation, involving several steps before and after the well is put into production. Primary oil-recovery operations include drilling the well, cementing the casing to the formation and completing the well prior to oil or gas production. Workover operations may be necessary during remedial work in producing wells, usually as an attempt to enhance or prolong the economic life of the well. When the flow rate of the fluid is diminished, the reservoir may be treated in some manner to increase the flow of fluid into the wellbore. This operation is called secondary recovery, known as fracturing/stimulation operations. They are performed either by acid wash or hydraulic fracturing. When the reservoir is depleted, enhanced oil recovery operations may be needed to increase the production rate. This operation is called tertiary recovery, and involves injection of fluids into the formation surrounding the production well to increase the flow rate of the formation fluid into the wellbore.

[00060] Drilling fluids are an integral element of the drilling program for primary oil recovery. They are especially designed to perform numerous functions that condition the success of drilling operations. Their principal functions include, but not limited to, are:
• An effective hole cleaning efficiency (H.C.E.).
• Maintaining the stability of the open hole-formation.
• Formation of a thin and low-permeability filter cake on the formation.
• Minimizing formation damage.
• Friction reduction between the drilling string and the formation.
• Cool and clean the drill bit.

[00061] To perform these functions, drilling fluids should possess particular properties with regard to rheology, density, and filtration control. Filtration control is a key performance attribute that affects all other properties. In fact, loss of a significant amount of water from the drilling fluid into the formation would result in irreversible change of the overall drilling fluid properties (density and rheology) that would seriously affect the stability of the borehole.

[00062] Among a variety of additives, carboxymethyl cellulose (CMC), HEC and polyanionic cellulose (PAC) are widely used to optimize water-based drilling fluid properties. High-viscosity types are used for rheology and fluid loss control properties while low viscosity types are exclusively used for filtration control properties. In most cases, these types are used together in a drilling fluid composition. During drilling operations, optimum drilling fluid attributes are further achieved by combining different components including clay, CMC/PAC, xanthan gum (primary rheology modifier), starches (improved filtration control) and other synthetics polymers that may be required for dispersing or shale inhibition properties.

[00063] Completion and workover fluids are specialized fluids used during well completion operations and remedial workover procedures. They are placed across the chosen pay zone after the well has been drilled but prior to putting it on production. These fluids must control not only subsurface pressure with density, but also must minimize formation damage during completion and workover operations to improve oil or gas production rate. Because all wells are susceptible to formation damage to some degree (from
a slight reduction in the production rate to complete plugging of specific zones) and the potential for permanent damage is greater during completion and workover operations than it is during drilling, it is imperative to use a fluid that causes the least possible damage to the pay zone formation. The principal functions of completion and workover fluids include, but not limited to, are:

- Control subsurface pressures.
- Minimize formation damage.
- Maintain well bore stability.
- Control fluid losses to the formation.
- Transport solids.
- Maintain stable fluid properties.

[00064] The types of completion and workover fluids can be categorized into clear solids-free brines, polymer viscosified brines with bridging/weighting agents, and other fluids including oil base, water base, converted muds, foam, etc. The primary selection criteria for an appropriate completion or workover fluid are density. Clear, solids free brines are the most commonly used fluids and are viscosified with polymers (CMC/PAC, xanthan gum, guar and guar derivatives, and HEC) and may incorporate solids that can be dissolved later, such as acid soluble calcium carbonate or sized sodium chloride salt, for increased density or bridging purposes. While HEC is the most suitable polymer for brine based systems, CMC/PAC and xanthan gum find their use in low density (up to 12 ppg) monovalent salts based brines.

[00065] Hydraulic fracturing may be defined as the process in which fluid pressure is applied to the exposed reservoir rock until failure or fracturing occurs. After failure of the rock, a sustained application of fluid pressure extends the fracture outward from the point of failure. This may connect existing natural fractures as well as provide additional drainage area from the reservoir. The fluid used to transmit the hydraulic pressure to the reservoir rock is called the fracturing fluid. To prevent the fracture from closing when
pumping is stopped, propping agents, such as sized sand, are added to the fracturing fluid. The propping agent acts as supports to hold the fracture open after the treatment and to provide an improved ability of the fracture to conduct oil or gas through the fracture to the wellbore.

[00066] The low HE-MS, water soluble HECs and derivatives thereof of the present invention can be used as rheology modifiers for aqueous based oilfield servicing fluids with improved efficiency.

CIVIL ENGINEERING SERVICING FLUIDS

[00067] Civil engineering applications include tunneling, diaphragm walling, pilling, trenching, horizontal drilling, and water-well drilling. These applications are often characterized by their closeness to agglomerations where strict environmental regulation is in effect to minimize any kind of pollution or contamination. The corresponding working sites are further characterized by the availability of very poor mixing equipment on-site to efficiently disperse and dissolve the water-soluble polymers (WSPs). There is a desire in civil engineering applications for polymer suspensions that are stable, environmentally friendly, and meet all discharge regulations.

[00068] The low HE-MS, water soluble HEC and derivatives thereof of the present invention are used as rheology modifiers in fluids for civil engineering applications including tunneling, pilling, diaphragm walling, drilling, and bentonite doping.

CONSTRUCTION / BUILDING COMPOSITIONS

[00069] Building compositions, also known as construction materials, include concrete, tile cement and adhesives, projection plasters, stuccos based on cement and synthetic binders, ready mixed mortars, manually applied mortars, underwater concrete, joint cement, joint compounds, gypsum board, crack fillers, floor screeds, and adhesive mortars. These compositions are essentially Portland cements, Plaster of Paris or vinyl copolymers.
containing functional additives to impart characteristics required for various construction applications.

[00070] The joint cement can contain clay and mica or can be clay free (i.e., contain less than 0.5 wt % clay). While lime was once the preferred material for controlling the water ratio in the building compositions, cellulose ethers are at present time the most used because of their contribution to improve the water retention characteristics and other physical properties such as workability, consistency, open time, tack, bleeding, adhesion, set time, and air entrainment.

[00071] The low HE-MS, water soluble HEC and derivatives thereof of the present invention are used as rheology modifiers in the above mentioned construction and building material compositions.

PHARMACEUTICALS

[00072] Pharmaceutical compositions normally are in the form of tablets, capsules, or granules. The sole purpose of a pharmaceutical composition, regardless of its form, is to deliver a therapeutically active medicament to the desired place of use. The most common form of the medicament delivery system is the tablet form. In the tablet or capsule form, it is common practice to use at least one inert ingredient for production, delivery, and economic considerations. Examples of inert ingredients are excipients, diluents, fillers, and binders. The combination of the medicament with the inert ingredients provides a formulation that can be directly compressed into tablets or made into granules or agglomerations for encapsulation. In order to provide a directly compressible product, these excipients must have certain physical properties, including flow ability, sufficient particle size distribution, binding ability, acceptable bulk and tap densities, and acceptable dissolution properties in order to release the medicament upon oral administration.

