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⑤④ **Viscosity reducers for coal-aqueous mixtures.**

⑤⑦ Heteric poly(oxyalkylene) nonionic surfactants are used as viscosity reducers in coal-aqueous mixtures. The heteric poly(oxyalkylene) nonionic surfactants are prepared by reacting a mixture of ethylene oxide and a higher epoxide with a hydrophobic initiator.

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VISCOSITY REDUCERS FOR COAL-AQUEOUS MIXTURES

This invention relates to coal-aqueous mixtures containing heteric poly(oxyalkylene) nonionic surfactants as viscosity reducers.

U.S. Patent 4,358,293 discloses coal-aqueous mixtures having high solids content. The solids are dispersed into the water by using selected poly(oxyalkylene) nonionic surfactants. Among the selected surfactants are block copolymers of ethylene oxide and propylene oxide derived from di- and higher functionality initiators. Particularly suitable for use in the invention were found to be block polymers of ethylene diamine and propylene oxide derived from nitrogen containing compositions such as ethylene diamine and having a molecular weight of at least 14,000, as described at column 3, lines 35-50 of the patent.

Although these products are effective in dispersing particulate coal into coal-aqueous mixtures, they do have a drawback. The high ethylene oxide content of the most effective viscosity reducers described causes the formation of gels when these materials are contacted by water. Detailed information on the gel regions of various block copolymers of ethylene oxide and propylene oxide can be found in technical data sheets on PLURONIC® polyols and TETRONIC® polyols published by BASF Corporation. For example, the TETRONIC surfactant 1307 specifically mentioned in the above patent forms permanent gels when 30 percent solutions in water of this material are attempted. Water solutions of lower concentration are also difficult to prepare due to the immediate formation, upon contact with water, of gel particles which redissolve slowly and only with vigorous agitation.

The solubility problems described above make it, therefore, difficult to prepare aqueous solutions of these additives to be blended with the aqueous slurry components during the commercial preparation of coal water mixtures.

The need of long solution times and to prepare stock solutions of the various viscosity reducers with relatively low concentrations will add to the cost of the final product. Furthermore, the solid nature of the heat products will require that they are transported and stored in heated vessels thus further increasing the processing costs.

The present application describes the composition of liquid additives which can be rapidly dissolved in water and are as effective or more effective than the selected poly(oxyalkylene) nonionic surfactants mentioned in U.S. Patent 4,358,293 in reducing the viscosity of coal water mixtures.

The subject invention relates to a coal-aqueous mixture comprising:

- (a) particulate coal as a dispersed solid material;
- (b) water as a carrier medium; and
- (c) a viscosity reducer which is a poly(oxyalkylene) nonionic surfactant containing a hydrophobic portion and a hydrophilic portion with such hydrophilic portion comprised of a mixture of ethylene oxide and a higher epoxide having 3 to 4 carbon atoms such that the weight ratio of ethylene oxide to higher epoxide is from about 5:1 to about 2:1 and the average molecular weight of the nonionic surfactant is from about 10,000 to about 50,000.

The subject invention also relates to a process for preparing a coal-aqueous mixture comprising (a) mixing the neat viscosity reducer with water to produce homogeneous solutions containing from 5 to 50 percent of the viscosity reducer, (b) adding the above solution to a particulate coal in such a way that the ratio of coal to viscosity reducer is from 1000:1 to 10:1, and (c) blending, under vigorous agitation, the particulate coal with a sufficient amount of water to produce slurries with a coal load varying from 40 to 90 percent by weight of the total slurry. Alternatively, the viscosity reducer solution in (a) can be admixed with a water stream in such a way that the resulting ratio of water to viscosity reducer is from 1000:1 to 10:1, and this solution can then be blended under vigorous agitation with particulate coal in sufficient amount to produce slurries with a coal load varying from 40 to 90 percent by weight of the total slurry.

The subject composition and process are particularly advantageous because the viscosity reducer is dissolvable in water at ambient temperature in shorter time periods than comparable products shown in the prior art as subsequent data will show. This feature is important because the viscosity reducer is mixed with the water before the particulate coal is added. Uniform mixing of the viscosity reducer and water is important in obtaining uniform viscosity.

The particulate coal used in the subject invention may be bituminous coal, anthracitic coal, sub-bituminous coal, lignitic coal, charcoal, and petroleum coke. The particle size of the particulate coal should range from 0.1 to 350 μ m, preferably 1 to 250 μ m. For best results, however, the particle size should not exceed about 200 μ m. The amount of particulate coal used in the coal-water mixture generally will be from 40 to 90 percent by weight, preferably 70 to 80 percent by weight, based upon the total weight of coal-water mixture.

