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(54) Title: IMPROVED COLLOIDAL STABILIZER

(57) Abstract: In one aspect, the present invention is directed to a stabilizer composition comprising a mixture of (a) co-atritted microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose; produced by the dry blending of components (a) and (b). In other aspects, the present invention is directed to an aqueous dispersion comprising such stabilizer composition; a method of making such a stabilizer composition; as well as to a food, pharmaceutical, nutraceutical or industrial product comprising such a stabilizer composition.



IMPROVED COLLOIDAL STABILIZER

FIELD OF THE INVENTION

[0001] In one aspect, the present invention is directed to a stabilizer composition comprising a mixture of (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose; produced by the dry blending of components (a) and (b). In other aspects, the present invention is directed to an aqueous dispersion comprising such stabilizer composition; a method of making such a stabilizer composition; as well as to a food, pharmaceutical, nutraceutical or industrial product comprising such a stabilizer composition.

BACKGROUND OF THE INVENTION

[0002] Microcrystalline cellulose (hydrolyzed cellulose), also known as MCC or cellulose gel, is commonly used in the food industry to enhance the properties or attributes of a final food product. For example, it has been used as a binder and stabilizer in food applications, including beverages. It has also been used as a suspending agent in liquid pharmaceutical formulations, a binder and disintegrant in pharmaceutical tablets, and as a pharmaceutical pellet former in extrusion-spheronization. It has also been used as a binder, disintegrant, and processing aid in industrial applications, in household products such as detergent and/or bleach tablets, in agricultural formulations, and in personal care products such as dentifrices and cosmetics.

[0003] Microcrystalline cellulose and/or hydrolyzed cellulose wet cake has been modified for a variety of uses. In food products it is used as a gelling agent, a thickener, a fat substitute and/or non-caloric filler, and as a suspension stabilizer and/or texturizer. It has also been used as an emulsion stabilizer and suspending agent in pharmaceutical and cosmetic lotions and creams. Modification for such uses is carried out by subjecting microcrystalline cellulose or wet cake to intense attrition (high shear), as a result of which the particles are substantially subdivided

to give colloidal microcrystalline cellulose. However, as particle size is diminished, the individual particles tend to hornify upon drying, and may not be redispersible in water. A protective colloid (such as carboxymethylcellulose (CMC)) may be added during attrition, or following attrition but before drying. The protective colloid wholly or partially neutralizes the hydrogen or other bonding forces between the smaller sized particles. Colloidal microcrystalline cellulose, including carboxymethylcellulose-coated microcrystalline cellulose is described in US Pat. 3,539,365 (Durand *et al.*).

[0004] When dispersed in water, colloidal microcrystalline cellulose forms white, opaque, thixotropic gels with most of the microcrystalline cellulose particles being less than 1 micron in size. FMC Corporation (Philadelphia, PA, USA) manufactures and sells various grades of this product which comprise co-processed microcrystalline cellulose and sodium carboxymethylcellulose under the designations of, among others, AVICEL[®] and GELSTAR[®].

[0005] However, while such products provide desirable effects there remains a need for producing stabilizer compositions which exhibit even more enhanced stabilization, gel strength (G') and other rheological properties, and acid stability.

[0006] One approach taken to improve certain of these rheological properties has been to co-attrite microcrystalline cellulose with carboxymethylcellulose(s) having various properties and by various methods. Thus, United States Patent Application 2013/0090391 (Tan et al) discloses a stabilizer composition formed by co-attriting microcrystalline cellulose with low viscosity (10-200 cps) or medium viscosity (200-4,000 cps) carboxymethylcellulose having a low degree of substitution (0.45-0.85). In another case, United States Patent Application 2013/0150462 (Tan et al) discloses a stabilizer composition produced by co-attriting microcrystalline cellulose with carboxymethylcellulose having or comprising a low viscosity (less than 100 cps) and a higher degree of substitution (0.95-1.5).

[0007] WO 2013/052114 (Tan et al) discloses stabilizer compositions produced by wet blending (a) a co-extruded (co-attrited) microcrystalline cellulose and low

substituted (DS of 0.45-0.85) carboxymethylcellulose; with (b) a second carboxymethylcellulose having a DS of 0.9-1.5; and subsequently drying such mixture. Comparative Example 1B of WO 2013/052114 indicates that when (a) a dry powder of co-attrited microcrystalline cellulose and low substituted/low viscosity carboxymethylcellulose is dry blended with (b) a dry powder of high substituted/medium viscosity carboxymethylcellulose, the resultant colloid produced upon resuspension exhibits a very low set-up gel strength G' of only 8 Pa.

[0008] Consequently, it is completely unexpected that stabilizer compositions produced by dry blending (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose, will exhibit desirable set up strengths, particularly as it is not commercially and economically practical to dry such components if they are wet blended. Further, it has been unexpectedly found that such stabilizer compositions exhibit desirable stability and particle suspending power under acidic conditions.

SUMMARY OF THE INVENTION

[0009] In one aspect, the present invention is directed to a stabilizer composition comprising a mixture of (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose; produced by the dry blending of components (a) and (b).