[00073] The low HE-MS, water soluble HECs or derivatives thereof of the present invention can be used as a pharmaceutical excipient in free flowing, directly compressible slow release granule compositions that can be prepared
by dry-blending, roller-compaction, or wet-agglomeration. The pharmaceutical composition may contain from about 5 to about 80 % by weight of the low HE-MS, water soluble HEC or HEC derivative. The pharmaceutical composition can also contain an inert filler in the amount of from about 0.01 to about 95 % by weight. Examples of the pharmaceutical fillers are monosaccharides, disaccharides, polysaccharides, polyhydric alcohols, inorganic compounds, and mixtures thereof. This pharmaceutical composition can also contain from about 0.01 to 50 % of an additional control release agent such as cellulose ethers, cellulose esters, polyethylene oxides, polyvinyl alcohol and copolymers, methacrylic acid derivatives, waxy-fatty materials, natural hydrocolloids, and Carbopol® derivatives.

[00074] In accordance with the present invention, a controlled release pharmaceutical tablet for oral administration is composed of from about 5 to about 80 % by weight of the total composition of the low HE-MS, water soluble HEC or derivatives thereof, up to about 90 % by weight of an inert pharmaceutical filler (as mentioned above), and an effective amount of a therapeutically active medicament to render a therapeutic effect. The ratio of medicament to the low HE-MS, water soluble HEC (hydrophilic material) is based in part upon the relative solubility of the medicament and the desired rate of release. By varying this ratio and/or the total weight of the tablet, one can achieve different slow release profiles, and may extend the dissolution of some medicaments to about 24 hours.

[00075] An immediate release tablet composition of the present invention is composed of from about 0.5 to 10 % by weight of the low HE-MS, water soluble HEC, suitable fillers and tableting aids, and an effective amount of a therapeutically active medicament. The amount of the active medicament depends on the desired amount needed to deliver the desired effect.
EXAMPLES

[00076] The following Examples indicate various possible methods for making, describing, and using the HECs 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. All parts and percentages are by weight unless otherwise stated.

PROCEDURES FOR PREPARING SAMPLES

[00077] Table 1 shows the details of the individual Examples. Cellulose, water, and solvent were charged to a nitrogen-sparged, reaction kettle per the ratios described in the various tables. The reactor was inerted with nitrogen. The caustic was added to reach the desired alkali to AGU molar ratio (AC1) and the alkali cellulose slurry temperature was maintained at 20° C for approximately 1 hour. Ethylene oxide was added to the reaction mixture. Acid was then added continuously over a 30 minute heat-up to 60 ° C and a 30 minute hold at 60° C in order to reach the desired alkali to AGU molar ratio (AC2). The temperature was raised to 100° C and held for 60 minutes to complete the hydroxyethylation. The reaction mixture was cooled down to ambient temperature and neutralized with sufficient acid to neutralize any excess alkali. The HEC product was then purified, dried, and ground to the desired particle size.

[00078] For modified HEC, after cooling the HEC reaction mixture to ambient temperatures, caustic was added to achieve the desired alkali/AGU molar ratio for modification (ACM). The modifying agents were charged. When the modification was hydrophobic, the reactor was heated to 115° C and the temperature was maintained for 2.5 hours. When the modification was anionic or cationic, the reactor was heated to 60° C and the temperature was maintained for 2.5 hours. Upon completing the modification reaction, the reaction mixture was cooled down to ambient temperature and neutralized with sufficient acid to neutralize any excess alkali. The product was then purified, dried, and ground to the desired particle size.
Table 1: Sample Preparation Descriptions

<table>
<thead>
<tr>
<th>EX</th>
<th>Cellulose Furnish&lt;sup&gt;A&lt;/sup&gt;</th>
<th>Cell. Bone Dry (g)</th>
<th>IPA (g)&lt;sup&gt;B&lt;/sup&gt;</th>
<th>Acid Type and Concentration</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O: AGU&lt;sup&gt;C&lt;/sup&gt;</th>
<th>NaOH: AGU&lt;sup&gt;D&lt;/sup&gt;</th>
<th>NaOH: AGU&lt;sup&gt;D&lt;/sup&gt;</th>
<th>NaOH: AGU&lt;sup&gt;D&lt;/sup&gt;</th>
<th>EO (g)</th>
<th>HM&lt;sup&gt;E&lt;/sup&gt; (g)</th>
<th>Cationic or Anionic Agent (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX 1</td>
<td>li</td>
<td>58</td>
<td>667</td>
<td>45% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.20</td>
<td>-</td>
<td>33.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 2</td>
<td>li</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>-</td>
<td>31.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 3</td>
<td>li</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>0.08</td>
<td>31.5</td>
<td>Butyl GE&lt;sup&gt;F&lt;/sup&gt; 5.8</td>
<td>-</td>
</tr>
<tr>
<td>EX 4</td>
<td>li</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>0.73</td>
<td>31.6</td>
<td>-</td>
<td>SCA&lt;sup&gt;G&lt;/sup&gt; 16</td>
</tr>
<tr>
<td>EX 5</td>
<td>li</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>0.73</td>
<td>31.9</td>
<td>-</td>
<td>60% Quat 188&lt;sup&gt;H&lt;/sup&gt; 8.54</td>
</tr>
<tr>
<td>EX 6</td>
<td>li</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>-</td>
<td>23.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 7</td>
<td>Paint Example</td>
<td>i</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>-</td>
<td>38.1</td>
<td>-</td>
</tr>
<tr>
<td>EX 8</td>
<td>i</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>-</td>
<td>31.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 9</td>
<td>iv</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>-</td>
<td>38.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 10</td>
<td>iii</td>
<td>58</td>
<td>667</td>
<td>45% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.20</td>
<td>-</td>
<td>35.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 11</td>
<td>iii</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.08</td>
<td>-</td>
<td>30.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 12</td>
<td>i</td>
<td>58</td>
<td>667</td>
<td>35% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.40</td>
<td>-</td>
<td>42.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 13</td>
<td>i</td>
<td>58</td>
<td>667</td>
<td>45% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.20</td>
<td>-</td>
<td>32.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 14</td>
<td>i</td>
<td>58</td>
<td>667</td>
<td>45% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.20</td>
<td>-</td>
<td>38.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EX 15</td>
<td>i</td>
<td>58</td>
<td>667</td>
<td>50% acetic in IPA</td>
<td>16.7</td>
<td>1.74</td>
<td>0.04</td>
<td>-</td>
<td>47.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>A</sup> Cotton Linter, Intrinsic Viscosity I.V.(d/l/g) > 20

<sup>B</sup> Wood Pulp, I.V.(d/l/g) 4 – 8

<sup>C</sup> Wood Pulp, I.V.(d/l/g) 11 – 15

<sup>D</sup> Wood Pulp, I.V.(d/l/g) > 18

<sup>E</sup> The solvent weight includes the solvent delivered to the reactor during the acid quench (total solvent).

