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(54) A method for the preparation of a uniform dispersion of a friable solid fuel, oil and water and the obtained fuel-oil-water dispersion.

(57) A uniform dispersion of a friable solid fuel, e.g. coal, oil and water is prepared by grinding the solid fuel in a medium consisting essentially of oil until the mean particle size of the solid fuel is reduced to a value in the range 1 to 15 micron. Air is excluded during the grinding operation. Water is added to the resulting dispersion of solid and oil and the resulting mixture of solid, oil and water is homogenised in the absence of added dispersant or emulsifier. The final dispersion contains 15 to 55% by weight solid, expressed as a percentage by weight of the total dispersion.

The water enhances the stability of the dispersion.

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TITLE MODIFIED
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SOLID FUEL-OIL MIXTURES

This invention relates to the production of dispersions of solid fuel, oil and water.

Coal oil-slurries have previously been disclosed, see for example British Patent Specification 975687. Whilst these have behaved as near-Newtonian non-settling fluids in pipelines, they separate on standing. Thus such slurries are suitable for use immediately after preparation or pipelining but are not suitable for transportation nor for storage.

Our British Patent Specification No. 1523193 describes and claims a method for the preparation of a uniform coal oil dispersion which method comprises grinding coal in a medium consisting essentially of gas oil and/or a heavier petroleum fraction until the particle size is reduced to a value below 10 micron and the dispersion contains 15 to 55% by weight coal, expressed as a percentage by weight of the total dispersion, and until a stable dispersion results on ceasing grinding.

British Patent Specification 1548402 discloses a method for making a fluid fuel which comprises the steps of mixing coal to a grain size of up to 6 mm with up to 30 wt % of water based on the mixture of coal and water, passing the wetted coal to a mixer wherein it is mixed with liquid hydrocarbon fuel, the coal forming no more than 50 wt % coal in the mixture and passing the so-formed mixture through a grinding mill wherein the coal grains are milled to particles of at most 500 micron in size to produce the fluid fuel.

1548402 states that it is essential that the water and coal be mixed before the addition of the liquid hydrocarbon fuel in order that the desired form of the product may be obtained, namely a flocculated structure in oil of the coal particles in which water preferentially wets part of the surface of each coal particle and links it to the other coal particles. It also states that if the mixing is carried out in any other sequence, as for example in United States Patent Specification 1431225, an emulsion of water in the oil is formed, the coal particles are not wetted by the water and the product is stabilised to a much smaller extent against settling. According to 1548402 adding water to the suspension of coal in liquid hydrocarbon fuel simply forms an emulsion in the hydrocarbon which does not aid stability for a long duration.

The aforesaid United States Patent Specification 1431225 discloses a method for the preparation of a fluid fuel in which a solid fuel is ground to a fineness of about 200 mesh (76 micron) or less. The powdered solid is then mixed with a liquid fuel, water is added and the mixture agitated to provide an emulsion. United States Patent Specification 1431225 acknowledges that under certain conditions there is a tendency for the emulsion to become unstable and separate into its constituents and to counteract this a stabilising agent such as soap may be added.

We have now surprisingly discovered that the stability of solid fuel-oil dispersions of the type disclosed in GB 1523193 can be improved by the addition of water after grinding. In particular, the stability is improved in the temperature range of 60° to 100°C. Alternatively, the grinding time required to produce a dispersion of desired stability is reduced.

Thus according to the present invention there is provided a method for the preparation of a uniform dispersion of a friable solid fuel, oil and water which method comprises grinding the solid fuel in a medium consisting essentially of oil until the mean particle size of the solid fuel is reduced to a value in the range of 1 to 15 micron, air being excluded during the grinding operation, adding water to the resulting dispersion of solid and oil and homogenising the resulting mixture of solid, oil and water in the absence of added dispersant or emulsifier, the final dispersion containing 15 to 55% by weight solid expressed as a percentage by weight of the total dispersion.

Suitable friable solid fuels include coals of various ranks, solvent refined coal, coal coke and petroleum coke. The preferred solid fuel is bituminous coal.

Preferably the solid fuel supplied to the grinding process is preground to a particle size not greater than 250 micron.

A suitable oil is a petroleum based fuel oil fraction having a viscosity of not more than 6000 seconds, preferably not more than 3500 seconds, Redwood No. 1 at 100°F (37.8°C). The required viscosity may be achieved by "cutting back" if necessary with, for example, gas oil.

In the case of certain heavier fuel oil fractions it may be necessary to heat them in order to render them sufficiently mobile to permit use as a grinding liquid.

The amount of solid fuel added is preferably in the range 30 to 45% by weight of the total weight of the dispersion of solid fuel, oil and water.

The amount of water added is suitably in the range 1 to 15%, preferably 5 to 10% of the total weight of the dispersion of solid fuel, oil and water.

