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⑤④ **A process for making fuel slurries of coal in water and the product thereof.**

⑤⑦ A process for making fluid, stable slurries of finely divided coal in water, which can be sufficiently highly loaded to serve as fuel, comprises:

a) Admixing:

- (i) ultrafine coal particles having a maximum size of 10 μm MMD in an amount comprising from 10 to 30% by weight of the slurry,
- (ii) larger coal particles within the size range of from 20 to 200 μm MMD in an amount sufficient to provide a desired total coal concentration in the slurry,
- (iii) water, and,
- (iv) a minor amount of dispersant consisting essentially of an alkaline earth metal salt of an organosulfonate in which the organic moiety is multifunctional, and

b) subjecting the mixture to high shear at a rate of at least 100 sec^{-1} .

Preferably, calcium lignosulphonate is used as the dispersant and the pH is maintained in the range of 5 to 8 using an inorganic alkali metal buffer salt.

The slurry thus produced exhibits thixotropic or Bingham fluid-like properties enabling prolonged periods of storage with subsequent restoration of fluid characteristics to enable use as a fuel.

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A process for making fuel slurries of coal in water
and the product thereof.

This invention relates to the production of fuel slurries of coal in water which can be injected directly into a furnace as a combustible fuel. A high fuel value coal slurry can supplant large quantities of increasingly
5 expensive fuel oil presently being used by utilities, factories, ships and other commercial enterprises. Since the inert water vehicle reduces fuel value in terms of BTU/lb (J/kg) it is desirable to minimise its concentration and maximise coal concentration for efficient use of the
10 slurry as a fuel. A high coal content also improves the combustion characteristics of the slurry.

It is important, therefore, that the slurry be loadable with finely-divided coal in amounts as high, for example, as about 50% to 70% of the slurry. Despite such high solids
15 loading, the slurry must be sufficiently fluid to be pumped and sprayed into the furnace. The coal particles must also be uniformly dispersed. The fluidity and dispersion must be stably maintained during storage.

An object of this invention is to provide an improved
20 process for producing a slurry suitable for this purpose.

According to the present invention there is provided a process for making substantially stable coal-water slurries comprising:

a) Admixing:

- 25 (1) ultrafine coal particles having a maximum size of $10\mu\text{m}$ MMD in an amount comprising from 10 to 30% by weight of the slurry,
(ii) larger coal particles within the size range of from 20 to $200\mu\text{m}$ MMD in an amount sufficient to
30 provide a desired total coal concentration in the slurry,
(iii) water, and,

- (iv) a minor amount of dispersant consisting essentially of an alkaline earth metal salt of an organo-sulfonate in which the organic moiety is multi-functional, and
- 5 b) subjecting the mixture to high shear at a rate of at least 100 sec^{-1} .

This invention further provides a coal-water slurry which comprises:

- a) ultrafine coal particles having a maximum size of $10\mu\text{m}$ MMD,
10 in an amount comprising from 10 to 30% by weight of slurry;
- b) larger coal particles within the size range of from 20 to $200\mu\text{m}$ MMD in an amount sufficient to provide a desired total coal concentration in the slurry;
- 15 c) water; and
- d) a minor amount of a dispersant consisting essentially of an alkaline earth metal organo-sulfonate in which the organic moiety is multi-functional.

Thus fluid, pourable slurries comprising up to about
20 70% or higher of coal stably dispersed in water are produced by admixing finely-divided coal having a critical distribution of particle sizes, water, and an organic dispersant in a high shear rate mixer. An inorganic buffer salt may also be added. The term "fluid" as used in this specification and
25 claims means a slurry which is fluid and pourable both at rest and in motion or a slurry which gels or flocculates into a substantially non-pourable composition at rest and becomes pourably fluid with stirring or other application of relatively low shear stress.

30 Controlled distribution of coal particles sizes is essential for both fluidity and stability. The partial size mixture, necessary for fluidity of the highly loaded slurry, comprises ultrafine (UF) particles having a maximum size of up to about $10\mu\text{m}$ MMD (mass mean diameter), preferably about
35 $1\mu\text{m}$ to $8\mu\text{m}$ MMD and larger particles (F/C) having a size

range of about 20 μ m to 200 μ m MMD, preferably about 20 μ m to 150 μ m MMD. For stability of the slurry, the UF particles should comprise about 10 to 30% by weight of the slurry, preferably about 15 to 25%.

