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(54) Coal-water mixture containing poly(alkylene oxide) surfactant and hydroxyalkyl polygalactomannan.

(57) Coal water mixtures are provided which contain a poly-(alkylene oxide) surfactant comprised of a hydrophilic portion derived from ethylene oxide and a hydrophobic portion derived from a higher alkylene oxide as a surfactant and a hydroxyalkyl ether of a polygalactomannan as a stabilizer. Particular examples of these surfactants and stabilizers include ethoxylated, propoxylated propylene glycol and hydroxypropyl guar, respectively. It has been found that coal water mixtures containing from 50 to 80% particulate coal exhibit excellent stability with respect to particle settling and bed compaction when this particular combination of surfactant and stabilizer is employed. Also provided is a process for preparing such coal water mixtures wherein a mixture of particulate coal, water, and the surfactant is formed to which the stabilizer is then added to form a stabilized homogeneous mixture. These coal water mixtures exhibit excellent stability when transported by a pipeline.

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COAL-WATER MIXTURE CONTAINING POLY(ALKYLENE OXIDE) SURFACTANT AND HYDROXYALKYL POLYGALACTOMANNAN

FIELD OF THE INVENTION

This invention relates to coal water mixtures having improved fluidity and stability. More particularly, this invention relates to coal-water mixtures comprised of a poly(alkylene oxide) surfactant and a hydroxyalkyl ether of a polygalactomannan.

BACKGROUND OF THE INVENTION

U.S. Patent No. 4,242,098 discloses the use of water-soluble polymers, e.g. hydroxypropyl guar gum or carboxymethylhydroxypropyl guar gum, in an aqueous coal slurry to permit the extrusion, pumping and transport of higher solids content aqueous coal slurries.

U.S. Patent No. 4,441,889 discloses examples of stable coal aqueous mixtures containing both xanthan gum and guar gum along with a nonionic surfactant. The patent discloses many examples of nonionic surfactants including ethoxylated alkylphenols; ethoxylated, propoxylated propylene glycols; and ethoxylated, propoxylated alkylene diamines.

SUMMARY OF THE INVENTION

This invention relates to coal-water mixtures comprising: a) a poly(alkylene oxide) surfactant comprised of a hydrophilic portion derived from ethylene oxide and a hydrophobic portion derived from a higher alkylene oxide; and b) a polymeric stabilizer comprising a hydroxyalkyl ether of a polygalactomannan. This invention also relates to a method of preparing the coal-water mixtures described above, comprising: i) forming a mixture comprised of particulate coal, water, and a poly(alkylene oxide) surfactant comprised of a hydrophilic portion derived from ethylene oxide and a hydrophobic portion derived from a higher alkylene oxide; ii) adding to the resultant mixture a stabilizer comprised of a hydroxyalkyl ether of

a polygalactomannan; and iii) mixing the resulting composition to form a homogeneous mixture.

DETAILED DESCRIPTION OF THE INVENTION

The coal-water mixtures of the instant invention are mixtures of coal and a water-based liquid containing a poly(alkylene oxide) surfactant and a modified polysaccharide stabilizer. The term coal is intended to be generic to the many types and grades of commercially available coals. Specific examples of preferred coals include low volatile bituminous coals from West Virginia, high volatile bituminous coals from Kentucky, Ohio or Arizona and subbituminous coals from Montana may be used in the practice of this invention. Anthracite, semi-anthracite, medium and high volatile bituminous, and lignite coals may also be used in this invention.

The coal for use in this invention can be obtained in a dry or wet form and mixed with fluid to form a coal-fluid slurry. Preferably, the coal for making a fine particle sized fraction is wet milled in known ways to prevent dust and explosion hazards. The wet milled coal fraction can be milled with all the water, or it can be mixed with sufficient additional water to make a slurry which will be readily pumpable in a pipeline when it further is mixed with a coarser pulverized coal fraction to form a coal-water slurry.

In one preferred embodiment, the coal utilized in the coal-fluid slurry of this invention is "pulverized". The term "pulverized coal" (or "P.C."), as used in this specification, refers to coal which has been milled or ground to a consistency of about 40 mesh X 0: see the Handbook of Chemistry and Physics, 51st Edition (CRC Publishing Co., Cleveland, Ohio, 1970-1971), page F-199, the disclosure of which is hereby incorporated herein by reference.

