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(54) Carbonaceous materials in water slurries.

(57) Stabilized carbonaceous materials in water slurries having reduced viscosity and improved pumpability are obtained by having present an ammonium salt of naphthalenesulfonic acid formaldehyde condensate as a stabilizer, the ammonium condensate being present in an amount sufficient to reduce viscosity of the aqueous carbonaceous slurry and to improve its pumpability. From about 0.01 to about 5% by weight of the ammonium condensate may be added to a coal water slurry containing from about 50 to about 80% or higher solids with the balance being water.

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CARBONACEOUS MATERIALS IN WATER SLURRIES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to carbonaceous materials in water slurries and more particularly to coal in water slurries stabilized with ammonium salts of naphthalenesulfonic acid formaldehyde condensates.

2. Description of the Prior Art

Transport is one of the major problems involved in use of particulate carbonaceous materials such as coal. One method of transport involves aqueous slurries. However, aqueous slurries of finely ground coal containing over 55 weight percent solids are difficult to pump with slurry pumps. This is because as the solids level is increased above 50 weight percent, water and solids tend to separate causing coal particles to build up in various areas in the pumping system. This dewatering of the slurry causes blockage and jamming in the pumping system.

On the other hand, decreasing the weight percent of water in aqueous coal slurries is desirable because water is a major contributor to the cost of transport and processing operations. The less water transported the greater is the volume of coal that can be moved, resulting in transport efficiencies. Further, water resources are limited. Also, during burning of coal, a significant amount of heat is required to vaporize the water. As the weight percent of water decreases, the efficiency of the coal burning process increases. Hence, use of higher

weight percent solids aqueous carbonaceous slurries than were heretofore feasible would be of great importance.

U.S. Patent No. 4,282,006 - Funk, August 4, 1981, describes a pipeline pumpable coal water slurry having a high content of coal particles with a minimum of void spaces and a maximum of particle surface area to enhance dispersing effects generated by electrolytes and/or dispersing agents added to the slurry. For dispersing agents, see Column 29, line 53 to Column 31, line 9, including condensed mononaphthalene sulfonic acid and its sodium and ammonium salts (Column 30, lines 19 and 20).

SUMMARY OF THE INVENTION

Stabilized carbonaceous materials in water slurries having reduced viscosity and improved pumpability are obtained by having present an ammonium salt of naphthalenesulfonic acid formaldehyde condensate as a stabilizer, the ammonium condensate being present in an amount sufficient to reduce viscosity of the aqueous carbonaceous slurry and to improve its pumpability.

DETAILED DESCRIPTION

The ammonium salt of naphthalenesulfonic acid formaldehyde condensate, hereinafter referred to as ammonium condensate for convenience, is present in the slurry in amounts sufficient to reduce viscosity of the slurry and improve its pumpability. Concentration of the ammonium condensate added, based on the total weight of the carbonaceous materials water slurry, can be up to 10% by weight, preferably from about 0.01% by weight to about 5.0% by weight. For example, from about 0.05% by weight to about 0.5% by weight of the ammonium condensate, based on the total weight of the slurry, i.e., solids plus water, can be used. Amount of the ammonium condensate is easily determined by introducing the condensate in an amount sufficient to form a soft sediment. The resulting

slurries will generally have from about 50 to about 80% by weight solids or higher with the balance being water. Ammonium salts of naphthalenesulfonic acid formaldehyde condensates have the following advantages over sodium or other metal salts of these condensates:

(a) Ammonium condensates do not contribute to ash or slag formation during combustion of slurry;

(b) Ammonium condensates have improved performance as slurry stabilizers;

(c) Solutions of ammonium condensates have lower manufacturing cost; and

(d) Solutions of ammonium condensates have improved cold storage stability.

Ammonium condensates are introduced into slurries at any convenient point during their preparation.