5 The actual degree of coal loading is not critical and will vary with the given use and operating equipment. The concentration of coal successfully incorporated into a given slurry varies with such factors as the relative amounts of UF and F/C particles, size of the F/C particles used within
10 the effective range, and the like. In general, percentage loading increases with increasing F/C size. An organic dispersant is essential to maintain the coal particles in stable dispersion. It has been found that the highly-loaded slurries are very sensitive to the particular type of
15 surfactant used, especially with respect to fluidity and storageability. The dispersants which have proven to be effective in producing stable fluid mixes are high molecular weight alkaline earth metal (e.g. Ca, Mg) organosulfonates in which the organic moiety is poly-functional. Molecular
20 weight of the organosulfonate is desirably about 1,000 to 25,000. The surfactant is used in minor amount, e.g. about 0.5 to 5 pph of coal, preferably about 1 to 2 pph.

In some cases, particularly at higher coal loadings, it has been found desirable to add an inorganic, alkali metal
25 (e.g. Na, K) buffer salt to stabilize pH of the slurry in the range of from pH 5 to 8, preferably from pH 6 to 7.5. The salt improves aging stability, pourability and handling characteristics of the slurry. It may be that the buffer counteracts potentially adverse effects of acid leachates
30 from the coal. The salt, such as sodium or potassium phosphate or carbonate, including their acid salts is used in minor amounts sufficient to provide the desired pH, e.g. about 0.1 to 2% based on the water. The inorganic salts also serve to reduce gaseous sulfur pollutants by forming
35 non-gaseous sulfur compounds.

The ultrafine and larger F/C coal particles, water, dispersant, and inorganic salt components are mixed in a blender or other mixing device which can deliver high shear rates. High shear mixing, e.g. at shear rates of at least about 100 sec^{-1} , preferably at least about 500 sec^{-1} , is essential for producing a stable slurry free from substantial sedimentation. The use of high shear mixing and the dispersant appears to have a synergistic effect. Dispersant with low shear mixing results in an extremely viscous, non-pourable slurry, while high shear mixing without dispersant produces a slurry which is unstable towards settling. With both dispersant and high shear mixing a fluid, pourable, stable slurry can be obtained.

The slurries are viscous, fluid dispersions which can generally be characterized as thixotropic or Bingham fluids having a yield point. In some cases, the slurries may gel or flocculate when at rest into a substantially non-pourable composition but are easily rendered fluid by stirring or other application of relatively low shear stress. They can be stored for considerable periods of time without excessive settling or sedimentation. The slurries can be employed as fuels by injection directly into a furnace previously brought up to ignition temperature of the slurry. The finely divided state of the coal particles improves combustion efficiency. Since the dispersants are organic compounds, they may be biodegraded with time. This can readily be prevented by addition of a small amount of biocides.

The ultrafine coal particles can be made in any suitable device, such as a ball mill or attritor, which is capable of very fine comminution. Preferably, though not essentially, the coal is milled with water so that the UF particles are in water slurry when introduced into the mixer. Some of the dispersant can be included, if desired, in the UF milling operation to improve flow and dispersion characteristics of the UF slurry.

The required larger size coal particles (20 μ m to 200 μ m) can be made from crushed coal in a comminuting device such as a hammermill equipped with a grate having appropriately sized openings. Excessively sized coal residue can be used
5 for making the UF particles.

The coal concentrations as used in the specification and in the following examples is on a dried coal basis which normally equals 98.5% by weight of bone-dried coal.

The 3.6 μ m MMD UF particles employed in Examples 3 - 8
10 were prepared in accordance with Example 1 and the UF particles were introduced in the form of the Example 1 aqueous slurry containing a portion of the dispersant. The total amount of dispersant given in the Examples includes the portion introduced in this way.

15 The 34 μ m MMD and 110 μ m MMD particles used in the Examples were prepared in accordance with Example 2.

Example 1

50% by wt. crushed coal, 1% calcium lignosulfonate (Marasperse C-21) and 49% water were ball milled for 2 hours.
20 The size of the resulting UF coal particles was 3.6 μ m MMD. The UF coal-water slurry was fluid and pourable.

Example 2

A. Crushed coal was comminuted in a hammermill at 3,450 RPM with a 27 HB grate. The particle size of the
25 product was 110 μ m MMD.

B. Crushed coal was comminuted in a hammermill at 13,800 RPM with a 10 HB grate. The particle size of the resulting product was 34 μ m MMD.

