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(54) **Aqueous slurry of coal and related preparation processes.**

(57) An aqueous slurry of coal is disclosed, together with the related processes for producing it, said aqueous coal slurry having a concentration comprised within the range of from 60 to 80% by weight and containing a polyelectrolyte selected from the monovalent cation salts of polymerized naphthalenesulphonic acids, the characteristic of such a slurry consisting in that on the surface of coal, constituted by particles with a granulometry not greater than 300 μm, a heavy liquid is present, which is obtained by means of the distillation of pit coal tar, or a fuel oil deriving from mineral oil, in an amount comprised within the range of from 0.1 to 2% by weight relatively to same coal.

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"AQUEOUS SLURRY OF COAL AND RELATED PREPARATION PROCESSES"

The present invention relates to an aqueous slurry and to the related preparation processes.

Several processes are known for producing aqueous slurries of coal.

In patent application DE-28 23 568, a process is disclosed for the preparation of an aqueous coal slurry, which comprises a grinding of coal to a size smaller than 100 μm, a beneficiation of ground coal by using an alkaline ammonium polycarboxylic salt endowed with the property of charging the prevailingly organic portion of coal with a higher charge than that of the inorganic portion, a settling, so as to separate, according to as stated in said patent application, said portions, and finally a slurrying of coal, separated from the inorganics, in water. The most striking disadvantages are due both to the fact that coal must be ground to a very fine size, and to the fact that the separation of coal from the inorganic matter results very difficult, in as much as a sharp boundary line between the two phases does not exist.

In BE-893,247 patent, an aqueous coal slurry is disclosed, which contains two separate groups of coal particles, wherein the particles of the first group have an average size comprised within the range of from 210 to 60 μm, the maximum size being not greater than 300 μm, and the particles of the second group have a size comprised within the range of from 1/6th to 1/20th of those of the first group.

In this patent, the slurry is only obtained with non-beneficiated coals.

We have surprisingly found that overcoming the drawbacks of the prior art is possible by using a heavy liquid obtained from the distillation of pit-coal tar, or a fuel oil deriving from mineral oil.

One of the advantages due to the use of either of the two above-mentioned liquids consists in that the coal surfaces are given a higher affinity for the dispersant additive used for the formulation of the aqueous slurry, with the efficaciousness of this latter being boasted, and the amount thereof being considerably reduced.

A first object of the present invention is an aqueous coal slurry at a concentration comprised within the range of from 60% to 80% by weight, comprising a polyelectrolyte selected from the monovalent cation salts of the polymerized naphthalenesulphonic acids having a molecular weight comprised within the range of from 800 to 3,000, preferably around 2,000, characterized in that on coal surface, which coal is constituted by particles having a granulometry not greater than 300 μm, a liquid which is obtained by the distillation of pit-coal tar, or a fuel oil derived from mineral oil, is present, in an amount comprised within the range of from 0.1% to 2%, preferably of from 0.2% to 1.2%, by weight, relatively to same coal.

The presence of either of said liquids on coal surface renders uniform the surface chemical-physical characteristics of different coals, thus rendering efficacious the used dispersant towards coals of even different origin.

The liquid obtained from the distillation of pit-coal tar is preferably selected from those having a distillation range comprised within 200 and 400°C, more preferably between 250 and 350°C.

For example, creosote oil can be used.

Hereunder to informative purposes a typical composition is reported for creosote oil, as relates to some more characteristic components:

Naphthalene	10	% by weight
Methyl-naphthalene	5-7	% by weight
Dimethyl-naphthalene	5-7	% by weight
Acenaphthene	8	% by weight
Diphenyl	1-2	% by weight
Diphenyl-oxide	4	% by weight
Fluorene	8	% by weight
Phenanthrene	15-20	% by weight
Anthracene	1	% by weight
Carbazole	2	% by weight
Nitrogenous bases	2-25	% by weight
Higher phenols	2-15	% by weight

The fuel oil deriving from mineral oil is selected from those having a viscosity at 50° preferably not lower than 3°E.