<sup>F</sup> IPA=Isopropanol

<sup>G</sup> Molar ratio of water to anhydroglucose (AGU)

<sup>H</sup> Molar ratio of sodium hydroxide (NaOH) to anhydroglucose (AGU)

<sup>I</sup> Hydrophobe modification (HM)

<sup>J</sup> GE=Glycidal Ether

<sup>K</sup> SCA=Sodium MonoChloroacetate

<sup>L</sup> Quat 188=cationizing agent -- N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride
Examples 1 - 6

[00079] HECs that have an HE-MS between 0.7 and 1.3, high water solubility, and an unsubstituted trimer ratio less than 0.21 are the basis of this invention. The properties for HECs of Examples 1 – 5 of this invention are shown in Table 2. Table 1 describes how the lowly hydroxyethylated HECs are prepared by completely opening up the cellulose fiber with high initial caustic level (AC1) and then "quenching" continuously to a low caustic level (AC2) during the reaction. This process drives a more uniform substitution so as to render high water solubility at low HE-MS. Examples 1-5 in Table 2 have an unsubstituted trimer ratio (U3R) less than 0.12 indicative of a very uniform structure and water solubility well over 90%. Example 6 describes an HEC with HE-MS of 0.7 having 100% water solubility, whereas the U3R is 0.26 setting the lower HE-MS limit of the invention.

[00080] Also shown in Table 2 are the properties of commercial Natrosol HECs with HE-MS in the range of 1.5 to 1.8. Commercial HECs with HE-MS in the range of 0.7 to 1.3 are not available due to poor water solubility and viscosifying power. For HECs of the invention, unprecedented water-solubility and unsubstituted trimer ratios are achieved at significantly lower HE-MS. Examples 3 - 5 demonstrate that further modification with hydrophobic, cationic, and anionic reagents is feasible.
### Table 2 – Water Soluble Low HE-MS HEC and Derivatives

<table>
<thead>
<tr>
<th>Example</th>
<th>HE-MS</th>
<th>Derivative</th>
<th>1% Aq. Viscosity (cP)</th>
<th>Solubility</th>
<th>Unsubstituted Trimer Ratio U3R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>1.2</td>
<td>-</td>
<td>244 – 2%</td>
<td>94</td>
<td>0.075</td>
</tr>
<tr>
<td>Example 2</td>
<td>1.0</td>
<td>-</td>
<td>191 – 2%</td>
<td>99</td>
<td>0.110</td>
</tr>
<tr>
<td>Example 3</td>
<td>1.0</td>
<td>Butyl 0.6%</td>
<td>227 – 2%</td>
<td>95</td>
<td>0.079</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.9</td>
<td>Carboxymethyl DS 0.23</td>
<td>105 – 2%</td>
<td>95</td>
<td>N/A</td>
</tr>
<tr>
<td>Example 5</td>
<td>0.9</td>
<td>Quat 1.5 %</td>
<td>221 – 2%</td>
<td>95</td>
<td>0.119</td>
</tr>
<tr>
<td>Example 6</td>
<td>0.7</td>
<td>-</td>
<td>24,200 – 2%</td>
<td>100</td>
<td>0.260</td>
</tr>
<tr>
<td>Comparative Natrosol 150GXR</td>
<td>1.5</td>
<td>-</td>
<td>200 – 2%</td>
<td>94</td>
<td>0.191</td>
</tr>
<tr>
<td>Comparative Natrosol 150GBXR</td>
<td>1.6</td>
<td>-</td>
<td>185 – 2%</td>
<td>97</td>
<td>0.031</td>
</tr>
<tr>
<td>Comparative Natrosol 180GXR</td>
<td>1.8</td>
<td>-</td>
<td>325 – 2%</td>
<td>93</td>
<td>0.167</td>
</tr>
<tr>
<td>Example 7</td>
<td>1.1</td>
<td>-</td>
<td>24,860</td>
<td>94</td>
<td>0.070</td>
</tr>
<tr>
<td>Example 8</td>
<td>0.9</td>
<td>-</td>
<td>24,360</td>
<td>92</td>
<td>0.102</td>
</tr>
<tr>
<td>Example 9</td>
<td>1.1</td>
<td>-</td>
<td>10,680</td>
<td>93</td>
<td>0.088</td>
</tr>
<tr>
<td>Example 10</td>
<td>1.3</td>
<td>-</td>
<td>5,280</td>
<td>95</td>
<td>0.099</td>
</tr>
<tr>
<td>Example 11</td>
<td>0.9</td>
<td>-</td>
<td>4,860</td>
<td>90</td>
<td>0.142</td>
</tr>
<tr>
<td>Example 12</td>
<td>1.3</td>
<td>-</td>
<td>10,100</td>
<td>98</td>
<td>0.181</td>
</tr>
<tr>
<td>Example 13</td>
<td>1.1</td>
<td>-</td>
<td>27,200</td>
<td>95</td>
<td>0.102</td>
</tr>
<tr>
<td>Example 14</td>
<td>1.0</td>
<td>-</td>
<td>32,100</td>
<td>90</td>
<td>0.180</td>
</tr>
<tr>
<td>Example 15</td>
<td>0.8</td>
<td>-</td>
<td>29,600</td>
<td>95</td>
<td>0.119</td>
</tr>
</tbody>
</table>

**Examples 7 - 15**

**[00081]** Examples 7-15 demonstrate that the synthesis procedure can be performed on a wide range of cellulose furnishes from cotton linters to wood pulps in order to generate a family of water-soluble, low HE-MS HEC products.

**[00082]** Examples 7, 8, and 12-15 show that high molecular weight, low HE-MS, water soluble HECs produced from cotton linters have 1 wt % Brookfield viscosities (spindle 3, 3 rpm, at 25°C) up to 32,000 cps. Commercially available high molecular weight HECs such as those marketed under the trademarks Natrosol 250 HHBR & HHR, Natrosol HI-VIS, Cellosize QP 100 MH, and Tylose H 200000 YP2 products typically have 1 wt% viscosities in the range of 4,500 – 6,000 cP.
Example 16

**Architectural Coatings**

[00083] Water-soluble, low HE-MS HEC shows enhanced thickening efficiency in architectural coating applications. Example 7 and Natrosol 250HHR were evaluated in the Ucar Latex 379G 70-PVC flat paint formulation shown. The novel thickener was 30% more efficient than 250HHR while maintaining similar paint properties as shown in Table 3.