Example 3

30 A. 65% by wt. of coal comprising 55% 110 μ m MMD coal and 45% 3.6 μ m MMD coal, 1.3% Marasperse C-21 (calcium ligning sulfonate) and 33.7% water were mixed in a blender at 6,000 RPM at a shear rate of 1,000 sec⁻¹. The resulting slurry was a paint-like gel that set into a soft gel which was
35 easily stirred to a liquid. After 23 days, it exhibited no

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sedimentation and was easily restirrrable to a uniform dispersion having relatively low viscosity - 6.7p.

B. A mix was made identical to A except that 34 μ m MMD particles were substituted for the UF particles. The mix, though initially fluid was unstable. Within 3 days it separated, forming a large supernatant and a highly packed subsidence. It could not be remixed into a uniform, pourable dispersion.

Example 4

10 A. A 65% coal slurry comprising 15% 3.6 μ m MMD and 50% 34 μ m MMD particles by wt. of the slurry, 1.3% Marasperse C-21 and 33.7% water were mixed in a blender at 6000 RPM. The resulting product was an uniformly dispersed gel which after 12 days in storage exhibited no supernatant, subsidence or
15 sedimentation. The gel was non-pourable at rest and became a pourable fluid with stirring.

B. A mix was made identical to A except that the blender was run at a low shear rate of 60 RPM (10 sec⁻¹). The resulting slurry was unstable. Within 4 days it had
20 separated into liquid and aggregated sediment.

Example 5

A. A 65% coal slurry comprising 26% 3.6 μ m MMD particles and 39% 110 μ m MMD particles, 13% Marasperse C-21 and 33.7% water were mixed in a blender at 6,000 RPM. The resulting
25 product was a uniformly dispersed slurry which was fluid and pourable and after 10 days was still pourable and substantially free from subsidence or sedimentation.

B. A mix was made identical to A except that the blender was run at a low shear rate of 10 sec⁻¹. The
30 resulting slurry was unstable. Within 3 days, it had separated into supernatant and aggregated sediment.

Example 6

A 65% coal slurry was made identical to Example 3A except that no dispersant was added. The resulting product
35 had the consistency of a stiff grease.

Example 7

A. A 70% coal slurry comprising 45.5% 110 μ m MMD particles and 24.5% 3.6 μ m MMD particles, 1.4% Marasperse C-21, and 28.6% water solution buffered to pH 7 by 0.15% Na₂HPO₄ added in the blender was mixed at 6,000 RPM. The resulting slurry has an EOM viscosity of 1.48 Kp, is fluid and pourable. After 7 days in storage it exhibited no supernatant liquid, settling or aggregation.

10 B. A mix was made identical to A except that phosphate salt was not added. The resulting slurry set up into a stiff non-pourable mass within 3 days.

C. A mix identical to A, except that the buffer salt was added to the ballmill producing the UF particles, was run in a blender at the low shear rate of 60 RPM (10 sec⁻¹).
15 The slurry was unstable and within 5 days separated into supernatant and stiff aggregated sediment.

Example 8

A mix was made identical to Example 4A except that Na₂HPO₄ in amount providing buffered pH 7 was added in the
20 blender. The resulting slurry was fluid and pourable. Its viscosity was EOM-T-bar 0.92 Kp. It retained its stability and pourability during storage and after 12 days was free from separation.

Example 9

25 A. 30 wt.% of hammermilled coal fines (30 μ m MMD), 0.3% Marasperse C-21 (1 pph coal), and 69.7% water were milled in an attritor for 30 minutes. The resulting slurry was very fluid. The UF coal particle size was 3.88 μ m MMD.

B. A 65 wt. % coal slurry comprising 50 wt.% 34 μ m MMD
30 coal particles, 15 wt.%, 3.88 μ m MMD (using 50 wt.% of slurry from 9A supra), 2 pph on coal of Marasperse C-21, and the remainder water, was mixed in a blender at a shear rate of 6,000 RPM (1000 sec⁻¹). The product was a uniformly-dispersed, pourable slurry. After 56 days the slurry was a stable, soft,
35 non-pourable gel free from settling or sedimentation. There

was a very slight supernatant. Probably caused by water evaporation and condensation on the surface. The thixotropic gel became easily pourable with slight stirring. At rest it returned to a stable non-pourable state within a short time.

- 5 After 61 days it retained its stable characteristics after several stirrings to pourability.