The term "carbonaceous materials", as used herein, encompasses solid particulate carbonaceous fossil fuel materials which may have been powdered or pulverized to a size where at least 80% will pass through a 200 mesh screen (U.S. Series). Useful carbonaceous materials include bituminous and anthracite coals, coke, petroleum coke, lignite, charcoal, peat, admixtures thereof and the like. These materials are crushed and milled to obtain finely divided particles suitable for use in pumpable water slurries.

Water used in slurries may be taken from any available source 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 and corrosion of milling facilities, pipelines and furnaces will be minimized and controllable.

The ammonium salt of naphthalenesulfonic acid formaldehyde condensate may be prepared by reacting naphthalene with formaldehyde and sulfuric acid and ultimately treating with ammonium hydroxide. Useful processes are described in U.S. Patent No. 2,141,569 - Tucker et al - December 27, 1938; U.S. Patent No. 3,193,575 - Nebel et al - July 6, 1965 and U.S. Patent No. 3,277,162 - Johnson - October 4, 1966.

A naphthalenesulfonic acid formaldehyde condensate is a mixture of condensation products of naphthalenesulfonic acid and formaldehyde. It can be chromatographed by size exclusion chromatography through a column containing pore sizes which selectively separate molecular volumes according to size. The solvent chosen for the acid in chromatography should minimize solute-packing interaction and solute-solute interaction. The chromatogram gives a true molecular volume profile when the eluents are displayed on a detector-strip chart recorder display. The chromatogram for a sample of the sulfonic acid used in the examples is the same as that for the sodium naphthaleneformaldehyde sulfonate in U.S. Patent No. 3,954,491 - Adrian et al - May 4, 1976, and the two anionic materials are identical. That is, the anionic materials from the sulfonic acid have the same profile as the anionic materials from the sodium naphthaleneformaldehyde sulfonate having lowest elution volumes of from about 61 to about 70% of the total elution volume and equivalent elution volumes of from about 61 to about 70% of the total elution volume. The teachings in U.S. Patent No. 3,954,491 relating to chromatography are incorporated by reference herein. This chromatographic method was described by Dr. Harold Edelstein in a paper entitled, "Aqueous Gel Permeation Chromatograph of Some Naphthalene Sulfonic Acid Formaldehyde Condensates" presented at the Mini Symposium of the North Jersey Chromatography Group

Subsection of the A.C.S. on March 6, 1978 at Hoffman La Roche Auditorium, Clifton N.J.

Evaluation of Stabilizers for Aqueous Carbonaceous Slurries

The following procedure is used in the evaluation of ammonium salts of naphthalenesulfonic acid formaldehyde condensates in aqueous coal slurries in the examples given below. This procedure determines ability of these ammonium condensates to disperse or suspend coal dust uniformly in water by measuring viscosity.

Apparatus Used

8-oz. paint can
Low shear mechanical mixer with a double blade
Spatula
Stormer viscometer

Reagents Used

Water of known record hardness
Coal dust - Reference coal is Pittston Coal, 80% through 200 mesh (U.S. Series). Other types of coal and grind sizes can be substituted.
Stabilizing agent

Procedure

1. A slurry of coal dust in water is prepared as follows. Coal dust is slowly added to water under agitation by a low shear mechanical mixer with a double blade. Sides of the container are scraped regularly while mixing. The slurry is agitated for an additional hour to ensure uniformity. The weight % solids in the slurry is determined by difference.

2. Viscosity of the aqueous coal slurry is determined by weighing out 200 gram samples of the slurry into 8 oz. paint cans. A specific quantity of the ammonium condensate is added to each can under vigorous agitation. A concentration range of ammonium condensate of from 0.10 to 1 gram/200 grams is used. Each can can is closed tightly to prevent evaporation of water.