<table>
<thead>
<tr>
<th>Ucar Latex 379G 70-PVC Formulation</th>
<th>Grams/13,000g</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Paint</strong></td>
<td></td>
</tr>
<tr>
<td>Pigment Grind</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>2,521 g</td>
</tr>
<tr>
<td>Nuosept 95</td>
<td>32.4</td>
</tr>
<tr>
<td>Tamol 731A Dispersant</td>
<td>64.7</td>
</tr>
<tr>
<td>Igepal CO-660</td>
<td>31.0</td>
</tr>
<tr>
<td>Igepal CO-897</td>
<td>43.6</td>
</tr>
<tr>
<td>AMP-95</td>
<td>14.1</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>182.9</td>
</tr>
<tr>
<td>Rhodine 640</td>
<td>14.1</td>
</tr>
<tr>
<td>Water, Discretionary,</td>
<td>1,407</td>
</tr>
<tr>
<td>Ti-Pure R-931 TiO2</td>
<td>1,055</td>
</tr>
<tr>
<td>ASP NC Clay</td>
<td>2,814</td>
</tr>
<tr>
<td>ECC #10 White Calcium Carbonate</td>
<td>2,110</td>
</tr>
<tr>
<td>Cellite 281 Silica</td>
<td>352</td>
</tr>
<tr>
<td>-Disperse to Hegman 4 to 5 –</td>
<td></td>
</tr>
</tbody>
</table>

**Letdown**

- All Discretionary Water in –

| Ucar Latex 379G                    | 2,079        |
| Texanol                            | 11.1         |
| PA-454 Antifoam                    | 26.7         |
| Propylene Glycol                   | 140.7        |
| **Total**                          | 13,000 g     |

**Thickened Paints**

| Base Paint                         | 220 g        |
| Thickener Solution + Water to 95 KU| 50           |

| **Total**                          | 270 g        |

pH, Initial (8.5 Target)

Density, lb/100 gal

Solids, Weight %

VOLUME%  47.8

PVC, % 69.9
Table 3: Ucar Latex 379G 70-PVC Paint Properties

<table>
<thead>
<tr>
<th>Thickener</th>
<th>Thickener Conc. (wt%)</th>
<th>Stormer (KU) Initial/Overnight</th>
<th>HSV (Poise)</th>
<th>Sag</th>
<th>Leveling</th>
<th>Hiding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natrosol 250HHR</td>
<td>0.43</td>
<td>100/100</td>
<td>0.6</td>
<td>8</td>
<td>5</td>
<td>0.984</td>
</tr>
<tr>
<td>Example 7</td>
<td>0.33</td>
<td>100/100</td>
<td>0.6</td>
<td>8</td>
<td>4</td>
<td>0.983</td>
</tr>
</tbody>
</table>

Example 17

Completion / Workover Fluids

[00084] The HECs of the invention exhibit novel thickening of heavy brines. Completion fluids are composed of a variety of brines of different salinity characterized by a density ranging from 8.5 ppg (pound per gallon) for seawater up to 19.2 ppg for heavy brines containing zinc and calcium bromide salts. Standard high viscosity HEC is commonly used as a viscosifier for brines ranging from 9 – 13 ppg. There presently is not an efficient viscosifier for heavy brines with a density ranging from 14 ppg (CaBr₂) to 19.2 ppg (ZnBr₂/CaBr₂). These brines have a very low level of free water content available, and therefore, do not promote optimum hydration of standard HECs. These brines are characterized by a very low pH (pH< 1 for ZnBr₂/CaBr₂).

[00085] Invention HEC Examples 13 and 15 were evaluated in 4 different brine systems (freshwater, salt-saturated water, CaBr₂ and ZnBr₂/CaBr₂) at 0.57 wt %. These were compared to a standard HEC widely used in completion fluids (Natrosol Hi-VIS). The viscosity and fluid loss properties were measured after static aging overnight at room temperature. Detailed results are reported in Tables 4-a to 4-d.

[00086] Invention Examples 13 and 15 showed exceptional thickening in the high density, heavy brine solutions (characterized by low water activity) as detailed by the high apparent viscosities (A.V.) and yield values (YV) that developed in these systems (Tables 4 c-d). In contrast, commercial Hi-VIS did not go into solution in these low water activity systems. Additionally, the invention HEC examples developed appreciable low-end rheology as
reflected by the 6 and 3-rpm Fann dial readings, and showed appropriate fluid loss values.

[00087] Among the water soluble, low HE-MS HEC samples, Example 15 provided outstanding thickening efficiency in all systems (fresh water, seawater, and high-density brines). Solutions made with this invention example were so viscous in the heavy brines that the viscosity reading was out of scale suggesting an extremely versatile and efficient viscosifier in a variety of solutions.
### Table 4-a: Rheology/Fluid Loss performance of various HEC samples in Demineralized water

<table>
<thead>
<tr>
<th>Fluid System</th>
<th>Sample Ref.</th>
<th>Final</th>
<th>Fann DR</th>
<th>Rheology</th>
<th>Fluid Loss (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine</td>
<td>Density ppg</td>
<td>Initial pH</td>
<td>Ph Aft. Ag.</td>
<td>6 rpm</td>
<td>3 rpm</td>
</tr>
<tr>
<td>Water</td>
<td>8.3</td>
<td>7.3</td>
<td></td>
<td>11.1</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Invention HEC Example 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Invention HEC Example 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Natrosol Hi-VIS</td>
<td>10.1</td>
<td>12</td>
</tr>
</tbody>
</table>

### Table 4-b: Rheology/ Fluid Loss performance of various HEC samples in 36% NaCl Solution

<table>
<thead>
<tr>
<th>Fluid System</th>
<th>Sample Ref.</th>
<th>Final</th>
<th>Fann DR</th>
<th>Rheology</th>
<th>Fluid Loss (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine</td>
<td>Density ppg</td>
<td>Initial pH</td>
<td>Ph Aft. Ag.</td>
<td>6 rpm</td>
<td>3 rpm</td>
</tr>
<tr>
<td>Saturated Salt (36% NaCl)</td>
<td>10.0</td>
<td>8.1</td>
<td></td>
<td>10.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Invention HEC Example 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Invention HEC Example 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Natrosol Hi-VIS</td>
<td>10.2</td>
<td>11</td>
</tr>
</tbody>
</table>
### Table 4-c: Rheology/Fluid Loss performance of various HEC samples in CaBr² Brine

<table>
<thead>
<tr>
<th>Fluid system</th>
<th>Sample</th>
<th>Final</th>
<th>Fann DR</th>
<th>Rheology</th>
<th>Fluid Loss (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaBr²</td>
<td>Ref.</td>
<td>PH Aft. Ag.</td>
<td>6 rpm</td>
<td>3 rpm</td>
<td>A.V. cPs</td>
</tr>
<tr>
<td></td>
<td>Invention HEC Example 13</td>
<td>7.5</td>
<td>52</td>
<td>38</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>Invention HEC Example 15</td>
<td>7.6</td>
<td>84</td>
<td>66</td>
<td>Out of Scale</td>
</tr>
<tr>
<td></td>
<td>Natrosol Hi-VIS</td>
<td>7.7</td>
<td>7</td>
<td>4.4</td>
<td>49</td>
</tr>
</tbody>
</table>

### Table 4-d: Rheology/Fluid Loss performance of various HEC samples in ZnBr²/CaBr² Brine

<table>
<thead>
<tr>
<th>Fluid system</th>
<th>Sample</th>
<th>Final</th>
<th>Fann DR</th>
<th>Rheology</th>
<th>Fluid Loss (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBr²/CaBr²</td>
<td>Ref.</td>
<td>PH Aft. Ag.</td>
<td>6 rpm</td>
<td>3 rpm</td>
<td>A.V. cPs</td>
</tr>
<tr>
<td></td>
<td>Invention HEC Example 13</td>
<td>1.4</td>
<td>104</td>
<td>85</td>
<td>Out of Scale</td>
</tr>
<tr>
<td></td>
<td>Invention HEC Example 15</td>
<td>1.2</td>
<td>130</td>
<td>108</td>
<td>Out of Scale</td>
</tr>
<tr>
<td></td>
<td>Natrosol Hi-VIS</td>
<td>1.2</td>
<td>Did not go into solution</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Did not fully go into solution
Example 18

Oil-well Cementing

[00088] Water soluble, low HE-MS HEC shows exceptional fluid loss properties at high temperature and in the presence of high salt. Oil-well cementing is the process of mixing a slurry of cement, water, and additives and pumping it down through steel casing to critical points in the annular space between the wall of the well and the outside of the casing. Additives are incorporated into cement slurries to deliver various functional properties, such as set time control, friction reduction, slurry density modification, cement bonding and fluid loss control. Among these properties, fluid loss control is a critical concern, especially difficult to control under severe environment conditions such as high salt and high temperature. To prevent early dehydration of cement slurries and related problems, fluid loss control additives are added to help maintain the integrity of designed slurry properties.