The viscosity reducer which is liquid at ambient temperature is a heteric poly(oxyalkylene) nonionic surfactant having an average molecular weight of from 10,000 to 50,000, preferably from 15,000 to 30,000. The viscosity reducer is prepared by reacting a mixture of ethylene oxide and a higher epoxide having 3 to 4 carbon atoms such as propylene oxide or butylene oxide with a hydrophobic initiator preferably obtained by reacting an aliphatic diamine such as ethylene diamine with a higher epoxide having 3 to 4 carbon atoms such that the ratio of ethylene oxide to higher epoxide in the hydrophilic portion is from 10:1 to 1:1, preferably from 5:1 to 1:1.

The heteric poly(oxyalkylene) nonionic surfactant is prepared by methods well known in the art. Essentially, the initiator is reacted with a mixture of ethylene oxide and a higher epoxide having 3 to 4 carbon atoms such as propylene oxide or butylene oxide at increased temperatures in the presence of an oxyalkylation catalyst.

the amount of liquid viscosity reducer used is generally from 0.1 to 10.0 percent by weight, preferably from 0.3 to 3.0 percent by weight, based upon the total weight of the coal-aqueous mixture.

Water is the other component of the coal-aqueous system and is used in amounts of from 60 to 10 percent by weight, preferably from 50 to 25 percent by weight, based upon the total weight of the coal-aqueous system.

Additional components may be added to the coal-aqueous mixture such as defoaming agents, thickeners, salts, bases, other flow modifying agents and combinations of these materials.

Generally, the defoaming agents that can be used are conventional and include both silicon and non-silicon containing compositions.

The thickeners that can be added to the mixture are also conventional. They are added to increase the non-settling characteristics of the composition. Suitable thickeners include xanthan gum, guar gum, glue or combinations of these materials, in amounts ranging from about 0.01 to 3.0 percent by weight, based in the total weight of the mixture.

In preparing the compositions, the heteric poly(oxyalkylene) nonionic surfactant is preferably mixed with water at atmospheric or nearly atmospheric temperature and pressure to obtain a concentrated solution which is then mixed with pulverized coal and water to obtain a flowable liquid. A defoaming agent can be added to the water at this point to assist in processing. If desired, a thickener can be added to provide protection against settling. Other additives such as salts or bases can also be added to assist in dispersing.

The following examples will illustrate in more detail how to practice this invention and are designated to disclose the best mode for practicing the invention at the time this patent application was filed. All embodiments of the invention are not intended to be disclosed in the examples. Those skilled in the art will recognize many equivalents.

In order for a viscosity reducer to work effectively, it must readily dissolve in water. A readily dissolvable viscosity reducer will save time and expense. The following examples compare the dissolvability of TETRONIC® 1307 (hereinafter referred to as BCS) nonionic surfactant, which is a block copolymer, disclosed in U.S. Patent 4,358,293, with a heteric analogue (hereinafter referred to as HCS) of TETRONIC® 1307 nonionic surfactant initiated with ethylenediamine.

Table I, which follows, shows the dissolution time for various concentrations of BCS both molten and in water:

TABLE I

	<u>Surfactant</u>	<u>Concentration in Water</u>	<u>Dissolution Time, hrs.</u>
5	BCS (molten)	10%	2.5
	BCS (molten)	20%	>8.0
10	BCS (molten)	30%	>24.0
	BCS (flaked)	10%	0.7
15	BCS (flaked)	20%	2.4
	BCS (flaked)	30%	>24.0

Table I shows that flaked BCS at concentrations of 10 percent in water has the lowest dissolution time.

TABLE II

	<u>Surfactant</u>	<u>% of Propylene Oxide in Heteric Chain</u>	<u>Concentration in Water</u>	<u>Dissolution Time, hrs.</u>
25	HCS/20	20.0	10.0	1.1
	HCS/20	20.0	20.0	1.4
30	HCS/20	20.0	30.0	>8.0
	HCS/25	25.0	10.0	1.2
35	HCS/25	25.0	20.0	1.9
	HCS/25	25.0	30.0	>24.0
	HCS/30	30.0	10.1	0.3
40	HCS/30	30.0	20.0	0.6
	HCS/30	30.0	30.0	1.00
45	HCS/40	40.0	10.0	1.1
	HCS/40	40.0	20.0	1.25
50	HCS/40	40.0	30.0	>24.0

Table II illustrates the dissolution time for various concentrations of HCS containing different percentages of propylene oxide in the heteric chain. The molecular weights of all the HCS products was approximately 15,000. In comparing Table I and Table II, it can be seen that all of the HCS products performed better than the molten BCS products at comparative concentrations. The flaked BCS did perform better at 10 percent concentrations than all the HCS products except that containing 30 percent propylene oxide. All of the HCS products performed better at 20 percent concentrations. The best dissolution time for all of the surfactants tested was HCS/30 containing 30 percent propylene oxide.