Coal can be constituted by one single group of particles, or by two particle groups.

In case of two particle groups, the first group may contain particles having an average granulometry comprised within the range of from 210 to 60 μm, the maximum size being however not greater than 300 μm; the second group can contain particles having an average granulometry comprised within the range of from 1/6th to 1/20th of the average granulometry of the particles of the first group, by "average granulometry of the particles" the granulometry corresponding to 50% of the cumulative mass distribution of that group being meant.

The particles of the first group should preferably be at least 40% of total, more preferably at least 60% by weight of total particles.

The cumulative particle distribution curve, by resulting from two fractions (i.e., two distinct groups of coal particles), should show, if reported on a bilogarithmic scale (log-log chart), a flat zone comprised between the values of the average dimensions of component fractions; wherein by "flat zone" a length of the curve is meant, wherein the derivative, computed on a bilogarithmic scale (log-log chart), is lower than 0.4, and preferably lower than or equal to 0.1, and still more preferably equals zero.

The cumulative granulometric distribution should hence be such that always two particle size values d_1 and d_2, comprised between the average values of the diameters of the two fractions exist, for which the numeric value of the following expression

$$\frac{\log(\%CM1) - \log(\%CM2)}{\log d_1 - \log d_2}$$

is lower than 0.4, preferably lower than or equal to 0.1, and, still more preferably, equals 0.

By "(%CM1)" and "(%CM2)" the values are indicated of the cumulative percentages of the mass of particles, respectively having a size lower than d_1 and d_2.

The numerical value of the expression is, obviously, independent from the unit of measure (micrometres or millimetres) according to which the particle size is expressed.

When preparing a slurry is desired, from a coal previously submitted to a beneficiation by agglomeration, the addition of the liquid obtained by means of distillation of pit-coal tar is carried out during the same beneficiation treatment, by performing such a treatment in the presence of a light hydrocarbon of from 4 to 8, preferably from 5 to 6, carbon atoms, said hydrocarbon being flashed off after the agglomeration.

Among the preferred hydrocarbons, we mention here n-pentane and n-hexane.

The Light hydrocarbon is preferably present in a percentage comprised within the range of from 5% to 30% by weight relatively to coal.

A second object of the present invention is the process for preparation of the aqueous coal slurries.

In case coal must also be beneficiated, the process comprises a beneficiation by agglomeration in water of a coal having a granulometry not higher than 300 μm with a liquid obtained by means of the distillation of pit-coal tar, or with a fuel oil deriving from mineral oil, in an amount comprised within the range of from 0.2% to 2% by weight relatively to coal, and a light hydrocarbon comprising a number of carbon atoms comprised within the range of from 4 to 8, in an amoung ranging from 5% to 30% by weight relatively to coal, the flashing of the light hydrocarbon, after that the prevailingly organic portion has agglomerated and separated from the aqueous solution in which the inorganic components have remained suspended or dissolved, and, finally, the slurrying in an aqueous solution comprising a polyelectrolyte, as the dispersant, selected from the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800 to 3,000, preferably around 2,000, the percent amount of the dispersant being comprised within the range of from 0.05 to 0.5% by weight relatively to the weight of the slurry.

Among said polyelectrolytes there can be used, e.g., the chemical compounds known under the tradename of DAXAD 15 and DAXAD 19 by W.R. Grace, and Reoplast 203 by Fratelli Lamberti S.p.A.

On the contrary, in case coal has not to be beneficiated, the process comprises the slurrying of a coal having a granulometry not greater than 300 μm, in a solution containing a liquid obtained by means of the distillation of pit-coal tar, or a fuel oil deriving from mineral oil, in an amount comprised between 0,2% and 2% by weight relative to coal, and a light hydrocarbon liquid comprising a number of carbon atoms comprised within the range of from 4 to 8, in an amount comprised within the range of from 50% to 200% by weight relatively to coal, followed by the flashing of the light hydrocarbon and by the formation of an aqueous slurry by means of the addition of a dispersant constituted by a polyelectrolite selected from the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800 to 3,000, preferably around 2,000, the percent amount of the dispersant being comprised within the range of from 0.05% to 0.5% by weight relatively to the weight of the slurry.