[00089] A wide variety of fluid loss control additives are currently used in formulating cement slurries depending upon the oil well environment. For medium temperature operations, cellulosics such as carboxymethylhydroxyethylcellulose (CMHEC) and hydroxyethylcellulose (HEC) are the most commonly used fluid loss additives. Among cellulosics, low molecular weight ones are preferred to achieve a good balance between fluid loss control and rheological properties by allowing higher flexibility of the polymer dosage under different operating conditions. While these polymers provide acceptable fluid loss control under moderate operating conditions, they are unsatisfactory under high temperature and salt environments. Hence, there is a need for improved fluid loss control additives under a wide range of operating conditions.

[00090] It has been surprisingly discovered that low molecular weight HECs with low HE-MS and high solubility, significantly reduce the fluid loss in oil well cements. The HECs of the invention show outstanding temperature and salt tolerance over standard commercially available cement grade HEC (Natrosol 180 GXR, available from Aqualon Company). Furthermore, butyl modified low
HE-MS, water soluble HEC Example 3 performs better than any other comparative samples.

[00091] Invention examples 2 and 3, and Natrosol 180 GXR were evaluated in the cement slurry formulation shown containing 0 and 18% salt (based on water content). The slurry density was around 15.8-16.2 ppg. Fluid Loss performance was measured at moderate and high temperatures, 80 °F and 180 °F, respectively.

<table>
<thead>
<tr>
<th>Formulation Cement Slurry Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ingredients</strong></td>
</tr>
<tr>
<td>Cement</td>
</tr>
<tr>
<td>Dispersant</td>
</tr>
<tr>
<td>Fluid Loss Additive</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Salt</td>
</tr>
<tr>
<td>Retarder</td>
</tr>
</tbody>
</table>

[00092] Table 5 demonstrates the superior performance of Invention Examples 2 and 3. The fluid loss control provided by the invention examples is less affected by temperature and salt than standard HEC. The invention examples show outstanding performance at 180 °F with 18% salt. Under these extreme conditions, the fluid loss performance of Examples 2 and 3 are 10-20 times better than commercial HEC.

**Table 5: American Petroleum Institute (API) Fluid Loss Control Properties**

<table>
<thead>
<tr>
<th>Sample</th>
<th>MS</th>
<th>C-4 modification</th>
<th>Fluid Loss @ 80 °F w/o NaCl</th>
<th>Fluid Loss @ 80 °F with 18% NaCl</th>
<th>Fluid Loss @ 180 °F w/o NaCl</th>
<th>Fluid Loss @ 180 °F with 18% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEC 180GXR</td>
<td>1.8</td>
<td>0</td>
<td>30 ml</td>
<td>224 ml</td>
<td>54 ml</td>
<td>786 ml</td>
</tr>
<tr>
<td>Invention</td>
<td>1.0</td>
<td>0</td>
<td>24 ml</td>
<td>144 ml</td>
<td>49 ml</td>
<td>62 ml</td>
</tr>
<tr>
<td>Example 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Invention</td>
<td>1.0</td>
<td>0.56%</td>
<td>23 ml</td>
<td>127 ml</td>
<td>46 ml</td>
<td>37 ml</td>
</tr>
<tr>
<td>Example 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example 19

Paper

[00093] Low HE-MS, water solube HEC is a highly efficient thickener and water retention agent in paper coatings. Invention HEC Examples 1 and 2, commercial samples Aqualon 7L1T CMC, and Natrosol 250GR were evaluated as thickeners and water retention aids in the paper coating formulation as shown below. The amount of rheology modifier necessary to maintain the Brookfield viscosity at 1500 +/- 50 cps, the water loss, and Hercules high shear viscosity are shown in Table 6. Low HE-MS, water soluble HECs Examples 1 and 2 and HEC 250GR are of similar molecular weights and solution viscosities; however, the low HE-MS, water soluble HEC products have a significantly higher dosage efficiency than HEC 250GR (up to 50% more efficient) while maintaining its low water loss rate. In addition Examples 1 and 2 have much lower water loss and higher dosage efficiency than Aqualon 7L1T CMC.

Paper coating formulation

<table>
<thead>
<tr>
<th>Parts</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC 60*</td>
<td>60</td>
</tr>
<tr>
<td>HC 90*</td>
<td>40</td>
</tr>
<tr>
<td>Dow 620 SB latex</td>
<td>12</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>1.00</td>
</tr>
<tr>
<td>Dispex N-40</td>
<td>0.25</td>
</tr>
<tr>
<td>(dispersing agent)</td>
<td></td>
</tr>
<tr>
<td>Solids (%)</td>
<td>68 +/- 0.5</td>
</tr>
<tr>
<td>Viscosity (cps):</td>
<td>1500 cps at ambient</td>
</tr>
<tr>
<td>Rheology modifier</td>
<td>Aqualon CMC7L1T, HEC 250GR, Invention Examples 1 and 2</td>
</tr>
</tbody>
</table>

* Ground Calcium Carbonate (HydroCarb) from OMYA Inc.
Table 6: Paper Coating Properties

<table>
<thead>
<tr>
<th>Thickener</th>
<th>HE-MS or DS</th>
<th>2% Viscosity (cPs)</th>
<th>Parts thickener/100 part filler</th>
<th>Water Loss (g/sq meter, 0.6 Bar/1min)</th>
<th>High Shear Rheology 1st Pass 2400/4400 RPM</th>
<th>High Shear Rheology 2nd Pass 2400/4400 RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natrosol HEC 250G</td>
<td>2.5</td>
<td>300</td>
<td>0.75</td>
<td>91</td>
<td>54/55</td>
<td>54/48</td>
</tr>
<tr>
<td>Aqualon 7L1T CMC</td>
<td>0.7</td>
<td>100</td>
<td>0.99</td>
<td>168</td>
<td>42/34</td>
<td>34/30</td>
</tr>
<tr>
<td>Invention Example 1</td>
<td>1.2</td>
<td>244</td>
<td>0.50</td>
<td>98</td>
<td>66/50</td>
<td>55/46</td>
</tr>
<tr>
<td>Invention Example 2</td>
<td>1.0</td>
<td>191</td>
<td>0.55</td>
<td>101</td>
<td>66/51</td>
<td>52/45</td>
</tr>
</tbody>
</table>

**Example 20**

**Construction**

[00094] Low HE-MS, water soluble HEC shows enhanced viscosity in joint compounds. Example 9 and Natrosol 250HHR product were evaluated as thickeners at 0.30 wt % in an all-purpose joint compound formulation, as described below. Table 7 shows that the formulation containing invention example HEC was more efficient (higher joint compound viscosity) while maintaining good adhesion, workability, and cratering properties.