3. Each can is opened and each slurry is stirred with a spatula before viscosity measurements are made with a Stormer Viscometer. Weights are adjusted in order to find a reading as close as possible to 30 seconds and the correct weight for a 30-second viscosity is determined. Readings are repeated twice after stirring each time. Readings should not differ by more than 2 seconds. Readings are repeated until consistent and the average of two readings taken. Readings on slurries covering a broad concentration range of ammonium condensate are taken to the point where the ammonium condensate no longer reduces viscosity of the slurry and/or coal precipitates from the slurry.

4. Seconds and weight are converted into krebs units. Krebs units are then converted to centipoise readings.

For a fuller understanding of the nature and advantages of this invention, reference may be made to the following examples. These examples are given merely to illustrate the invention and are not to be construed in a limiting sense. All quantities, proportions and percentages are by weight and all references to temperature are °C unless otherwise indicated.

EXAMPLE I

Samples of coal water slurries were treated with the quantities of solutions of sodium condensate (sodium salt of naphthalenesulfonic acid formaldehyde condensate) and ammonium condensate (ammonium salt of naphthalenesulfonic acid formaldehyde condensate) shown in the table below. The coal water slurries were 60% by weight slurries of Pittston coal dust in tap water. A sample of coal slurry on drying was found to contain 59.1% solids. Quantity in the table is the quantity of additive solution added to 200 g of coal water slurry. An untreated sample of the coal slurry was used as the blank and samples treated with sodium condensate were used as the control. The additive solution used as a control was a 34% sodium condensate solution. The other two additive solutions were a 40% ammonium condensate solution having a pH of 6.5 and a 42.3% ammonium condensate solution having a pH of 4.0. Samples of the blank, control and ammonium condensate treated slurries were then evaluted by the procedure described above to obtain the following results:

Quantity (g)	Additive Solution (% by weight)	Additive (g) / Coal (g)	Stormer wt	sec	KU	cps
-	Blank	-	800	32	132	4000
0.10	34% sodium condensate	0.00028	300	28	93	1230
0.15	34% sodium condensate	0.00043	200	30	82	925
0.20	34% sodium condensate	0.00057	175	29	76	766
0.25	34% sodium condensate	0.00071	150	25	66	460
0.35	34% sodium condensate	0.00099	125	31	68	500
0.10	40% ammonium condensate	0.00033	200	32	83	950
0.15	40% ammonium condensate	0.00050	175	29 (30)	76	766
0.20	40% ammonium condensate	0.00067	175	30	77	800
0.25	40% ammonium condensate	0.00083	125	30	67	480
0.10	42.3% ammonium condensate	0.00035	250	27	86	1033

0.15	42.3% ammonium condensate	0.00053	175	29	76	766
0.20	42.3% ammonium condensate	0.00070	150	30	72	633
0.25	42.3% ammonium condensate	0.00088	125	29	66	460

While the invention has been described with reference to certain specific embodiments thereof, it is understood that it is not to be so limited since alterations and changes may be made therein which are within the full intended scope of the appended claims.

WHAT IS CLAIMED IS:

1. In a water slurry of carbonaceous materials composition comprising water and carbonaceous materials, the improvement of having present therein an effective amount of an ammonium salt of a naphthalenesulfonic acid formaldehyde condensate sufficient to reduce viscosity and to improve pumpability.

2. The composition of claim 1 wherein there is present up to about 10% by weight of the condensate.

3. The composition of claim 1 wherein there is present from about 0.01 to about 5% by weight of the condensate.

4. The composition of claim 1 wherein the carbonaceous materials are coal.

5. In a process of pumping a water slurry of carbonaceous materials composition in a pipeline, the improvement comprising having present the composition of claim 1.

6. In a process of pumping a water slurry of carbonaceous materials composition in a pipeline, the improvement comprising having present the composition of claim 2.

7. In a process of pumping a water slurry of carbonaceous materials composition in a pipeline, the improvement comprising having present the composition of claim 3.

8. In a process of pumping a water slurry of carbonaceous materials composition in a pipeline, the improvement comprising having present the composition of claim 4.