[0010] In a further aspect, the present invention is directed to an aqueous suspension comprising: (A) a stabilizer composition comprising a mixture of (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose; produced by the dry blending of components (a) and (b); and (B) water.

[0011] In another aspect, the present invention is directed to a method of making a stabilizer composition comprising dry blending (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose.

[0012] In yet another aspect, the present invention is directed to a food, pharmaceutical, nutraceutical or industrial product comprising such a stabilizer composition.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In one aspect, the present invention is directed to a stabilizer composition comprising a mixture of (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose.

[0014] As is employed herein, “colloid” and “colloidal” are used interchangeably in the specification to define particles that may be suspended in a mixture. As known to those of ordinary skill in the art, colloidal particles are of a certain average particle size, for example, on the order of about 0.1 to 10 microns. The colloidal particles described herein may be of any suitable particle size, provided that they are able to form colloidal suspensions.

[0015] In addition, as employed herein, “gel” refers to a soft, solid, or solid-like material which consists of at least two components, one of which is a liquid present in abundance (Almdal, K., Dyre, J., Hvidt, S., Kramer, O.; Towards a phenomenological definition of the term ‘gel’. *Polymer and Gel Networks* **1993**, *1*, 5-17).

[0016] The co-attrited component of the stabilizer of this invention comprises microcrystalline cellulose (“MCC”) and a low or medium viscosity carboxymethylcellulose (“CMC”).

[0017] MCC from any source may be employed in such component. Suitable feedstocks from which MCC may be obtained include, for example, wood pulp (such as bleached sulfite and sulfate pulps), corn husks, bagasse, straw, cotton, cotton linters, flax, hemp, ramie, seaweed, cellulose, and fermented cellulose. Additional feedstocks include bleached softwood Kraft pulps, bleached hardwood Kraft pulps, bleached Eucalyptus Kraft pulps, paper pulps, fluff pulps, dissolving

pulps, and bleached non-wood cellulosic pulps. In one embodiment, the MCC used is one approved for human consumption by the United States Food and Drug Administration.

[0018] If desired, the MCC may be made from a low cost pulp or mixtures of low cost pulp and specialty pulp. If a mixture is desired, then, for example, 30-80% of the total MCC can be from made from low cost pulp, and the colloidal content of the resulting MCC product can be at least 60%. Examples of low cost pulp include any paper grade pulp and fluff pulp, such as Southern Bleached Softwood Kraft Pulp, Northern Bleached Softwood Pulp, Bleached Eucalyptus Kraft Pulp, Bleached Hardwood Kraft Pulp, Bleached Sulfite Pulps, Bleached Soda Pulps, and bleached non-wood pulps. Specific low cost pulps include CPH pulp from Weyerhaeuser and Viscose grade dissolving pulps.

[0019] Chemical or mechanical treatments make MCC more amenable to extrusion/attrition intensity. For instance, during MCC acid hydrolysis cooking (or after MCC acid cooking), the MCC slurry can be treated with peroxide, peracetic acid, performic acid, persulfate, peroxymonosulfate (Oxone), or ozone at acidic pH. The acid hydrolysis process to make MCC may also be enhanced with other additives (such as iron salts, *i.e.*, ferric chloride, ferrous sulfate). Another approach is to extend the cooking time of MCC acid hydrolysis as shown in Example 5 of US 2013/0090391. The effect of extended cooking time may also be achieved by varying other conditions of the acid hydrolysis, including a higher acid concentration and/or increased cooking temperature.

[0020] The techniques of boosting MCC wet cake solids content and mechanically or chemically varying the treatment of the MCC may be combined to increase the elastic modulus G' of the final product more than by use of any technique alone.

[0021] The carboxymethylcellulose employed in the co-attrited component of the present stabilizer composition comprises an alkali metal carboxymethylcellulose, for instance, sodium, potassium, or ammonium CMC. Most preferably, the carboxymethylcellulose is sodium CMC.

[0022] The CMC is characterized by its viscosity, as measured in a 2% aqueous solution, at 25°C (Brookfield). Such viscosity may be determined by devices and settings well known to one of ordinary skill in the art, such as those described in the brochure AQUALON[®] CMC, An Anionic Water-Soluble Polymer, Hercules Incorporated, 1999, the disclosure of which is hereby incorporated by reference. As is employed herein, “low viscosity” CMC has a range of 10 to 200 cps (measured at 60 rpm using a Spindle Number 1 or 2). As is employed herein, “medium viscosity” CMC has a range of 200 to 4000 cps (measured at 30 rpm using a Spindle Number 2). As is employed herein, a “high viscosity” CMC has a viscosity which has a viscosity higher than medium viscosity CMC as defined and measured above. High viscosity CMC has a viscosity higher than 4,000 cps when tested at 2% solids. Typically, however, high viscosity CMC is tested at 1% solids (measured at 30 rpm using a Spindle Number 3 or 4).