**All-Purpose Joint Compound Formulation**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Supplier</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground CaCO3</td>
<td>Georgia White #9</td>
<td>61</td>
</tr>
<tr>
<td>Attapulgite Clay</td>
<td>Gel B, Milwhite</td>
<td>2.0</td>
</tr>
<tr>
<td>Mica</td>
<td>4-K, Oglebay Norton</td>
<td>3.00</td>
</tr>
<tr>
<td>Latex dispersion</td>
<td>EVA or PVA latex (see Note 1)</td>
<td>2.5</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>Aldrich</td>
<td>0.35</td>
</tr>
<tr>
<td>Biocide</td>
<td>Trosan 174, Troy chemical</td>
<td>0.05</td>
</tr>
<tr>
<td>Defoamer</td>
<td>Foamaster PD1WD, Cognis</td>
<td>0.02</td>
</tr>
<tr>
<td>Thickener</td>
<td></td>
<td>0.30</td>
</tr>
<tr>
<td>Water</td>
<td>Tap water</td>
<td>30.6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>
Table 7: All Purpose Joint Compound Properties

<table>
<thead>
<tr>
<th>Thickener</th>
<th>Joint Compound Viscosity (Brabender Units)</th>
<th>Adhesion</th>
<th>Cratering (1-10) 10 best</th>
</tr>
</thead>
<tbody>
<tr>
<td>250HHXRX HEC</td>
<td>480</td>
<td>100%</td>
<td>7</td>
</tr>
<tr>
<td>Commercial HEC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Invention</td>
<td>500</td>
<td>100%</td>
<td>8</td>
</tr>
<tr>
<td>Example 9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Example 21

Personal Care

[00095] Low HE-MS, water soluble HEC shows enhanced viscosity in personal care formulations. Natrosol® hydroxyethyl cellulose type 250HHR and low HE-MS, water soluble HEC Example 8 were compared at 0.7 wt% for thickening efficiency in the hair conditioner formulation shown below.

Hair Conditioner

90.94g Deionized water
00.70g Thickening polymer (Natrosol® 250HHR, HEC example 2)
02.00g Cetyl alcohol
00.50g Potassium Chloride
02.00g Isopropyl Myristate
As required – citric acid to adjust pH
As required – Sodium hydroxide to adjust pH
00.50g Germaben II

Procedure:

[00096] The thickening polymer was added to water under agitation. Next, the pH was adjusted to 8.0 to 8.5. The slurry was stirred for at least 30 minutes or until the polymer dissolved. The solution was heated to about 65°C and cetyl alcohol was added and mixed until homogeneous. The mixture was cooled to about 50°C and potassium chloride was added. Isopropyl myristate was added and mixed until the mixture looked homogeneous. The pH of the mixture was adjusted to 5.3 - 5.5 with citric acid and/or NaOH solution. The conditioner was preserved with 0.5 g Germaben II and mixed until the mixture reached room temperature.

[00097] The viscosity of the conditioning formulation containing low HE-MS, water soluble HEC Example 8 was 3,730 cP, as compared to the control containing Natrosol® 250HHR at 910 cPs, a 4-fold improvement.
Example 22

Oral Care – Lean Solvent Gels

[00098] Low HE-MS, water soluble HECs form strong gels in lean solvents unlike other commercial high molecular weight HEC. There is a need for efficient viscosifiers and gelling agents in personal and oral care applications that function well in low water activity compositions such as hydro-alcoholic and lean solvent solutions. Lean solvents are the basis of toothpaste formulations and are typically a mixture of water and a miscible organic solvent such as sorbitol or glycerol. Often hydrophilic polymers have difficulty fully hydrating in these lean solutions similarly to solutions with high salt levels as there is less water accessible to the polymer.

[00099] It has been discovered that these water-soluble low HE-MS HEC samples act as efficient gelling agents in glycerol-water solutions, unlike commercial HECs. 1 wt% solutions of Examples 12 and 14 and Natrosol 250 HHX were prepared in water. These three samples are of similar molecular weight. Upon diluting the low HE-MS samples with glycerol to 0.5 wt %, elastic gels developed over the course of a couple of days. Undisturbed samples of the gels did not exhibit significant syneresis over the course of 3 weeks. This behavior is unlike any of our standard Natrosol HEC materials that yield free-flowing solutions under both conditions.

[00100] Visual assessment of the 0.5 wt% solution quality and zero-shear viscosity for the three HECs tested are listed in Table 8. The distinctive behavior of the low HE-MS HEC samples is particularly evident when comparing zero shear viscosities in the 50:50 glycerol:water solutions. Examples 12 and 14 reveal solution viscosities that are 6 - 10 times greater than expected. Furthermore, the rheological profiles are indicative of elastic gels with yield points.

[00101] The assembly is not instantaneous, but takes some time (hours-days) to form. This may find use in PC applications such as toothpaste
formulations where the ability to easily pump a material into end-use packaging is desirable via in situ thickening after final packaging. Development of a yield stress is also advantageous in suspending solid ingredients. It is important to point out that all operations described here were performed without heating or a drastic change in solution pH. Competing technologies for the development of a yield stress, such as carrageenan (heating/cooling) or synthetic carbomer (pH control) employ those strategies, which can be incompatible with other ingredients in the formulation.

[000102] In order to develop the gel-like character observed with these systems, the initial dissolution of the polymer in a strong solvent (i.e water) followed by dilution with a non-solvent as described above was followed. The use of 50:50 glycerol:water is one example of this. Replacement of the glycerol with any water miscible cosolvent (e.g. alcohols) should provide similar behavior.