In view of the manner in which coal fractures during milling, coal particles will have irregular shapes which, however, are of a body (or maximum side-to-side thickness) such that the sub-sieve sized discrete particles will pass through a specified mesh of a sieve. The size of the discrete particle can be expressed in terms of a spherical diameter which, as used herein, is defined as a U.S.

sieve size of from 16 mesh (1.18 mm) to 400 mesh (0.038 mm) or its equivalent in microns through which a coal particle from a sample of coal or coal-water slurry will pass. For particles finer than 200 mesh, the size of the particles can be expressed in mm as determined by means of a sieve, or a sedimentometer, or a scanning electron microscope (SEM). In a preferred embodiment, from about 85% to about 90% of the particles are less than 200 mesh.

Mixtures of coals also can be used in the slurry of this invention. By way of illustration and not limitation, one can use a mixture of a coarse coal fraction which contains less than about 30 weight percent of volatilizable hydrocarbons (such as, e.g. anthracite or low volatile bituminous coal) and a fine coal fraction which contains more than about 35 weight percent of volatilizable hydrocarbons (such as, e.g. lignite or high volatile bituminous coal). One can use a mixture of two or more of said coarse coal fractions and one of said fine fractions, one of said coarse coal fractions and two or more of said fine fractions, or two or more of said coarse coal fractions and two or more of said fine fractions.

The slurry of this invention is comprised of one or more water-based liquids. As used in this specification, the term liquid refers to water, and mixtures of water and water-miscible alcohols. The water-based liquid used in the slurry of this invention preferably performs at least two functions--it fills the interstitial pores of the carbonaceous solid material, and it provides the vehicle for separation of the particles of the carbonaceous solid material to minimize collisions between said particles; thus, the preferred water-based liquid is a carrier water-based liquid.

In one preferred embodiment, the water-based liquid used in the slurry of this invention is carrier water. As used in this specification, the term "carrier water" means the bulk of free water dispersed between the coal particles and contiguous to the bound layers of the particles, and it is to be distinguished from bound water. The term "bound water" means water retained in the "bound water layer," as defined and illustrated in Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Vol. 22, pages

90-97 (at p. 91).

The kind of water used as carrier water in the coal-water slurry of this invention may be any available water, such as mine, well, river, or lake water or desalinated ocean water having a sufficiently low mineral salt content such that the electrochemistry of the bound water layer and carrier water interface can be controlled, in accordance with the invention and corrosion of milling facilities, pipe lines and furnaces will be minimized and controllable.

When water is added to a carbonaceous powder comprised of finely divided particles, and if the water "wets" the powder, a surface water film is adsorbed on each particle which is known to be structurally different from the surrounding "free" or bulk water, in that the film may be described as "semi-rigid", or "bound water film". Depending on the fundamental electrical potential of the surface, this "semi-rigid" or bound water film may be of several molecules thickness.

In another embodiment, a mixture of water and à water-miscible alcohol is the water-based liquid used in the slurry of this invention. The alcohols are completely or partially water miscible, e.g. methanol, ethanol, n-propanol, isopropanol, t-butanol, glycerol, etc. Thus, by way of illustration and not limitation, one may use mixtures of water and an alcohol, e.g. methanol. One can use mixtures comprised of from about 1 to about 49 volume percent of alcohol and from about 51 to about 99 volume percent of water. In one preferred embodiment, the mixture is comprised of from about 1 to about 15 volume percent of alcohol with the remainder of the liquid consisting essentially of water. It is preferred that the alcohol be liquid and water miscible and that it contain from about 1 to about 10 carbon atoms, e.g. methanol, ethanol, isopropanol, t-butanol, glycerol, etc.

High solids content aqueous coal slurries and, in particular, the transport thereof by pipeline are well known. A high solids content aqueous coal slurry is generally defined as containing from about 50% to about 80% by weight of particulate coal based on the weight of the coal water mixture. The coal slurries of this in-

vention may contain from about 50% to about 80% by weight particulate coal, but preferably contain from about 65% to about 70% by weight particulate coal.

The poly(alkylene oxide) surfactant useful in this invention is a long chain organic compound, or a mixture thereof, having a distinct hydrophilic portion derived from ethylene oxide and a distinct hydrophobic portion derived from a higher alkylene oxide. The surfactant, when added to aqueous solutions at a level of about 0.1% by weight or higher, yield aqueous solutions having a surface tension below 50 dynes/cm. Examples of suitable surfactants include water-started block copolymers of ethylene oxide with a higher alkylene oxide such as propylene oxide. Specific examples include the block co-polymers of ethylene oxide and propylene oxide sold by BASF under the tradename Pluronic.