Homogenisation may take place in a high speed vortex mixer.

Grinding can be carried out in commercially available ball mills, e.g. agitatory, vibratory or tumbling ball mills.

When using an agitatory or vibratory ball mill, the preground coal is preferably premixed with the oil before grinding, e.g. in a high speed vortex mixer.

Grinding is preferably carried out until the solid fuel mean particle size is reduced to a value in the range 2 to 8 micron.

The grinding time will depend on the nature of the mill. However, this time will generally be about half the time required to produce a dispersion of similar stability when no water is subsequently added. For example, when using an agitatory ball mill the grinding time may be reduced from about 6 minutes to 3 minutes.

It is necessary to exclude air during the grinding operation. This can easily be achieved in the case of vibratory and agitatory ball mills by filling the mill completely.

When using a ball mill it is, of course, desirable to use balls made of a material which does not react with the solid and which does not wear unduly either itself or the interior surface of the mill during the grinding. Ball mills usually contain steel or glass balls and these are suitable for the present purpose.

The dispersions will generally be prepared, used and stored at elevated temperature and under these conditions will be more stable than corresponding dispersions prepared without adding water. They are suitable for use in blast furnaces, cement kilns and in industrial, marine and utility boilers.

The stability of the solid fuel-oil-water dispersion is a function of three important variables - the method of grinding, the final particle size and the concentration of solid in oil - enhanced by a fourth - the addition of water after grinding. If all four are chosen correctly, then the dispersion is of enhanced stability at elevated and ambient temperatures.

At ambient temperature, the dispersion is in the form of a weak, thixotropic gel in which a physical network is formed by solid particles which interact with the oil reinforced by water links between the solid particles. It is a uniform structure from which the solid particles cannot settle out because they form part of it.

This is unlike previous solid fuel-oil-water dispersions which have been dispersions of water-wet coal particles suspended in oil or dispersions of coal particles suspended in an emulsion of oil and water.

At elevated temperature, although the gel-like structure is less apparent, the same interactions occur to confer enhanced stability.

If the solid particles are not ground in the oil in the absence of air, the solid particles will become oxidised and interact unfavourably. If the solid particle size is too great, the forces will be insufficient to confer stability. The concentration of the solid particles is also critical. If it is too low the dispersion will be unstable. If it is too high the dispersion will become too solid-like for pumping. The water enhances stability by a complex mechanism probably involving bridges between the solid particles.

According to another aspect of the present invention there is provided a solid fuel-oil-water dispersion which comprises 15 to 55% by weight of solid fuel particles dispersed in a medium consisting essentially of a major proportion of oil and a minor proportion of water, the solid fuel particles having a mean particle size in the range 1 to 15 micron and having both hydrophilic and oleophilic properties.

The minor proportion of water is preferably in the range 1 to 15% by weight of the total weight of the dispersion of solid, oil and water.

The invention is illustrated by the following examples:

Example 1

The fuel oil was a mixed-source fuel oil with a viscosity of 3500 Redwood 1 seconds at 37.8°C. It had the following properties:

Sulphur content	% wt	:	2.3
Water content	% wt	:	0.10
Specific gravity 15.6°C/15.6°C		:	0.966
Kinematic viscosity at 60°C cSt		:	247
80°C cSt		:	74.3
100°C cSt		:	36.8

The coal was a bituminous coal ex Durham coal field of Rank 501 with the following ultimate and initial particle size analyses (air-dried basis):

Carbon content	% wt	:	78.1
Hydrogen content	% wt	:	4.87
Nitrogen content	% wt	:	1.7
Total sulphur content	% wt	:	1.74
Chlorine content	% wt	:	0.25
Water content	% wt	:	2.3
Ash content at 815°C	% wt	:	5.1
+ 500 micron	% wt	:	0.1
- 500 + 212 micron	% wt	:	1.6

- 212 + 75 micron	% wt	:	21.0
- 75 + 53 micron	% wt	:	14.2
< 53 micron	% wt	:	63.1

The fuel oil (24.3 kg) was warmed to 35°C and the pulverised coal (15.2 kg) was added gradually, stirring continuously with a high speed vortex mixer. The resulting slurry was then pumped at a rate of 2.5 litre/min giving a residence time of 3 minutes, to a stirred-ball mill sold under the name of Dyno Mill, Type KD 15 by Willy Bachofen Maschinefabrik, Basle, Switzerland.

The mill grinding chamber was a horizontally mounted cylinder of volume 15 litres containing 2 mm steel balls (nominally 60 kg). The balls were stirred by agitator discs mounted on a horizontal shaft which was parallel with the axis of the cylinder. The shaft speed was set at 1,635 rpm to give a disc peripheral speed of 15 m/sec. The product was collected as it emerged from the mill. The mean particle size of the coal was approximately 5 micron.