Table 8: Appearance and Zero Shear Viscosity of 0.5 wt% HECs in Water and in 50:50 Glycerol:Water Solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>HE-MS</th>
<th>Solvent</th>
<th>Zero Shear Viscosity (Pa.s)</th>
<th>Solution Appearance @ 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natrosol 250HHX</td>
<td>2.4</td>
<td>Water</td>
<td>0.43</td>
<td>Clear fluid</td>
</tr>
<tr>
<td>Example 12</td>
<td>1.3</td>
<td>Water</td>
<td>0.49</td>
<td>Clear fluid</td>
</tr>
<tr>
<td>Example 14</td>
<td>1.0</td>
<td>Water</td>
<td>0.90</td>
<td>Clear fluid</td>
</tr>
<tr>
<td>Natrosol HHX</td>
<td>2.4</td>
<td>Glycerol:water</td>
<td>3.2</td>
<td>Clear fluid</td>
</tr>
<tr>
<td>Example 12</td>
<td>1.3</td>
<td>Glycerol:water</td>
<td>20.9</td>
<td>Clear gel</td>
</tr>
<tr>
<td>Example 14</td>
<td>1.0</td>
<td>Glycerol:water</td>
<td>33.9</td>
<td>Clear strong gel</td>
</tr>
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Example 23

Household

[000103] Low HE-MS, water soluble HEC shows excellent thickening ability in a common household care formulation. Natrosol® hydroxyethyl cellulose type 250HHR CS and low HE-MS, water soluble HEC Example 8 were evaluated at 0.2 wt% for their compatibility, thickening efficiency, and clarity in
an all-purpose cleaner. Table 9 shows that example 8 thickens the all-purpose cleaner nearly 2.5 times better than Natrosol® 250HHR CS which is of similar molecular weight. Furthermore, the clarity remains high indicating compatibility with this household cleaner.

Procedure: [000104] 20 g of a 1 wt% polymer solution was added to 80 g of Lysol All-Purpose Cleaner (pH 8). Final product viscosity was measured using the Brookfield LVT viscometer once the product had been conditioned for at least two hours at 25°C. The product clarity was measured at 600 nm using a spectrophotometer. The clarity measurements are reported as % transmittance (% T) with 100% being perfect clarity.

Table 9: Viscosity and Transmittance of 0.2 wt% HEC in Lysol All-Purpose Cleaner

<table>
<thead>
<tr>
<th>Thickener</th>
<th>HE-MS</th>
<th>Viscosity (cPs)</th>
<th>T (%)</th>
</tr>
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<tbody>
<tr>
<td>Control - Polymer-Free</td>
<td>-</td>
<td>9</td>
<td>96.9</td>
</tr>
<tr>
<td>Invention Example 8</td>
<td>0.9</td>
<td>44</td>
<td>96.0</td>
</tr>
<tr>
<td>Natrosol 250HHR CS</td>
<td>2.5</td>
<td>18</td>
<td>98.9</td>
</tr>
<tr>
<td>Lysol All-Purpose Cleaner as.</td>
<td>-</td>
<td>3</td>
<td>99.0</td>
</tr>
</tbody>
</table>

Example 24

Pharmaceuticals [000105] Low HE-MS, water soluble HEC excipients provide superior tablet hardness. HEC is used in the pharmaceutical industry as an excipient to provide a swellable diffusion barrier in controlled release applications. The gel matrix it forms limits the diffusion of aqueous fluids into a system and dissolves actives out of the system.

[000106] HEC has some unique modified release properties not duplicated by hydroxypropylmethyl cellulose (HPMC) and hydroxypropyl cellulose (HPC). However, current knowledge is that commercial grades of HEC show significantly inferior compression properties when compared to HPMC and
HPC. The poor compactivity of this polymer generally makes the polymer suitable for only wet granulation processing, rather than direct compression processing which is frequently the industry preference.

[000107] In order to improve this limitation, scientists at Astra Zeneca in International Patent Application, WO 02/19990 A1 describe a procedure whereby HEC is purified by dissolution in water before precipitation via addition of organic solvent. The precipitate is washed and then milled in a specific manner. The purified HEC has markedly improved tablet compactability.

[000108] In accordance with the present invention is the use of a low HE-MS, water soluble HEC material that is highly compressible for making direct compressible tablets for use in compaction applications such as sustained release tablets for pharmaceutical, household, and agricultural applications.

[000109] Table 10 shows the strength of pure polymer tablets (with 1% stearic acid for lubrication) made from low HE-MS HEC and commercial Natrosol 250 HHX Pharm HEC. Water soluble HEC with HE-MS 1.1 achieves a 9-fold increase in tablet hardness as compared to regular Natrosol 250 HHX Pharm. In a typical modified release formulation, these materials all showed excellent direct compression performance and drug release kinetics as compared to commercial Natrosol 250 HHX Pharm.

Table 10: Hardness of 99 wt% HEC with 1 wt% Stearic Acid Tablets

<table>
<thead>
<tr>
<th>Water Soluble HEC</th>
<th>HE-MS</th>
<th>1 wt% Solution Viscosity (cps)</th>
<th>Mean Particle Diameter (um)</th>
<th>Tablet Hardness (kP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invention</td>
<td>1.1</td>
<td>27,200</td>
<td>121</td>
<td>24.6</td>
</tr>
<tr>
<td>Example 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natrosol 250 HHX</td>
<td>2.4</td>
<td>3,850</td>
<td>105</td>
<td>2.7</td>
</tr>
</tbody>
</table>

[000110] While the invention has been described with respect to specific embodiments, it should be understood that the invention should not be limited thereto and that many variations and modifications are possible without departing from the spirit and scope of the invention.
WHAT IS CLAIMED:

1. A composition comprising hydroxyethylcellulose (HEC) having hydroxyethyl groups that are uniformly distributed on the cellulose backbone wherein the unsubstituted trimer ratio (U3R) is less than about 0.21, the water solubility is greater than about 90 %, and the hydroxyethyl molar substitution is greater than about 0.7 and less than about 1.3.

2. The composition of claim 1, wherein the hydroxyethylcellulose is further modified with one or more substituents having chemical functionality selected from the group consisting of nonionic, anionic, and cationic and mixtures thereof.

3. The composition of claim 2, wherein the substituents are attached to the hydroxyethylcellulose backbone via an ether, ester, or urethane linkage moiety.

4. The composition of claim 2, wherein the substituents present have nonionic chemical functionality.

5. The composition of claim 4, wherein the substituents have the formula

--R, or --A-R,

wherein

A is selected from the group consisting of

CH₂-CH(OH),
CH₂-CH(OH)-CH₂,
(CH₂-CH₂-O)ₙ where n = 1 – 100,
CH₂-CH(OH)-CH₂-O-(CH₂-CH₂-O)ₙ where n = 1 – 100, and
CH(R)-C(O)-CH₂,

and

R is selected from the group consisting of
i) an acyclic or cyclic, saturated or unsaturated, branched or linear hydrocarbon moiety having 1 to 30 carbon atoms,

ii) an acyclic or cyclic, saturated or unsaturated, branched or linear heterohydrocarbon moiety having 1 to 30 carbon atoms and one of more oxygen, nitrogen, or silicone atoms,

iii) an acyclic or cyclic, saturated or unsaturated, branched or linear hydrocarbon moiety having 1 to 30 carbon atoms and one or more aromatic hydrocarbon groups,

iv) an acyclic or cyclic, saturated or unsaturated, branched or linear heterohydrocarbon moiety having 1 to 30 carbon atoms and one or more oxygen, nitrogen, or silicone atoms and one or more aromatic groups, and

v) an acyclic or cyclic, saturated or unsaturated, branched or linear, heterohydrocarbon moiety having 1 to 30 carbon atoms and one or more oxygen, nitrogen, or silicone atoms and one or more heteroaromatic groups containing one or more oxygen, nitrogen, or silicone groups.