[0023] The degree of substitution (DS) of the CMC employed is not critical for many applications. The degree of substitution represents the average number of hydroxyl groups substituted per anhydroglucose unit. For example, in CMC, each anhydroglucose unit contains three hydroxyl groups, which gives CMC a maximum theoretical DS of 3.0.

[0024] The MCC and low and/or medium viscosity CMC can be co-attrited by means well known to one of ordinary skill in the art, such as those described in US Patent Application 2013/0090391 which is hereby incorporated by reference. The methods include mixing a water-soluble carboxymethylcellulose with microcrystalline cellulose wet cake of at least 42% solids, wherein the weight ratio of the microcrystalline cellulose to the carboxymethylcellulose is about 95:5 to about 70:30. A particular weight ratio of the microcrystalline cellulose to the carboxymethylcellulose is about 90:10 to about 70:30; a more particular weight ratio of the microcrystalline cellulose to the carboxymethylcellulose is about 90:10 to about 80:20.

[0025] The moist mixture is extruded with sufficient intensity to achieve co-attrition and interaction among the components. As used in this specification, the terms

“attrited” and “attrition” are used interchangeably to mean a process that effectively reduces the size of at least some if not all of the particles to a colloidal size. The processing is a mechanical processing that introduces shearing force either to an MCC wet cake before blending with CMC or to an admixture of MCC wet cake and CMC. “Co-attrition” refers to application of high shear forces to an admixture of the MCC and CMC component. Suitable attrition conditions may be obtained, for example, by co-extruding, milling, or kneading.

[0026] The extrudate can be dried or be dispersed in water to form a slurry. The slurry can be homogenized and dried, preferably spray dried. Drying processes other than spray drying include, for example, fluidized bed drying, drum drying, bulk drying, and flash drying. Dry particles formed from the spray drying can be reconstituted in a desired aqueous medium or solution to form the compositions, edible food products, pharmaceutical applications, and industrial applications described herein.

[0027] The MCC:CMC extrusions employed herein are done at high intensity with high shear and high compression, so that the resulting colloidal MCC product is sufficiently attrited. As used herein, “shear force” refers to an action resulting from applied force that causes or tends to causes two contiguous parts of a mixture to slide relative to each other in a direction generally parallel to their plane of contact. The amount of force applied must be sufficient to create associations between the microcrystalline cellulose particles and the carboxymethylcellulose. If the force applied is insufficient, the components remain too “slippery” to transfer the shear force applied to the material or admixture to accomplish intimate associations. In that case, the shear force is primarily dissipated as mechanical energy by sliding action. Any means to increase the extrusion intensity may be used, including, but not limited to, extruder designs, duration/passes of extrusions, extrusion with attriting aids including all mentioned by FMC patent US Pat. 6,037,380 (Venables *et al.*), high shear/high solids levels, and anti-slip agents.

[0028] A preferred way of effecting high extrusion intensity is to control the solids level of the microcrystalline cellulose wet cake to be extruded. A wet cake solids

level below about 41% yields a colloidal MCC with a given gel strength G' . However, if the wet cake solids content is higher than about 42%, the final colloidal MCC product shows a significant increase in gel strength G' . The comprehensive range of the effective wet cake solids level is between about 42% to 60%, preferably 42.5% to 60%, more preferably 42.5% to 55%, and most preferably 43% to 50%.

[0029] Strategies to increase the wet cake solids content include, but are not limited to, better dewatering during washing/filtering with more vacuum/felting/pressing/filter surface areas, in-line evaporation of water from the wet cake before CMC addition by steam heating, hot air flows, Infrared irradiation, and RF/microwave heating. Another strategy is to add dry (or higher solids) MCC (or colloidal MCC such as Avicel RC591 or Avicel CL611 powders) into the wet cake, thereby increasing the total MCC solids content of the composition.

[0030] Improved extrusion/attrition intensity may be done with extended extrusion residence time (or more passes), and may also be achieved by cooling the extrusion temperature. The use of any common coolants is included in the invention's embodiments, and includes, but is not limited to, water cooling, and ammonia cooling.

[0031] In another embodiment, sufficient extrusion/attrition may be achieved in two or more separate steps. For instance, the MCC wet cake may be extruded/attrited first and then followed by CMC addition and extrusion/attrition. In addition to various types of extruders as practiced in current MCC manufacturing, equipment for attriting MCC wet cake or MCC:CMC include compression rolls/belts, calendaring rolls, mechanical refiner discs, ultrasonic refiners, high pressure homogenizers (including Micro-fluidic devices), high compression planetary mixers, and shockwave/cavitation devices.

[0032] The high viscosity carboxymethylcellulose, which is to be blended or combined with the above co-attrited MCC/CMC, can be of any degree of substitution, usually from 0.45% to 1.5%. Such carboxymethylcellulose can be an alkali metal carboxymethylcellulose, more particularly sodium, potassium, or

ammonium carboxymethylcellulose, and most preferably sodium carboxymethylcellulose.