As relates to the preferred granulometries, the preferred liquids obtained from the distillation of pit-coal tar, the preferred fuel oils deriving from mineral oil, the preferred light oils, and the preferred polyelectrolytes, what above said for the aqueous slurries holds true as well.

The following Examples are supplied to the purpose of illustrating the invention, which however is not to be considered as being limited to them or by them.

Examples 1-4

A American bituminous coal (Pittsburgh Nr. 8) was dry-ground; it had the following analytical characteristics:

Immediate Analysis

Intrinsic Moisture	% w	1.19
Volatile Matter	% dry w	37.10
Ashes	% dry w	7.56
Fixed C (by difference)	% dry w	55.34

End Analysis

Carbon	% dry w	76.93
Hydrogen	% dry w	5.25
Nitrogen	% dry w	1.66
Sulphur	% dry w	1.63
Ashes	% dry w	7.56
Oxygen (by difference)	% dry w	6.97

Heat Value

Gross Heat Value	kcal/kg	7,627
Net Heat Value	kcal/kg	7,356

After the grinding, the end granulometry results to be the following:

Passing Through	% of Cumulative Weight
150 µm	99.3
74 µm	87.0
53 µm	61.9
44 µm	36.5

The coal having this granulometry was used for preparing the slurries after being coated with a creosote oil film.

The coating by the creosote oil was achieved by diluting this latter oil in n-hexane, subsequenty adding coal, under stirring, and finally flashing off the solvent.

The amount of creosote oil added to coal was 0.5% by weight based on dry coal, and the amount of n-hexane was 100% by weight.

With the used granulometry, samples were then prepared and analysed of water-coal slurries, with a solids concentration of 62% by weight, to which 0.2% 0.3% and 0.5% by weight of DAXAD 15, relatively to the suspension, was added.

The blend was characterized in terms of its apparent viscosity at 50 sec^{-1}.

The results of these measurements are reported in Table 1.

Examples 5-8 (Comparison Examples)

The same American coal (Pittsburgh Nr. 8), with the same granulometry as obtained in the foregoing Examples, was used without any creosote oil for preparing slurry samples to which respectively 0.2% (Example 5), 0.3% (Example 6), 0.4% (Example 7) and 0.5% (Example 8) of DAXAD 15 by weight was added.

The results are reported in Table 1 as well.

By comparing these results with the previous ones, it can be see from Table 1 how considerable is the effect of the treatment with creosote oil on apparent viscosity values.

Above all for low additive levels, the reduction in viscosity is very evident (50-60% at DAXAD 15 concentrations of 0.2-0.3% by weight).

The viscosity value observed at 0.2% of dispersant additive for creosote-treated coal as such is even lower than that obtained with non-treated coal with 0.5% of additive.

Example 9-11

A Polish coal, having the following analytical characteristics:

Immediate Analysis

Intrinsic Moisture	% w	1.60
Volatile Matter	% dry w	32.80
Ashes	% dry w	9.40
Fixed C (by difference)	% dry w	57.80

End Analysis

Carbon	% dry w	73.80
Hydrogen	% dry w	4.24
Nitrogen	% dry w	1.44
Sulphur	% dry w	0.86
Ashes	% dry w	9.40
Oxygen (by difference)	% dry w	10.26

Heat Value

Gross Heat Value	kcal/kg	7,167
Net Heat Value	kcal/kg	6,948

was partly dry-ground to the following end granulometry:

Passing Through	Weight %
250 µm	98.8
150 µm	82.0
125 µm	52.2

74 μm	20.2
44 μm	2.7

and the residual portion was micronized by wet-grinding by a laboratory micronizer, to an end granulometric distribution having an average value (d_{50}) of 6.5 μm.

With this granulometric distribution, obtaining a 66% concentration of coal in the slurry was possible.