In the following examples, HCS/30 was compared to BCS with respect to its effectiveness in reducing the viscosity of various coal-water mixtures. The coal-water mixtures were prepared by dissolving 30 percent of the surfactant in water and by adding the resulting solution to a blend of water and various coals such that 90 percent of the particles have a diameter smaller than 160 μ m and 100 percent is less than 250 μ m. The coal-load in the mixture was determined by heating the mixture in a microwave oven repeatedly for 15 minutes or until no more weight loss was measured. The viscosities were measured by using a Haake Viscometer (Model XV100) and a MV2P spindle. The viscosity was measured by increasing the shear rate from 0 to 512 rpm over a four minute period. The Viscometer was maintained at that rate for one minute. The shear rate was reduced to 0 over a four minute period. The same cycle was repeated and the viscosity was measured at 100 sec. on the second descending curve. The results of the experiments are shown in Table III.

TABLE III

	<u>Coal</u>	<u>Surfactant</u>	<u>Coal Load</u>	<u>Viscosity</u> <u>cps.</u>	
				<u>100 sec.-1</u>	<u>200 sec.-1</u>
20	Splash Dam Coal	HCS/30	65.3	244.5	348.0
	"	BCS	64.7	161.7	226.0
25	Blumental Coal	HCS/30	64.6	94.0	103.4
	"	BCS	64.2	101.5	94.0
30	Datong Coal	HCS/30	64.9	244.5	244.5
	"	BCS	65.1	394.9	479.5
	Polish Coal	HCS/30	64.2	101.5	112.8
35	"	BCS	65.2	451.3	479.5

Table III shows that HCS/30 is an effective viscosity reducer for all coals tested and is in some cases, (Datong coal and Polish coal) more effective than BCS, a well known viscosity reducer for coal-aqueous systems. HCS/30, as well as other types of HCS products, have the added advantage that they more readily dissolved in water and do not have to be molten or flaked. This saves time, money, and permits a more efficient operation.

45 Claims

1. A coal-aqueous mixture comprising:
 - (a) particulate coal dispersed as a solid material;
 - (b) water as a carrier medium; and
 - 50 (c) a viscosity reducer which is prepared by reacting a mixture of ethylene oxide and a higher epoxide having 3 to 4 carbon atoms with a hydrophobic initiator.
2. The coal-aqueous mixture of claim 1 wherein the viscosity reducer has an average molecular weight of from 10,000 to 50,000.
3. The coal-aqueous mixture of claim 2 wherein the hydrophobic initiator of the viscosity reducer is obtained by reacting an aliphatic diamine with a higher epoxide having 3 to 4 carbon atoms.
- 55 4. The coal-aqueous mixture of claim 2 wherein
 - (a) from 45 to 90 percent by weight of particulate coal is used based upon the total weight of the coal-aqueous mixture;

(b) from 15 to 60 percent by weight of water is used based upon the total weight of the coal-aqueous mixture; and

(c) from 0.1 to 5.0 percent by weight of viscosity reducer is used based upon the total weight of the coal-aqueous mixture.

5 5. The coal-aqueous mixture of claim 4 wherein the weight ratio of ethylene oxide to higher epoxide in the hydrophylic portion of the viscosity reducer is from 10:1 to 1:1.

6. The coal-aqueous mixture of claim 5 wherein the weight ratio of ethylene oxide to higher epoxide in the hydrophylic portion of the viscosity reducer is preferably from 5:1 to 2:1.

7. The coal-aqueous mixture of claim 5 wherein the higher epoxide is propylene oxide.

10 8. The coal-aqueous mixture of claim 5 wherein the higher epoxide is propylene oxide.

9. A process for forming a coal-aqueous mixture comprising:

(a) adding to water a viscosity reducer which is prepared by reacting a mixture of ethylene oxide and a higher epoxide having 3 to 4 carbon atoms with a hydrophobic initiator and water to produce homogeneous solutions containing from 5 to 50% of the viscosity reducer.

15 (b) adding the solution prepared in step a) to a blend of particulate coal and water such that the weight ratio of the coal-water mixture to the viscosity reducer is from 1000:1 to 10:1.

(c) agitating the resulting mixture under high speed agitation.

10. The process of claim 9 wherein the viscosity reducer has an average molecular weight of from 10,000 to 50,000.

20 11. The process of claim 10 wherein

(a) from 45 to 90 percent by weight of particulate coal is used based upon the total weight of the coal-aqueous mixture;

(b) from 15 to 60 percent by weight of water is used based upon the total weight of the coal-aqueous mixture; and

25 (c) from 0.1 to 5.0 percent by weight of viscosity reducer is used based upon the total weight of the coal-aqueous mixture.

12. The process of claim 11 wherein the weight ratio of ethylene oxide to higher epoxide in the hydrophylic portion of the viscosity reducer is from 10:1 to 1:1.

30 13. The process of claim 12 wherein the weight ratio of ethylene oxide to higher epoxide in the hydrophylic portion of the viscosity reducer is preferably from 5:1 to 1:1.

14. The process of claim 12 wherein the higher epoxide is propylene oxide.

15. The process of claim 13 wherein the higher epoxide is propylene oxide.

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