[0033] The high viscosity CMC can be products made by any company. For instance, for CMC products made by Ashland Inc., which may be employed include 7H, 7HOF, 7H3S, 7H4, 9H, 9H4 high viscosity grades. Other high viscosity CMCs such as Drispac (Ashland) may also be used.

[0034] The co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose (component a) and high viscosity carboxymethylcellulose (component b) may be dry blended by means well known to one of ordinary skill in the art such as various ribbon mixers, paddle blenders or plow mixers, vertical blenders, and various tumble blenders including V blenders. Various high shear mixers with single or multiple shafts, single or multiple axis, are also included. Some liquid may be present or may be added during the dry blending process so long as no drying step is required to produce a free flowing powder once the blending is complete.

[0035] The weight ratio of component (a):component (b) is typically between 99:1 and 40:60; and is preferably between 97:3 and 50:50. For acidic pH applications, ratios of 90:10 to 50:50 are typically employed.

[0036] In a further aspect, the present invention is directed to an aqueous suspension comprising: (A) a stabilizer composition comprising a mixture of (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose; produced by the dry blending of components (a) and (b); and (B) water.

[0037] The amount of stabilizer composition contained in such aqueous suspension will vary upon the particular application involved, but will typically range between 0.1 and 10 percent by weight, based upon the weight of stabilizer composition and water present. Such aqueous composition may optionally comprise additional components, for example, organic liquids such as ethanol, methanol, isopropanol,

glycols, and the like, depending upon the use of the product comprising such aqueous suspension.

[0038] As is demonstrated in the Examples below, the stabilizer compositions of this invention, when dispersed in water, exhibit unexpectedly desirable rheological properties, gel strength and acid stability. Rheological properties, including elastic modulus G' and thixotropy, are tested by rheometers as specified in the Examples. The Brookfield viscosity test is used in the Examples to obtain an initial viscosity on the activated compositions at 60 seconds (usually 2.6% solids dispersion of the material in deionized water), and repeated to obtain the set-up viscosity after 24 hours. A RVT viscometer, with an appropriate spindle, is used at 20 rpm, at 20° C to 23°C.

[0039] Thus, such compositions typically exhibit a gel elastic modulus (G') of at least 30 Pa, when dispersed in water at 2.6% by weight solids. Preferably, such compositions exhibit a G' of at least 40 Pa, more preferably of at least 50 Pa.

[0040] In addition, such compositions typically exhibit an improved thixotropy (relative to the particular co-attrited MCC/CMC component employed alone) by at least 50 Pa/s. In one embodiment, the improvement by 300 Pa/s or more; preferably by 450 Pa/s or more; and more preferably by 600 Pa/s or more.

[0041] Due to such properties, the compositions are suitable for a wide variety of food, pharmaceutical, nutraceutical and industrial applications including in cosmetic products, personal care products, consumer products, agricultural products, or in chemical formulations and in paint, polymer formulations.

[0042] Some examples in pharmaceutical applications include liquid suspending agents and/or emulsions for drugs; nasal sprays for drug delivery where the MCC/CMC gives increased residence and bioavailability; controlled release agents in pharmaceutical applications; and reconstitutable powders which are dry powders mixtures containing drugs which can be made into suspension by adding water and shaking by hand; topical drug applications, and various foams, creams, lotions for

medical uses, including compositions for oral care such as toothpaste, mouthwash and the like. One particular example is a suspension of benzoyl peroxide or similar agents which requires the stability of the MCC/CMC against oxidizing agent over time. Other examples include pharmaceutical suspensions (or reconstitutible powders) which are acidic or with high ionic strength.

[0043] Examples in nutraceutical applications include delivery systems for various nutraceutical ingredients and dietary supplements. Examples in industrial applications include various suspensions, thickeners, which can be used in foams, creams, lotions and sun-screens for personal care applications; suspending agents, which can be used with pigments and fillers in ceramics, or used in colorants, optical brighteners, cosmetics, and oral care in products such as toothpaste, mouthwash and the like; materials such as ceramics; delivery systems for pesticides including insecticides; delivery of herbicides, fungicides, and other agricultural products, and paints, and various chemical or polymer suspensions. One particular example is an industrial wash fluid, containing oxidizing or bleach agents, which demand strong and stable suspension systems.

[0044] The compositions may be used in a variety of food products including emulsions, beverages, sauces, soups, syrups, dressings, films, dairy and non-dairy milks and products, frozen desserts, cultured foods, bakery fillings, and bakery cream. It may also be used for the delivery of flavoring agents and coloring agents. The edible food products can additionally comprise diverse edible material and additives, including proteins, fruit or vegetable juices, fruit or vegetable pulps, fruit-flavored substances, or any combination thereof.

[0045] These food products can also include other edible ingredients such as, for example, mineral salts, protein sources, acidulants, sweeteners, buffering agents, pH modifiers, stabilizing salts, or a combination thereof. Those skilled in the art will recognize that any number of other edible components may also be added, for example, additional flavorings, colorings, preservatives, pH buffers, nutritional supplements, process aids, and the like. The additional edible ingredients can be soluble or insoluble, and, if insoluble, can be suspended in the food product.