A hydroxyalkyl ether of a polygalactomannan is the other essential component in the coal water mixtures of this invention. Useful in the practice of this invention are polygalactomannan polysaccharides that have been etherified by the reaction of the free hydroxyl groups of the polygalactomannans with an alkylene oxide lower alkanol-started, e.g. methanol, block copolymers of ethylene oxide and a higher alkylene oxide, lower glycol-started block copolymers, e.g. ethylene or propylene glycol, ethylene oxide and a higher alkylene oxide, and the like.

A polygalactomannan polysaccharide is a polysaccharide comprised of repeating units derived from galactose and mannose sugars. Sources of polygalactomannans include the endosperm sections of the seeds of leguminous plants such as guar seeds and locust beans.

The preferred hydroxyalkyl ethers are hydroxyalkyl guar gums, e.g. hydroxypropyl guar gum and hydroxyethyl guar gum, which are generally prepared by the base catalyzed reaction of an alkylene oxide, e.g. propylene oxide or ethylene oxide, respectively, with guar gum. The term "hydroxyalkyl ether of a polygalactomannan" also encompasses mixed derivatives, e.g. those wherein both an alkylene oxide and a second etherifying agent used to etherify the polygalactomannan. Suitable secondary etherifying agents include a

secondary alkylene oxide and/or alkylating agents such as alkyl halides, e.g. methyl chloride. The use of such secondary etherifying agents will produce a mixed hydroxyalkyl ether of a polygalactomannan. The amount of secondary etherifying agent should be controlled so as not to adversely affect the performance of the hydroxyalkyl ether of a polygalactomannan. For example, a hydroxyalkyl ether of a polygalactomannan having a hydroxypropyl molar substitution (m.s.) of from about 0.01 to about 3.0 in an aqueous system and from about 0.2 to about 4.0 in an alcohol system; a methyl degree of substitution of about 0.01 to about 2.0 is suitable for use in this invention.

Mixtures of hydroxyalkyl ether derivatives, are also contemplated e.g. a mixture of a hydroxypropyl guar and a hydroxyethyl guar or a mixture of a hydroxypropyl guar and a hydroxypropyl methyl guar.

The hydroxyalkyl ether of a polygalactomannan is added to the coal-water mixture in amounts such that the total concentration of etherified polygalactomannan in the coal-water mixture may vary from about 0.02% to about 0.2% based on the weight of the coal water mixture.

When preparing the coal water mixtures of the present invention, it is preferred that the nonionic surfactant be added to the carbonaceous slurry prior to the addition of the stabilizer to prevent any interaction between the surface of the coal and modified polysaccharide polymer used as a stabilizer, which may otherwise occur.

More particularly, in preparing the coal water mixtures of this invention, the surfactant and other optional additives such as conventional defoaming agents, if desired, are first added to water and mixed, under low speed agitation conditions such as at from about 500 rpm to about 1,500 rpm, preferably about 1,000 rpm for a time of from about 30 seconds to about 3 minutes, preferably about 1 minute. The aqueous mixture is charged to a ball mill containing coarsely ground coal; e.g., a topsize of 1/4". The amount of coal as a percentage of total material charged to the mill, coal, water, chemicals, may vary from 50 to 75% and is typically 70%. The ball

size and charge in relation to the amount of material to be milled is determined in accordance with commonly practiced techniques as are other milling parameters; e.g., speed and duration of rotation. In order to maintain a constant particle size distribution milling, parameters are adjusted to compensate for differences in coal types and/or chemical additives.

After the coal-water mixture has been prepared by wet milling, water is added to bring the solids to the desired level. Using mild agitation the polymeric stabilizer is slowly delivered to the mixture preferably in powder form, and the agitation, 3-4000 RPM, is continued for 30-40 minutes after which time the polymer is completely dissolved. Finally, a preservative, such as formaldehyde, is added in solution or powder form.

An alternate procedure by which a high solids, fluid coal-water mixture may be prepared is to disperse pulverized coal in a solution of surfactant, water, and if necessary, other processing aids such as defoamers or pH modifying agents. The pulverized coal is typically ground to 75-90% passing through a Tylêr 200 mesh screen size. By a preferred procedure 4 baffles, 90° apart, are inserted in a cylindrical vessel and a 4-paddle impeller is rotated at 500-1500 RPM. The dimensions of the baffles are impeller relative to the vessel geometry and are in accordance with standard engineering principles. The pulverized coal is slowly added to the agitated solution and after all has been charged, agitation is continued for an additional 15-60 minutes. The polymeric stabilizer is then added with mild agitation, 2-400 RPM, and allowed to thoroughly dissolve.