A sample (300 g) of the coal/fuel oil dispersion prepared above was warmed to ca 30°C. Water (26.1 g) was added and the mixture stirred with a high speed vortex mixer for 6 minutes. The dispersion of final composition 35% wt coal, 8% wt water and 57% wt fuel oil showed no sign of coal settling after standing for 3 months at ambient temperature. After standing for 24 hours at 100°C the dispersion also appeared quite stable.

For comparison, a coal-fuel oil dispersion was prepared containing 35% wt coal and 65% wt fuel oil (i.e. without added water). The premix slurry was ground in the KD 15 Dyno Mill under identical conditions as before. Although stable for 3 months at ambient temperature the dispersion showed signs of instability after 24 hours at 100°C with the formation of a layer of thick sludge. The mean particle size of the coal was 4.7 micron, as determined by an optical microscope technique.

Example 2

The fuel oil was a mixed-source fuel oil with a viscosity of 3500 Redwood 1 seconds at 37.8°C. The coal was drawn from a different batch of the Durham coal used in Example 1. The analytical details of the coal and fuel oil were similar to those used in Example 1.

A premix of pulverised coal (84 kg) in fuel oil (156 kg) was prepared as in Example 1. This slurry, containing 35% wt coal, was pumped at a rate of 5.8 litre/min,giving a residence time of 6.9 minutes, to a vibratory ball mill sold under the name of Palla 20U by Humboldt-Wedag, Cologne, Germany. This mill consisted of two horizontally-mounted cylinders as grinding chambers, the upper containing 140 kg steel cylinders (½ inch long x ¼ inch diameter), the lower containing 140 kg of steel balls (¼ inch diameter). The mill diameter of vibration was at its maximum setting of 10 - 12 mm. The product was collected and then passed through the KD 15 Dyno Mill at a rate of 3.0 litre/min, giving a residence time of 2½ minutes. Other Dyno Mill conditions were as in Example 1.

The product emerging from the Dyno Mill had a mean particle size of 6.3 micron and showed no signs of settling after storage at ambient temperature for 3 months, but after 24 hours at 100°C the dispersion was unstable forming a deposit of hard-packed coal.

A sample of this dispersion (200 g) was warmed to ca 30°C and to it was added distilled water (16 g). The mixture was stirred using a high speed vortex mixer for 6 minutes. The mixture of final composition 32.2% wt coal, 7.4% water, 60.4% wt fuel oil was stable after 24 hours at 100°C showing no sign of coal settling.

Claims:

1. A method for the preparation of a uniform dispersion of a friable solid fuel, oil and water which method comprises grinding the solid fuel in a medium consisting essentially of oil until the mean particle size of the solid fuel is reduced to a value in the range 1 to 15 micron, air being excluded during the grinding operation, adding water to the resulting dispersion of solid and oil and homogenising the resulting mixture of solid, oil and water in the absence of added dispersant or emulsifier, the final dispersion containing 15 to 55% by weight solid, expressed as a percentage by weight of the total dispersion.
2. A method according to claim 1 wherein the mean particle size of the solid fuel is reduced to a value in the range 2 to 8 micron.
3. A method according to either of the preceding claims wherein the dispersion contains 30 - 45% by weight of solid fuel.
4. A method according to any of the preceding claims wherein the dispersion contains 1 to 15% by weight of water.
5. A method according to claim 4 wherein the dispersion contains 5 to 10% by weight of water.
6. A method according to any of the preceding claims wherein the friable solid fuel is coal, solvent refined coal, coal coke or petroleum coke.
7. A method according to claim 6 wherein the friable solid fuel is bituminous coal.
8. A method according to any of the preceding claims wherein the solid fuel is preground to a particle size not greater than 250 micron before grinding in the oil medium.
9. A method according to any of the preceding claims wherein the oil is a petroleum fuel oil fraction having a viscosity of not more than 6000 seconds Redwood No. 1 at 37.8°C.
10. A method according to claim 9 wherein the oil is a petroleum fuel oil fraction having a viscosity of not more than 3000 seconds Redwood No.1 at 37.8°C.

11. A method according to any of the preceding claims wherein grinding is carried out in a ball mill.

12. A method according to any of the preceding claims wherein homogenisation is carried out in a high speed vortex mixer.

13. A solid fuel-oil-water dispersion which comprises 15 to 55% by weight of solid fuel particles dispersed in a medium consisting essentially of a major proportion of oil and a minor proportion of water, the solid fuel particles having a mean particle size in the range 1 to 15 micron and having both hydrophilic and oleophilic properties.

14. A solid fuel-oil-water dispersion according to claim 13 wherein the minor proportion of water is in the range 1 to 15% by weight of the total weight of the dispersion of solid, oil and water.