Routine adjustment of the composition is fully within the capabilities of one having skill in the art and is within the scope and intent of the present invention. These edible food products can be dry mix products (instant sauces, gravies, soups, instant cocoa drinks, etc.), low pH dairy systems (sour cream/yogurt, yogurt drinks, stabilized frozen yogurt, etc.), baked goods, and as a bulking agent in non-aqueous food systems and in low moisture food systems.

[0046] Suitable juices incorporating the stabilizer composition include fruit juices (including but not limited to lemon juice, lime juice, and orange juice, including variations such as lemonade, limeade, or orangeade, white and red grape juices, grapefruit juice, apple juice, pear juice, cranberry juice, blueberry juice, raspberry juice, cherry juice, pineapple juice, pomegranate juice, mango juice, apricot juice or nectar, strawberry juice, and kiwi juice) and vegetable juices (including but not limited to tomato juice, carrot juice, celery juice, beet juice, parsley juice, spinach juice, and lettuce juice). The juices may be in any form, including liquid, solid, or semi-solid forms such as gels or other concentrates, ices or sorbets, or powders, and may also contain suspended solids. In another embodiment, fruit-flavored or other sweetened substances, including naturally flavored, artificially flavored, or those with other natural flavors (“WONF”), may be used instead of fruit juice. Such fruit flavored substances may also be in the form of liquids, solids, or semi-solids, such as powders, gels or other concentrates, ices, or sorbets, and may also contain suspended solids.

[0047] Proteins suitable for the edible food products incorporating the stabilizer compositions include food proteins and amino acids, which can be beneficial to mammals, birds, reptiles, and fish. Food proteins include animal or plant proteins and fractions or derivatives thereof. Animal derived proteins include milk and milk derived products, such as heavy cream, light cream, whole milk, low fat milk, skim milk, fortified milk including protein fortified milk, processed milk and milk products including superheated and/or condensed, sweetened or unsweetened skin milk or whole milk, dried milk powders including whole milk powder and nonfat dry milk (NFDm), casein and caseinates, whey and whey derived products such as whey concentrate, delactosed whey, demineralized whey, whey protein isolate. Egg

and egg-derived proteins may also be used. Plant derived proteins include nut and nut derived proteins, sorghum, legume and legume derived proteins such as soy and soy derived products such as untreated fresh soy, fluid soy, soy concentrate, soy isolate, soy flour, and rice proteins, and all forms and fractions thereof. Food proteins may be used in any available form, including liquid, condensed, or powdered. When using a powdered protein source, however, it may be desirable to prehydrate the protein source prior to blending with stabilizer compositions and juice for added stability of the resulting beverage. When protein is added in conjunction with a fruit or vegetable juice, the amount used will depend upon the desired end result. Typical amounts of protein range from about 1 to about 20 grams per 8 oz. serving of the resulting stable edible food products, such as beverages, but may be higher depending upon the application. For protein beverage applications, it is preferable that the high viscosity CMC (component b) would have also a high degree of substitution, from 0.85%-1.5%.

[0048] In certain embodiments, the compositions are formulated as dry blends. The dry blends are suitable intermediates that can be dosed and dispersed with other ingredients including surfactants, fillers, or active substances. Sufficient water and agitation with heat are added as appropriate to activate the stabilizer in a desired food product, pharmaceutical product, nutraceutical product, personal care product, cosmetic product, consumer product, agricultural product, or chemical formulation.

[0049] Suitable surfactants include, but are not limited to, ionic or nonionic with an HLB of 1 to 40. Active substances may be added to the compositions and include, but are not limited to, at least one of a nutraceutical agent, a vitamin, a mineral, a coloring agent, a sweetener, a flavorant, a fragrance, a salivary stimulant agent, a food, an oral care agent, a breath freshening agent, a pharmaceutical active, agricultural active, therapeutic agent, cosmetic agent, chemical, buffer, or pH modifier. Active substances can be encapsulated or otherwise processed or treated to modify their release properties.

[0050] It should also be noted that the food/beverage compositions may be processed by heat treatment in any number of ways. These methods may include,

but are not limited to, pasteurization, ultra pasteurization, high temperature short time pasteurization (“HTST”), and ultra high temperature pasteurization (“UHT”). These beverage compositions may also be retort processed, either by rotary retort or static retort processing. Some compositions, such as juice-added or natural or artificially flavored soft drinks may also be cold processed. Many of these processes may also incorporate homogenization or other high shear/high compression methods. There may also be co-dried compositions, which can be prepared in dry-mix form, and then conveniently reconstituted for consumption as needed. The resulting beverage compositions may be refrigerated and stored for a commercially acceptable period of time. In the alternative, the resulting beverages may be stored at room temperature, provided they are filled under aseptic conditions.

[0051] It is to be understood that each component, compound, substituent, or parameter disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent, or parameter disclosed herein.