6. The composition of claim 5, wherein R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, alkyl aryl, aryl alkyl, alkenyl aryl, aryl alkenyl, and mixtures thereof, having when possible, from 1 to 30 carbon atoms.

7. The composition of claim 2, wherein the substituents present have anionic chemical functionality.

8. The composition of claim 7, wherein the anionic chemical functionality is selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate, phosphonate and mixtures thereof.
9. The composition of claim 7, wherein the substituents are selected from the group consisting of carboxymethyl, sulfoethyl, phosphonomethyl, and mixtures thereof.

10. The composition of claim 2, wherein the substituents present have cationic chemical functionality.

11. The composition of claim 10, wherein the substituents have the formula $R^1R^2R^3R^4N^+ (A^-)$

   wherein
   $R^1$ is $-CH_2-CHOH-CH_2$-- or $-CH_2-CH_2$--,
   $R^2$, $R^3$, $R^4$ each independently is selected from the group consisting of
   an alkyl or aryalkyl group having 1 to 20 carbon atoms, and
   $A^-$ is a halide, sulfate, phosphate, or tetrafluoroborate.

12. The composition of claim 11, wherein the substituents are selected from the group consisting of 2-hydroxypropyltrimethylammoniumchloride,
   2-hydroxypropyldecylimidethylammoniumchloride,
   2-hydroxypropylcoocalkyldimethylammoniumchloride,
   2-hydroxypropyloctadecylimidethylammoniumchloride, and mixtures thereof.

13. The composition of claim 10, wherein the cationic group is derived from the grafting reaction of the HEC composition with
diallyldimethylammonium chloride.

14. The composition of claim 2, wherein the modified hydroxyethylcellulose is selected from the group consisting of methyl
    hydroxyethylcellulose, ethyl hydroxyethylcellulose, octyl
    hydroxyethylcellulose, cetyl hydroxyethylcellulose, cetoxy-2-hydroxypropyl
    hydroxyethylcellulose, butoxy-2-hydroxypropyl hydroxyethylcellulose, butoxy-2-
    hydroxypropyl cetyl hydroxyethylcellulose, butoxy-2-hydroxypropyl cetoxy-2-

15. The composition of claim 1, wherein the unsubstituted trimer ratio (U3R) is less than 0.18.

16. The composition of claim 1, wherein the hydroxyethyl molar substitution is greater than about 0.8 and less than about 1.3.

17. A slurry process for making the hydroxyethylcellulose composition of claim 1 comprising

A) mixing and reacting cellulose, water and alkali in an organic solvent for a sufficient time and at a sufficient temperature in order to form an alkali cellulose mixture, wherein the water to anhydroglucose (AGU) molar ratio is in the range of about 5 to 35 and the alkali to AGU molar ratio is greater than about 1.6,
B) adding a sufficient amount of ethylene oxide to produce the desired HE-MS

C) adding a sufficient amount of acid continuously in order to reduce the alkali to AGU molar ratio to less than about 0.4 and preferably greater than about 0.04, while reacting the ethylene oxide with the alkali cellulose at a sufficient temperature and for a sufficient time to form a water soluble HEC product with a hydroxyethyl molar substitution of greater than about 0.7 and less than about 1.3.

18. The slurry process of claim 17, wherein the organic solvent is selected from the group consisting of ethanol, isopropanol, tert-butanol, acetone, methyl ethyl ketone, and dimethoxyethane and mixtures thereof.

19. The slurry process of claim 17, wherein the alkali is selected from the group consisting of lithium hydroxide, sodium hydroxide, potassium hydroxide, and mixtures thereof.

20. The slurry process of claim 17, wherein the cellulose is selected from the group consisting of cotton linters, wood pulps, and mixtures thereof.

21. The slurry process of claim 17, wherein the HEC composition is further reacted with at least one other derivatizing reagent to form a modified hydroxyethylcellulose composition.

22. The slurry process of claim 21, wherein the derivatizing reagent is selected from the group consisting of nonionic, cationic, anionic organic compounds and mixtures thereof.

23. The slurry process of claim 22 wherein the organic compounds are selected from the group consisting of halides, epoxides, glycidyl ethers, carboxylic acids, isocyanates, and mixtures thereof.

24. The slurry process of claim 17 or 21, wherein the HEC or modified HEC composition is further reacted with a viscosity reducing agent.
25. The slurry process of claim 24, wherein the viscosity reducing agent is selected from the group consisting of peroxides, persulfates, peracids, cellulolytic enzymes, salts of halide oxo acids, oxygen, and ozone.

26. A composition comprising a) a functional system selected from the group consisting of personal care compositions, household care compositions, pharmaceutical compositions, building and construction material compositions, emulsion polymerization compositions, oil field servicing fluid compositions, civil engineering servicing fluid compositions, paper coating compositions, paper making compositions, architectural coating compositions, industrial coating compositions, printing ink compositions, adhesive compositions, and mineral processing and recovery compositions and b) a hydroxyethylcellulose (HEC) of claim 1 or modified hydroxyethylcellulose of claim 2.

27. The composition of claim 26, wherein the functional system is an aqueous based architectural or industrial coating composition.

28. The composition of claim 27 further comprising a binder selected from the group consisting of a latex, an alkyd resin, a urethane resin, a silicone resin, and an epoxide resin.

29. The composition of claim 26, wherein the functional system is a building or construction material composition selected from the group consisting of concrete, tile cements and adhesives, plasters, stuccos, mortars, underwater concrete, joint compound or cement, crack fillers, floor screeds, and adhesive mortars.

30. The composition of claim 26, wherein the functional system is a personal care composition.
31. The composition of claim 30, wherein the personal care composition is selected from the group consisting of skin care, hair care, oral care, nail care, and personal hygiene products.

32. The composition of claim 26, wherein the functional system is a household care composition.

33. The composition of claim 32, wherein the household care composition is selected from the group consisting of fabric care, laundry detergent, hard surface cleaner, industrial institutional liquid soaps, and dish detergents.

34. The composition of claim 26, wherein the functional system is an oil field servicing fluid composition.

35. The composition of claim 34 wherein the oil field servicing fluid composition is selected from the group consisting of drilling fluid, completion or workover fluid, fracturing fluids, and oil well cementing fluids.

36. The composition of claim 26, wherein the functional system is a paper coating composition.

37. The composition of claim 26, wherein the functional system is a paper making composition.

38. The composition of claim 26, wherein the functional system is a pharmaceutical composition.

39. The composition of claim 38, wherein the pharmaceutical composition is selected from the form consisting of tablet, capsule, and granules.

40. The composition of claim 38, wherein the component b is used as an excipient.
INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/007663

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08B11/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 6 482 940 B1 (KLOHR ERIK-ANDREAS ET AL) 19 November 2002 (2002-11-19) column 1, lines 53-59; examples 5,6 column 2, lines 5-8</td>
<td>1-16, 26-40</td>
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Date of the actual completion of the International search

4 July 2006

Date of mailing of the international search report

19/07/2006

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Lanz, S

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US 4024335 A 17-05-1977 NONE

US 3709876 A 09-01-1973 NONE