Typical mixing or dispersing apparatus employed herein include for example Premiere Mill Company's Hi-Vispersator High Speed Disperser.

It is to be understood that the above indicated residence times, mixing speeds, etc., may vary according to the specific process requirements such as the volume of ingredients, size of apparatus, mixing efficiency, etc. Thus, for example, depending on the scale of the operation, e.g. pilot plant, plant, etc., these process conditions of the present invention may be adjusted accord-

ingly. As indicated above, additives that can be added to the coal water mixtures include defoaming agents, salts, bases, or other modifying agents, and accommodations of these materials. Generally, the defoaming agents that can be used are conventional and include both silica and non-silica containing compositions. A commercially available defoaming agent suitable for use in the mixtures is COLLOID® 691, supplied by Colloids, Inc. This composition generally comprises a mixture containing mineral oil, amide and an ester.

In preparing the compositions the weight ratio of the nonionic surfactants to the water is from about 0.1:40 to about 1:25. In the preferred embodiments a defoaming agent is added to assist in processing. The weight ratio of defoaming agent to water is from about 1:25 to about 0.01:40. The pulverized coal is then mixed with water in a portion of about 65 parts to about 75 parts by weight coal to the above described mixture to obtain a flowable liquid. The amount of etherified polygalactomannan described above can then be added to stabilize the mixture with respect to particle settling and bed compaction. Other additives such as salts or bases, antibacterial agents such as formaldehyde, and the the like, viscosity stabilizers such as ammonia, etc. can also be added in about 0.1 to about 0.3 parts by weight of the total mixture to further assist in dispersing the coal and providing other advantages.

EXAMPLE I

Initially a cold water mixture was prepared without the addition of the formaldehyde or hydroxypropyl galactomannan. The base coal-water mixture was prepared by charging a ball mill with the following materials in the proportions indicated and milling until 83% by weight of the particles passed through a tyler 200 mesh screen. The following ingredients were combined in the following weight percents:

TABLE 1

	Amount
Bituminous Coal (Pittston Moss #1 1/4 Top Size)	70 Wt. %
Ethoxylated Nonylphenol Surfactant (Igepal® CO-990; GAF Corp)	0.55 Wt. %
A Hydrocarbon Based Defoamer	0.30 Wt. %
Water	29.15 Wt. %

After milling had decreased the particle size to the stated, the material was then split into 4 equal samples and 0.05% by wt. of formaldehyde was added to each sample as a preservative. Hydroxypropyl galactomannan (Galactasol® 416; Henkel Corp.) was added to 3 of the samples in the amounts indicated below in Table 2.

A Haake Rv 12 Rotovisco Rheometer was used to determine the initial apparent viscosity, (shear stress divided by shear rate at a shear setting of 57.6 S^{-1}. After the determination of apparent viscosity, all four samples were placed in static storage at ambient conditions for a period of 8 weeks. After this static storage time, the amount of hard-packed sediment accumulating at the bottom of the sample jar was determined by inserting a 6 inch metal machinist's ruler. The ruler penetrated the slurry with the use of light hand pressure until the hard pack sediment is detected. When the hard pack sediment is reached, the depth of penetration is read from the ruler. The amount of sediment is expressed as a percentage of the total sample height: $(h_o-h)/h_o \times 100g$ where h_o = total sample height in the container, h = depth of non-sedimented and loosely packed material.

TABLE 2

% Concentration of Hydroxypropyl Galactomannan	Initial Reading of Apparent Viscosity (CPS)	Percent Sediment 8 Weeks after Viscosity Reading
0.0	456	70.4
0.05	1070	48.1
0.075	1980	18.8
0.1	2700	5.0

EXAMPLE II

Initially a coal water mixture was prepared without the addition of the formaldehyde or hydroxypropyl galactomannan. The base coal-water mixture was prepared by charging a ball mill with the following materials in the proportions indicated and milling until 83% by weight of the particles passed through a tyler 200 mesh screen. The following ingredients were combined in the following weight percents:

TABLE 3

	Amount
Bituminous Coal (Pittston Moss #1, 1/4" top size)	70 Wt. %
Ethylene Oxide Propylene Oxide Block Co-polymer Surfactant	0.45 Wt. %
Hydrocarbon Based Defoamer (Colloids® 691; Colloids Inc.)	0.3 Wt. %
Water	29.25 Wt. %

After milling had decreased the particle size to the stated, the material was then split into 4 equal samples and 0.05% by wt.

of formaldehyde was added to each sample as a preservative. Hydroxypropyl galactomannan (Galactasol® 416; Henkel Corp.) was added to 3 of the samples in the amounts indicated below in Table 2.