C. A slurry similar to 9B was prepared except that the mix was buffered to pH 7 by the addition of Na_2HPO_4 . The product was a uniformly-dispersed fluid slurry of relatively
 10 low viscosity. After 55 days the slurry was a weak, non-pourable gel free from settling or sedimentation. As in 9B there was a very slight supernatant. With slight stirring, it became very fluid and pourable. It was still stable and pourable after 24 hours and, although somewhat more viscous,
 15 retained its stability and pourability 5 days after the initial stirring.

Example 3 demonstrates the need for the UF particles in controlled size distribution to impart stability. Examples 4 and 5 show the need for high shear rate mixing.
 20 Example 6 shows the importance of the dispersant. Example 7 illustrates the improvement made in a highly-loaded 70% slurry by use of an inorganic buffer salt and the adverse effect of low shear mixing. Example 8 shows that the use of the pH buffer salt maintained the slurry in a stable fluid
 25 condition. Example 9 shows that the buffer salt improved aging and its user and handling characteristics.

The stable, fluid coal-water slurries are efficient and considerably lower cost alternatives to fuel oil. Their flame temperatures and heating values compare very favorably
 30 with fuel oil, as is shown in the following Tables:

TABLE I

ADIABATIC FLAME TEMPERATURE AT 20% EXCESS AIR

(in a typical furnace)

No. 6 Fuel Oil	3095°F
35 70% coal-water slurry	3089°F
65% coal-water slurry	3028°F

TABLE IIHEATING VALUE IN BTU/lb OF COMBUSTION PRODUCTS

	No. 6 fuel oil	991.0
	70% coal-water slurry	983.3
5	65% coal-water slurry	975.5

The cost of the coal-water slurries including processing is about 1/2 that of No. 6 fuel oil at present prices.

TABLE IIICOST PER MILLION BTU

10	No. 6 fuel oil	\$4.94
	70% coal-water slurry	\$2.24
	65% coal-water slurry	\$2.34

Claims:

1. A process for making substantially stable coal-water slurries comprising:

a) Admixing:

- (i) ultrafine coal particles having a maximum size of $10\mu\text{m}$ MMD in an amount comprising from 10 to 30% by weight of the slurry,
- (ii) larger coal particles within the size range of from 20 to $200\mu\text{m}$ MMD in an amount sufficient to provide a desired total coal concentration in the slurry,
- (iii) water, and,
- (iv) a minor amount of dispersant consisting essentially of an alkaline earth metal salt of an organo-sulfonate in which the organic moiety is multi-functional, and

b) subjecting the mixture to high shear at a rate of at least 100 sec^{-1} .

2. A process according to claim 1, in which an inorganic alkali metal buffer salt is added to maintain pH in the range of from 5 to 8.

3. A process according to claim 2, in which the buffer salt is an alkali metal phosphate.

4. A process according to any one of claims 1, 2 or 3 in which:

- a) The ultrafine particles are within the size range of from 2 to $8\mu\text{m}$ MMD and comprise from 15 to 25% by wt. of the slurry; and
- b) the larger coal particles are within a size range of from 20 to $150\mu\text{m}$ MMD.

5. A process according to any one of claims 1 to 4 in which the dispersant is calcium lignosulfonate.

6. A process according to any one of claims 1 to 5 in which the minimum shear rate is 500 sec^{-1} .
7. A process according to any one of claims 1 to 6 in which the ultrafine particles are produced in the presence of water and at least a portion of the dispersant.
8. A coal-water slurry which comprises:
 - a) ultrafine coal particles having a maximum size of $10\mu\text{m}$ MMD, in an amount comprising from 10 to 30% by weight of slurry;
 - b) larger coal particles within the size range of from 20 to $200\mu\text{m}$ MMD in an amount sufficient to provide a desired total coal concentration in the slurry;
 - c) water; and
 - d) a minor amount of a dispersant consisting essentially of an alkaline earth metal organo-sulfonate in which the organic moiety is multi-functional.
9. A slurry according to claim 8 in which:
 - a) the ultrafine particles are within a size range of from 1 to $8\mu\text{m}$ MMD, and,
 - b) the larger particles are within the size range of from 20 to $150\mu\text{m}$ MMD.
10. A slurry according to claim 8 or 9 in which the dispersant is calcium lignosulfonate.
11. A slurry according to any one of claims 8 to 10 which is buffered to a pH of from 5 to 8 by means of an inorganic alkali metal buffer salt.
12. A slurry according to any one of claims 8 to 11 in which the buffer salt is an alkali metal phosphate.
13. A slurry according to any one of claims 1 to 12 in which the slurry is a substantially thixotropic or Bingham fluid.