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

(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 a major proportion of oil and a minor proportion of water in the absence of added dispersant or emulsifier. Air is excluded during the grinding operation. The solid fuel is present in amount 15 to 55% by weight of the dispersion and is ground until the mean particle size of the solid fuel is reduced to a value in the range 1 to 15 micron.

The water enhances the stability of the dispersion.

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1 TITLE MODIFIED
see front page

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-
5 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
10 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.

15 British Patent Specification No. 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 %
20 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
25 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 No. 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. USP 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 prior to or during 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 a major proportion of oil and a minor proportion of water in the absence of added dispersant or emulsifier, air being excluded during the grinding operation, the solid fuel being present in amount 15 to 55% by weight of the dispersion and being ground until the mean particle size of the solid fuel is reduced to a value in the range 1 to 15 micron.

Suitable friable solid fuels included 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.

The water can be added to the oil prior to mixing with the solid fuel or the solid fuel added to the oil prior to mixing with water or all three added simultaneously prior to grinding.

The initial mixing 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 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 grinding in the absence of water. 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.

5 The dispersions will generally be prepared, used and stored at elevated temperature and under these conditions will be more stable than corresponding dispersions prepared in the absence of water.

They are suitable for use in blast furnaces, cement kilns and industrial, marine and utility boilers.

10 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 presence of water during grinding. If all four are chosen correctly, then the dispersion is of enhanced stability at elevated and ambient temperatures.

15 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.

20 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.

25 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, 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
30 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.

The invention is illustrated with reference to the following examples.

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Example 1

The fuel oil was a mixed-source fuel oil with a viscosity of 3500 Redwood No. 1 seconds at 37.8°C. It had the following properties.

	Sulphur content	% wt	: 2.3
5	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

10 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
15	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
20	+ 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

25 The fuel oil (3.42 kg) was warmed to 35°C and the pulverised coal (2.1 kg) was added with continuous stirring to a vortex mixer. To the resulting mixture water was added (0.48 kg) and further mixing was continued until the mixture attained 54°C. The resulting slurry containing 35% wt coal, 8% wt water and 57% wt fuel oil was pumped at

30 a rate of 480 ml/min giving a nominal residence time of 1.5 minutes, to a stirred ball mill sold under the name of Dyno Mill Type KD Pilot by Willy Bachofen Maschinefabrik, Basle, Switzerland. The mill grinding chamber, a horizontally mounted cylinder of volume 1.4 litres, contained 2 mm steel balls (nominally 5 kg). The balls were stirred by agitator

35 discs mounted on a horizontal shaft which ran parallel with the axis of

the cylinder. The shaft speed was set at 3350 rpm to give a disc peripheral speed of 14 m/sec. The product was collected as it emerged from the mill. The mean particle size of the coal was 5.7 micron, as measured by an optical microscope technique.

5 The coal-fuel oil-water dispersion showed no signs of coal settling after 6 weeks storage at ambient temperature. It showed no signs of instability after standing for 24 hours at 100°C.

10 For a comparison a coal-fuel oil dispersion was prepared containing 35% wt coal in fuel oil in exactly the same grinding conditions as above. This sample again showed no signs of settling after 6 weeks storage at ambient temperature but showed considerable instability after 24 hours at 100°C with the formation of a layer of sludge. It did not contain added water. The mean particle size of the coal was 5.1 micron.

15 In order to produce a product of comparable stability a residence time of approximately 3.5 minutes was required in the mill. The mean particle size of the coal had been reduced to 4.1 micron.

This illustrates how the presence of water reduces the grinding time and thus energy requirements.

Example 2

20 The fuel oil was a mixed-source fuel oil with a viscosity of 3500 Redwood No. 1 seconds at 100°F (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.

25 Water (0.48 kg) was added to the fuel oil (3.42 kg) and stirred briefly with a high speed vortex mixer. Coal (2.1 kg) was then added and stirred in. The resulting slurry containing 35% wt coal, 8% wt water and 57% wt fuel oil was pumped at a rate of 440 ml/min giving a nominal residence time of 1.6 minutes, to the stirred ball mill described in the previous example. The product was collected as it emerged from
30 the mill and was similar in properties to the coal-oil-water dispersion of Example 1. The mean particle size of the coal was 5.3 micron.

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 a major proportion of oil and a minor proportion of water in the absence of added dispersant or emulsifier, air being excluded during the grinding operation, the solid fuel being present in amount 15 to 55% by weight of the dispersion and being ground until the mean particle size of the solid fuel is reduced to a value in the range 1 to 15 micron.
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 to 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 the coal is added to the oil prior to mixing with the water.
12. A method according to any of claims 1 to 10 wherein the water is added to the oil prior to mixing with the coal.
13. A method according to any of the preceding claims wherein grinding is carried out in a ball mill.