A Haake Rv 12 Rotovisco Rheometer was used to determine the initial apparent viscosity, (shear stress divided by shear rate at a shear setting of 57.6 S^{-1}. After the determination of apparent viscosity, all four samples were placed in static storage at ambient conditions for a period of 8 weeks. After this static storage time, the amount of hard-packed sediment accumulating at the bottom of the sample jar was determined by inserting a 6 inch metal machinist's ruler. The ruler penetrated the slurry with the use of light hand pressure until the hard pack sediment is detected. When the hard pack sediment is reached, the depth of penetration is read from the ruler. The amount of sediment is expressed as a percentage of the total sample height:$(h_o-h)/h_o$ x 100g where h_o = total sample height in the container, h = depth of non-sedimented and loosely packed material.

TABLE 4

Polymer Concentration	Initial Reading of Apparent Viscosity	Percent sediment 8 weeks after viscosity reading
0.00	965	61.21
0.05	2220	7.2
0.075	2830	0.0
0.10	5540	0.0

WHAT IS CLAIMED IS

1. A coal water mixture comprising: a) a poly(alkylene oxide) surfactant comprised of a hydrophilic portion derived from ethylene oxide and a hydrophobic portion derived from a higher alkylene oxide; and b) a stabilizer comprising a hydroxyalkyl ether of a polygalactomannan.

2. A composition in accordance with claim 1 wherein the surfactant is present in an amount sufficient to wet the coal particles present in the mixture and wherein the amount of the stabilizer is sufficient to stabilize the coal water mixture with respect to particle settling and bed compaction.

3. A composition in accordance with claim 1 wherein the coal is pulverized coal.

4. A composition in accordance with claim 1 wherein the coal is present in an amount from about 50% to about 80% by weight of the coal water mixture.

5. A composition in accordance with claim 1 wherein the higher alkylene oxide of the surfactant is propylene oxide.

6. A composition in accordance with claim 1 wherein the surfactant is an ethoxylated, propoxylated propylene glycol.

7. A composition in accordance with claim 1 wherein the hydroxy-alkyl ether of a polygalactomannan is a hydroxy-propyl ether.

8. A composition in accordance with claim 1 wherein the hydroxy-alkyl ether of a polygalactomannan is a hydroxyalkyl ether of guar.

9. A composition in accordance with claim 1 wherein the stabilizer is hydroxypropyl guar.

10. A composition in accordance with claim 1 wherein the stabilizer is a hydroxypropyl methyl guar.

11. A process for preparing a coal water mixture comprising: i) forming a mixture of particulate coal, water and a poly(alkylene oxide) surfactant comprised of a hydrophilic portion derived from ethylene oxide and a hydrophobic portion derived from a higher alkylene oxide; ii) adding to the resultant mixture a stabilizing amount of a stabilizer comprised of a hydroxyalkyl ether of a polygalactomannan; and iii) mixing the resultant composition to form a homogeneous mixture.

12. In a method for transporting or pumping a coal-water mixture, the improvement of having present in the coal water mixture: a) a poly(alkylene oxide) surfactant comprised of a hydrophilic portion derived from ethylene oxide and a hydrophobic portion derived from a higher alkylene oxide; and b) a stabilizer comprising a hydroxyalkyl ether of a polygalactomannan.

European Patent Office

EUROPEAN SEARCH REPORT

0 209 122

EP 86 10 9728

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
A	EP-A-0 057 576 (GULF & WESTERN) * Claims 1,2,4,10; page 16, last paragraph; page 20, paragraph 2 *	1,3-6, 9,11	C 10 L 1/32 B 65 G 53/00
P,A	EP-A-0 153 206 (RHONE-POULENC) * Claim 1; page 1, lines 6-13 *	1	
A	GB-A-1 604 216 (HERCULES LTD.) * Claims 1-8,10-12; page 1, lines 11-16 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl 4)

C 10 L
B 01 F
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-10-1986	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document

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