The coal with the above described granulometry underwent a beneficiation treatment by selective agglomeration with n-pentane and creosote oil. Used amount of creosote oil equalled 0.5% by weight relatively to coal.

The beneficiation step was carried out on a batch equipment having a capacity of 10 litres of slurry, on a coal slurry in water at 20% of solids by weight, by using a concentration of n-hexane of 20% relatively to dry coal.

The results of the beneficiation treatment are reported in Table 2.

At the end of the agglomeration treatment, n-pentane was removed by drying under N_2 in oven at 40°C.

With the beneficiated product, according to the above disclosed modalities, samples were then prepared and analysed of coal-water slurries with solids concentration of 66% by weight and to which 0.2%, 0.3% amd 0.5% of weight of DAXAD relatively to the suspension was added.

The results of the rheological measurements are reported in Table 3.

Examples 12-14 (Comparison Examples)

The same Polish coal of Examples 9-11, with the same bimodal granulometry was beneficiated with n-pentane alone, without using any creosote oil, in the same equipment and with the same modalities as of the above Examples.

The results of the beneficiation treatment are shown in Table 2.

As it can be observed from Table 2, the presence of creosote oil in the agglomeration step led to an increase in yield, with the product quality being the same (from 85.8% to 90.7% by weight), i.e., an increase of 5 percent points in energy recovery (from 90.9% to 96.0%).

Furthermore, the induction times of the agglomeration phenomenon, i.e., the times necessary for agglomeration to begin, resulted sharply shorter: from the 15-minute time of the test with n-pentane only, a decrease to the 8-minute time of the test with n-pentane plus creosote oil as the agglomerating agent were obtained, with obvious advantages from the viewpoint of process economy.

At the end of the agglomeration process, n-pentane was removed by oven-drying under N_2 at 40°C.

With the beneficiated product, samples were then prepared and analysed of coal-water slurries with a solids concentration of 66% by weight, and to which 0.2% (Example 12), 0.3% (Example 13) and 0.4% (Example 14) by weight of DAXAD 15, based on slurry was added.

The results of the rheological measurements are reported in Table 3.

It can be observed from Table 3 that the slurries obtained with beneficiated coal plus pentane plus creosote oil show a lower viscosity than those obtained from coal beneficiated with pentane only.

Examples 15-17 (Comparison Examples)

The same Polish coal as of Example 9-11, with the same bimodal granulometry, not beneficiated, and without creosote oil, was used to prepare slurries to which 0.2% (Example 15), 0.3% (Example 16) and 0.5% by weight (Example 17) of DAXAD had been added.

With 0.2% of DAXAD 15, no fluid slurry was obtained, whilst with 0.3% and 0.5% by weight of DAXAD 15 the suspensions were obtained, the viscosities of which are reported in Table 3.

Always from Table 3, it can be observed that the viscosities are considerably higher than the preceding values.

TABLE 1

Examples	1	2	3	4	5	6	7	8
DAXAD %	0.2	0.3	0.4	0.5	0.2	0.3	0.4	0.5
Viscosity (cP)	996	710	745	740	2045	1754	1283	1174
Coal %	62	62	62	62	62	62	62	62

TABLE 2

Example	Yield, % by weight	Ashes, % by weight	Induction time
9-11	90.7	5.0	8 minutes
12	85.8	5.0	15 minutes

TABLE 3

Examples	9	10	11	12	13	14	15	16	17
DAXAD %	0.2	0.3	0.5	0.2	0.3	0.5	0.2	0.3	0.5
Viscosity (cP)	569	496	412	905	713	532	-	1889	1336
Coal %	66	66	66	66	66	66	-	66	66

Claims

1. Aqueous coal slurry at a concentration comprised within the range of from 60% to 80% by weight, comprising a polyelectrolyte selected from the monovalent cation salts of the polymerized naphthalenesulphonic acids having a molecular weight comprised within the range of from 800 to 3,000, preferably around 2,000, characterized in that on the surface of coal, which is constituted by particles having a granulometry not greater than 300 μm, a liquid, which is obtained by the distillation of pit-coal tar, or a fuel oil derived from mineral oil, is present in an amount comprised within the range of from 0.1% to 2% by weight, relatively to same coal.