[0052] It is also to be understood that each amount/value or range of amounts/values for each component, compound, substituent, or parameter disclosed herein is to be interpreted as also being disclosed in combination with each amount/value or range of amounts/values disclosed for any other component(s), compounds(s), substituent(s), or parameter(s) disclosed herein and that any combination of amounts/values or ranges of amounts/values for two or more component(s), compounds(s), substituent(s), or parameters disclosed herein are thus also disclosed in combination with each other for the purposes of this description.

[0053] It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range disclosed herein for the same component, compounds, substituent, or parameter. Thus, a disclosure of two ranges is to be interpreted as a disclosure of four ranges derived by combining each lower limit of each range with each upper limit of each range. A disclosure of three ranges is to be interpreted as a disclosure of nine ranges derived by combining each lower limit of each range with each upper limit of each

range, etc. Furthermore, specific amounts/values of a component, compound, substituent, or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound, substituent, or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent, or parameter.

EXAMPLES

[0054] The following examples are provided to illustrate the invention in accordance with the principles of this invention, but are not to be construed as limiting the invention in any way except as indicated in the appended claims.

Example 1

[0055] A colloidal microcrystalline cellulose product comprising co-attrited MCC and low DS medium viscosity CMC (Avicel RC591; FMC Corporation) was dry blended with a low degree of substitution, high viscosity (high molecular weight) carboxymethylcellulose product (Aqualon 7HF CMC; Ashland Inc.) at the weight ratios listed in Table 1 below. The mixtures were then dispersed in de-ionized water at 2.6% solids and their rheological properties tested with a TA-Instruments ARES-RFS3 Rheometer with the following conditions:

- 50 mm parallel plates with a 1.8 mm gap size and tested at 20°C.
- Strain Sweep test: 5 minutes equilibration, frequency = 6.2832 rad/sec or 1 Hz, 0.1 to 100% strain.

As a comparison, 2.6% Avicel RC591(1-CE1) and 1.3% Aqualon CMC (1-CE2) alone were tested as well. The results of such testing (at the ratios indicated) are presented in Table 1 below:

Table 1

Example or Comparative Experiment	1A	1B	1-CE1	1-CE2
Co-Attrited CMC/MCC (weight percent)	95	90	100	0
High Viscosity CMC (weight percent)	5	10	0	100
%CMC in aqueous dispersion	0.40	0.52	0.29	1.3
Initial Viscosity (cps)	7,200	17,000	2,500	
24 Hour Set Up Viscosity (cps)	9,400	17,000	4,500	
G' (Pa)	50	60	25	3

[0056] The results above indicate that the compositions of this invention exhibit unexpectedly desirable properties relative to their components alone.

Example 2

[0057] A colloidal microcrystalline cellulose product comprising co-attrited MCC and low DS low viscosity CMC (Avicel CL611; FMC Corporation) was dry blended with a low degree of substitution, high viscosity (high molecular weight) carboxymethylcellulose product (Aqualon 7HF CMC; Ashland Inc.) at the weight ratios listed in Table 2 below. The mixtures were then dispersed in de-ionized water at 2.6% solids and their rheological properties evaluated as described in Example 1. As a comparison, (2-CE) Avicel CL611 alone was tested as well. The results of such testing (at the ratios indicated) are presented in Table 2 below:

Table 2

Example or Comparative Experiment	2A	2B	2-CE
Co-Attrited CMC/MCC (weight percent)	95	90	100
High Viscosity CMC (weight percent)	5	10	0
Initial Viscosity (cps)	2,100	7,000	150
24 Hour Set Up Viscosity (cps)	7,900	12,000	2,500
G' (Pa)	12	22	6

[0058] The results above, including those for 1-CE2 above, indicate that the compositions of this invention exhibit unexpectedly desirable properties relative to their components alone.

Example 3

[0059] A colloidal microcrystalline cellulose product comprising co-attrited MCC and low DS medium viscosity CMC (Avicel RC591; FMC Corporation) was dry blended with moderately high degree of substitution, high viscosity carboxymethylcellulose (Aqualon 9 HF CMC; Ashland Inc.) in a 90:10 weight ratio. The mixture were dispersed in de-ionized water at 2.6% solids and its rheological properties evaluated as described in Example 1. The initial viscosity was 17,000 cps, and gel elastic modulus G' was 60 Pa.

Example 4

[0060] A colloidal microcrystalline cellulose product comprising co-attrited MCC and low DS low viscosity CMC was dry blended with a low degree of substitution, high viscosity (high molecular weight) carboxymethylcellulose product (Aqualon 7HF CMC; Ashland Inc.) in the amounts listed in Table 3. The samples so prepared were dispersed in de-ionized water with a propeller mixer for 30 minutes at 800 rpm; and their rheological properties measured at a 2.6% solids level. (2.6% in this

example). The dispersed samples were then tested with a TA Instrument AR2000ex Rheometer (TA Instruments) under the following conditions:

- Geometry: 60-mm acrylic parallel plate
- Gap: 800 μm
- a) Flow, Continuous Ramp test for Thixotropy measurement
 - Conditioning step: $T = 20^{\circ}\text{C}$; Equilibration = 1 minute
 - Up stepped ramp:
 - Shear rate: from 0 to 50 s^{-1}
 - Duration: 5 min
 - Linear Mode
 - Down stepped ramp:
 - Shear rate: from 50 to 0 s^{-1}
 - Duration: 5 min
 - Linear Mode
- b) Oscillation, Time sweep test for gel strength (G')
 - Conditioning step: $T = 20^{\circ}\text{C}$; Equilibration = 1 minute
 - Time sweep:
 - Test settings duration: 5 minutes
 - Delay time: 1 second
 - Controlled Variable, displacement: $5\text{ e}^{-5}\text{ rad}$
 - Frequency: 1 Hz
 - Controlled strain tab: continuous oscillation [direct strain]

[0061] The results of such testing are summarized in Table 3. As a comparison, the co-attrited MCC/CMC was evaluated alone at 2.6% solids (4-CE).

Table 3

Example or Comparative Experiment	4A	4B	4C	4C-E
Co-Attrited CMC/MCC (weight percent)	90	80	50	100
High Viscosity CMC (weight percent)	10	20	50	0
Gel Elastic Modulus G' (Pa) (from Time Sweep)	37	48	58	29

Example 5

Impact on Thixotropy as Tested by Rheometer at Low Shear and High Shear
Dispersions

[0062] A colloidal microcrystalline cellulose product comprising co-attrited MCC and low DS low viscosity CMC was dry blended with a low degree of substitution, high viscosity (high molecular weight) carboxymethylcellulose product (Aqualon 7HF CMC; Ashland Inc,) in the weight percentages listed in Table 3. (Examples 5A, 5B and 5C)

[0063] In addition, a colloidal microcrystalline cellulose product comprising co-attrited MCC and high DS low viscosity CMC was dry blended with a low degree of substitution, high viscosity (high molecular weight) carboxymethylcellulose product (Aqualon 7HF CMC; Ashland Inc,) in a 80:20 weight ratio (Example 5D).

[0064] The impact on thixotropy at high and low shear was measured as set forth in Example 4.

[0065] In low shear dispersion, samples were dispersed in de-ionized water with a propeller mixer for 30 minutes at 800 rpm at target solids levels (2.6% in this example). The dispersed samples were then tested with a TA Instrument AR2000ex Rheometer with flow, continuous ramp for thixotropy measurement.

[0066] In high shear dispersion, samples were dispersed first in de-ionized water with a propeller mixer for 5 minutes at 800 rpm. Then, the suspension was passed through an inline high shear mixer (IKA T25 basic) at maximum speed (24000 rpm), at 150 pump speed (Tubing size 24) and. The dispersed samples were then tested with a TA Instrument AR2000ex Rheometer with flow, continuous ramp for thixotropy measurement.

[0067] As a comparison, the co-attrited MCC/CMC products alone were also tested (5CE-1 and 5CE-2). The results of such testing are summarized in Table 4 below.

[0068] A thixotropic fluid will form a hysteresis loop when shear stress is plotted against shear rate, which is captured by the rheograms of this experiment. Table 4 below shows the magnitude of the hysteresis loop area which is traditionally considered as a measure of thixotropy effect.

Table 4

Example or Comparative Experiment	5A	5B	5C	5D	5CE-1	5CE-2
Co-Attrited MCC/ LowDS-Low Visc. CMC (weight percent)	90	80	50	0	100	0
Co-Attrited MCC/ HighDS-Low Visc. CMC (weight percent)	0	0	0	80	0	100
High Viscosity CMC (weight percent)	10	20	50	20	0	0
Thixotropy at Low Shear Dispersion 2.6% solids, 25 hrs. (Pa/s)	1,300	1,900	1,950	1,050	380	65
Thixotropy at High Shear Dispersion 2.6% solids, 25 hrs. (Pa/s)	950	1,400	2,950	1,350	560	75

Example 6

[0069] The stability of gels formed by colloidal co-attrited MCC/CMC compositions with and without being dry blended with high viscosity CMC was evaluated by producing compositions having the components indicated in Table 5; and testing the stability of such compositions at pH 3.6 in accordance with the following procedure:

- Sieve powders through 1000 micron sieve, and mix with the glass beads in the Turbula blender T2F for 10 minutes at 49 rpm.
- Then add de-ionized water to the dry powder, and shake by hand for 1 minute until homogeneous suspensions is obtained.

- Observe the suspension stability, and watch out for glass beads sedimentation at given time periods.

Table 5

Formula Composition	% w/v
D-Sorbitol	20.00
Glass Beads	11.00
Colloidal MCC	4.00
Citric Acid	1.44
Sodium Citrate	0.72
Sodium Benzoate	0.20
Deionized Water	Add to make up the 100% total formula

[0070] It was visually observed that suspensions based on co-atrited MCC:CMC without added high viscosity 7HF CMC settled out into two phases, with complete glass beads sedimentation at the bottom in 24 hrs. However, it was found surprisingly that the when the same co-atrited colloidal compositions were blended with high viscosity CMC (Aqualon 7HF CMC; Ashland Inc) at ratios of 50:50 and 80:20, respectively, the gels formed remained stable at pH 3.6, without any glass bead sedimentation after 24 hours.

CLAIMS

What is claimed is:

1. A stabilizer composition comprising a mixture of (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose; produced by the dry blending of components (a) and (b).
2. The stabilizer composition of claim 1 wherein the weight ratio of microcrystalline cellulose:low or medium carboxymethylcellulose in component (a) is between 95:5 and 70:30.
3. The stabilizer composition of claim 2 wherein the weight ratio of microcrystalline cellulose:low or medium carboxymethylcellulose in component (a) is between 90:10 and 80:20.
4. The stabilizer composition of any of claims 1-3 wherein the weight ratio of component (a) to component (b) is between 99:1 and 40:60.
5. The stabilizer composition of claim 4 wherein the weight ratio of component (a) to component (b) is between 97:3 and 50:50.
6. The stabilizer composition of any of claims 1-5 wherein such composition exhibits a gel elastic modulus (G') when dispersed in water at 2.6% by weight solids of at least 30 Pa.
7. The stabilizer composition of claim 6 wherein such composition exhibits a gel elastic modulus (G') when dispersed in water at 2.6% by weight solids of at least 40 Pa.

8. The stabilizer composition of claim 7 wherein such composition exhibits a gel elastic modulus (G') when dispersed in water at 2.6% by weight solids of at least 50 Pa.
9. The stabilizer composition of any of claims 1-8 wherein such composition exhibits an improved thixotropy, relative to the co-attrited microcrystalline cellulose/carboxymethylcellulose employed as component (a) alone, of at least 50 Pa/s.
10. The stabilizer composition of claim 9 wherein such composition exhibits an improved thixotropy, relative to the co-attrited microcrystalline cellulose/carboxymethylcellulose employed as component (a) alone, of at least 300 Pa/s.
11. The stabilizer composition of claim 10 wherein such composition exhibits an improved thixotropy, relative to the co-attrited microcrystalline cellulose/carboxymethylcellulose employed as component (a) alone, of at least 450 Pa/s.
12. An aqueous suspension comprising: (A) the stabilizer composition of any of claims 1-11; and (B) water.
13. The aqueous suspension of claim 12 wherein the stabilizer composition comprises between 0.1 and 10 percent by weight, based upon the total weight of stabilizer composition and water.
14. A method of making a stabilizer composition comprising dry blending (a) co-attrited microcrystalline cellulose and low or medium viscosity carboxymethylcellulose; and (b) high viscosity carboxymethylcellulose
15. A food, pharmaceutical, nutraceutical or industrial composition comprising the stabilizer composition of any of claims 1-11.

16. A pharmaceutical composition in accordance with claim 15 wherein such composition is a liquid suspending agent for drugs, a nasal spray, a controlled release agent, a reconstitutable powder, or a topical drug formulation.

17. An industrial composition in accordance with claim 15 wherein said industrial product is a personal care product, a paint, an industrial wash fluid, a ceramic or an agricultural chemical formulation.

18. The industrial composition of claim 17 wherein such composition is a toothpaste or a mouthwash.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/042373**A. CLASSIFICATION OF SUBJECT MATTER****C08L 1/08(2006.01)i, C08J 3/075(2006.01)i, A23L 1/0534(2006.01)i, A61K 47/38(2006.01)i, A61K 9/06(2006.01)i**

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)

C08L 1/08; A23L 1/0534; C08L 1/04; A23L 2/52; A23L 1/212; A23L 1/0532; C08J 3/075; A61K 47/38; A61K 9/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: stabilizer, co-atrited, co-extruded, microcrystalline cellulose, high viscosity, carboxymethylcellulose, dry blending, gel elastic modulus G', shear dispersion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013-052114 A1 (FMC CORPORATION) 11 April 2013 See paragraphs [0008]–[0013], [0025], [0038] and [0041]; and Example 3.	1–5, 14
A	US 2013-0150462 A1 (FMC CORPORATION) 13 June 2013 See paragraphs [0006]–[0008] and [0020]; and Examples 1–13.	1–5, 14
A	US 2013-0064953 A1 (BACHE, GEORG et al.) 14 March 2013 See paragraphs [0003]–[0007]; and claims 6–10.	1–5, 14
A	US 2007-0128333 A1 (TUASON, DOMINGO C. et al.) 07 June 2007 See paragraphs [0002]–[0004]; and Examples 1, 17 and 58.	1–5, 14
A	US 5789004 A (HOGAN, DANIEL T. et al.) 04 August 1998 See column 2, lines 32–67; and claim 1.	1–5, 14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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22 October 2015 (22.10.2015)

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2015/042373**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 7,8,10,11,13,16-18
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The above claims refer to claims which are not drafted in accordance with the third sentence of Rule 6.4(a). Thus, no meaningful search could be carried out.
3. ☒ Claims Nos.: 6,9,12,15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/042373

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