2. Aqueous coal slurry according to claim 1, wherein the liquid obtained by means of pit-coal tar distillation, or the fuel oil derived from mineral oil is in an amount comprised within the range of from 0.2% to 1.2% by weight relatively to coal.

3. Aqueous coal slurry according to clam 1, wherein the liquid obtained by means of the pit-coal distillation has a distillation range comprised between 200 and 400°C.

4. Aqueous coal slurry according to claim 3, wherein the liquid obtained by means of the pit-coal tar distillation has a distillation range comprised between 250°C and 350°C.

5. Aqueous coal slurry according to claim 4, wherein the liquid obtained by means of the pit-coal tar distillation is creosote oil.

6. Aqueous coal slurry according to claim 1, wherein the fuel oil derived from mineral oil has a viscosity at 50°C not lower than 3°E.

7. Aqueous coal slurry of coal according to claim 1, wherein coal is constituted by two groups of particles, wherein the particles of the first group have average granulometries comprised within the range of from 210 to 60 μm, with their largest dimensions not exceeding 300 μm, and those of the second group have average granulometries comprised within the range of from 1/6th to 1/20th of those of the first group.

8. Aqueous coal slurry according to claim 1, wherein the liquid obtained by means of the pit-coal tar distillation is added during the beneficiation of coal by agglomeration carried out in the presence of a light hydrocarbon containing a number of carbon atoms comprised within the range of from 4 to 8, said hydrocarbon being flashed off after the agglomeration.

9. Aqueous coal slurry according to claim 8, wherein the light hydrocarbon contains a number of carbon atoms comprised within the range of from 5 to 6.

10. Aqueous coal slurry according to claim 9, wherein the light hydrocarbon is n-pentane.

11. Aqueous coal slurry according to claim 9, wherein the light hydrocarbon is n-hexane.

12. Aqueous coal slurry according to claim 8, wherein the light hydrocarbon for carrying out the beneficiation by agglomeration is present in a percentage comprised within the range of from 5 to 30% by weight relatively to coal.

13. Process for preparing an aqueous coal slurry according to one or more of the preceding claims, comprising a beneficiation by agglomeration in water of a coal having a granulometry not greater than 300 μm with a liquid obtained by the distillation of pit-coal tar, in an amount comprised within the range of from 0.1 to 2% by weight relatively to coal, and a light hydrocarbon containing a number of carbon atoms comprised within the range of from 4 to 8, in an amount ranging from 5 to 30% by weight relatively to coal, the flashing of the light hydrocarbon, after that the prevailingly organic portion has agglomerated and separated from the aqueous solution in which the inorganic components have remained suspended or dissolved, characterized in that the beneficiated coal is dispersed in an aqueous solution comprising a polyelectrolyte, as the dispersant agent, selected from the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800 to 3,000, preferably around 2,000, the percent amount of the dispersant being comprised within the range of from 0.05 to 0.5% by weight relatively to the weight of the slurry.

14. Process for preparing an aqueous coal slurry according to one or more of the preceding claims, characterized in that it comprises the slurrying of a coal having a granulometry not greater than 300 μm, in a solution containing a liquid obtained by the distillation of pit-coal tar, in an amount comprised within the range of from 0.1 to 2% by weight relatively to coal, and a light hydrocarbon liquid comprising a number of carbon atoms comprised within the range of from 4 to 8, in an amount comprised within the range of from 50 to 200% by weight relatively to coal, followed by the flashing of the light hydrocarbon and by the formation of an aqueous slurry by means of the addition of a dispersant constituted by a polyelectrolyte selected from among the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800 to 3,000, preferably around 2,000, the percent amount of the dispersant being comprised within the range of from 0.05% to 0.5% by weight relatively to the weight of the slurry.