

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



11 Publication number:

**0 244 902 B1**

12

### EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: **19.06.91** 51 Int. Cl.<sup>5</sup>: **C10L 1/32**

21 Application number: **87200771.1**

22 Date of filing: **23.04.87**

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

30 Priority: **02.05.86 IT 2029586**

43 Date of publication of application:  
**11.11.87 Bulletin 87/46**

45 Publication of the grant of the patent:  
**19.06.91 Bulletin 91/25**

84 Designated Contracting States:  
**AT BE CH DE ES FR GB GR LI LU NL SE**

56 References cited:  
**BE-A- 893 247**  
**DE-C- 822 032**

73 Proprietor: **ENIRICERCHE S.p.A.**  
**Corso Venezia 16**  
**I-20121 Milan(IT)**

72 Inventor: **Meli, Salvatore**  
**Via Mazzarello 2**  
**I-20067 Paullo Milan(IT)**  
Inventor: **Passarini, Nello**  
**Via Moro 3**  
**I-20060 Colturano Milan(IT)**  
Inventor: **Vettor, Antonio**  
**Via Gramsci 47/A**  
**I-20097 San Donato Milanese Milan(IT)**

74 Representative: **Roggero, Sergio et al**  
**Ing. Barzanò & Zanardo Milano S.p.A. Via**  
**Borgonuovo 10**  
**I-20121 Milano(IT)**

**EP 0 244 902 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**Description**

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

Several processes are known for producing aqueous slurries of coal.

5 In DE-A-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  $\mu\text{m}$ , a beneficiation of ground coal by using an alkaline ammonium polycarboxylic salt endowed with the property of charging the prevailing 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 slurring of coal, separated  
10 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-A-893,247, 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  
15 210 to 60  $\mu\text{m}$ , the maximum size being not greater than 300  $\mu\text{m}$ , 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.

20 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  
25 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 grain size not greater than 300  $\mu\text{m}$ , 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  
30 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  
35 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:

40

45

50

55

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

The fuel oil deriving from mineral oil is selected from those having a Kinematic viscosity at 50°  
 25 preferably not lower than  $21,2 \cdot 10^{-6} \text{ m}^2/\text{s}$  (3° Engler).

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 grain size  
 comprised within the range of from 210 to 60  $\mu\text{m}$ , the maximum size being however not greater than 300  
 30  $\mu\text{m}$ ; the second group can contain particles having an average grain size comprised within the range of  
 from 1/6th to 1/20th of the average grain size of the particles of the first group, by "average grain size of  
 the particles" the grain size 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.

35 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.

40 The cumulative grain size 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

$$45 \quad \frac{\log(\%CM1) - \log(\%CM2)}{\log d_1 - \log d_2}$$

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

50 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.

55 When preparing a slurry is desired, from a coal previously submitted to a beneficiation by agglomer-  
 ation, 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  
5 water of a coal having a grain size not higher than 300  $\mu\text{m}$  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 amount ranging from 5% to 30% by weight relatively to coal, the flashing of the light hydrocarbon, after that the prevailing organic portion has agglomerated and  
10 separated from the aqueous solution in which the inorganic components have remained suspended or dissolved, and, finally, the slurring 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.

15 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 slurring of a coal having a grain size not greater than 300  $\mu\text{m}$ , 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  
20 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 polyelectrolyte selected from the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800  
25 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 grain sizes, 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.

30 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

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

40

45

50

55

Immediate Analysis

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

10 End Analysis

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

Heat Value

25	Gross Heat Value	31932 kJ (kcal/kg	7,627)
	Net Heat Value	30798 kJ (kcal/kg	7,356)

After the grinding, the end grain size results to be the following:

30	<u>Passing Through</u>	<u>% of Cumulative Weight</u>
	150 $\mu$ m	99.3
35	74 $\mu$ m	87.0
	53 $\mu$ m	61.9
40	44 $\mu$ m	36.5

45 The coal having this grain size 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, subsequently 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.

50 With the used grain size 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<sup>-1</sup>.

The results of these measurements are reported in Table 1.

55 Examples 5-8 (Comparison Examples)

The same American coal (Pittsburgh Nr. 8), with the same grain size 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.

5 By comparing these results with the previous ones, it can be seen 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).

10 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.

A Polish coal, having the following analytical characteristics:

15

Immediate Analysis

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

25

End Analysis

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

Heat Value

Gross Heat Value	30006KJ (kcal/kg	7,167)
40 Net Heat Value	29089KJ kcal/kg	6,948

Example 9-11 was partly dry-ground to the following end grain size:

45

<u>Passing Through</u>	<u>Weight %</u>
250 $\mu$ m	98.8
50 150 $\mu$ m	82.0
125 $\mu$ m	52.2
55 74 $\mu$ m	20.2
44 $\mu$ m	2.7

and the residual portion was micronized by wet-grinding by a laboratory micronizer, to an end grain size distribution having an average value ( $d_{50}$ ) of 6.5  $\mu\text{m}$ .

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

The coal with the above described grain size underwent a beneficiation treatment by selective  
5 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.

10 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  $\text{N}_2$  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%,  
15 0.3% and 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)

20 The same Polish coal of Examples 9-11, with the same bimodal grain size 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  
25 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  
30 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  $\text{N}_2$  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.

35 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)

40 The same Polish coal as of Example 9-11, with the same bimodal grain size, 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  
45 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.

50

55

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, dynamic $Ns/m^2$	0,996	0,710	0,745	0,740	2,045	1,754	1,283	1,174
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 $Ns/m^2$	0,569	0,496	0,412	0,905	0,713	0,532	-	1,889	1,336
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 grain size not greater than 300  $\mu m$ , 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 claim 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 Kinematic viscosity at 50% not lower than  $21,2 \cdot 10^{-6} m^2/s$  (3° Engler).
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 grain sizes comprised within the range of from 210 to 60  $\mu\text{m}$ , with their largest dimensions not exceeding 300  $\mu\text{m}$ , and those of the second group have average grain sizes comprised within the range of from 1/6th to 1/20th of those of the first group.

- 5 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.
- 10 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.
- 15 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.
- 20 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 grain size not greater than 300  $\mu\text{m}$  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 prevailing 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.
- 25 30 35 40 45
14. Process for preparing an aqueous coal slurry according to one or more of Claims 1 to 12 characterized in that it comprises the slurring of a coal having a grain size not greater than 300  $\mu\text{m}$ , 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.

Claims for the following Contracting States: AT, ES

- 50 55
1. Process for preparing an aqueous coal slurry containing from 60% to 80% by weight of coal and a monovalent cation salt of a polymerized naphthalenesulphonic acid as the dispersant polyelectrolyte, characterized in that it comprises the steps of slurring a coal having a grain size not greater than 300  $\mu\text{m}$  in an aqueous phase containing from 0,1% to 2% by weight relative to coal of a liquid obtained from the distillation of of pit-coal tar, and an amount of from 50% to 200% by weight relative to coal of a light liquid hydrocarbon having from 4 to 8 carbon atoms, flashing the light hydrocarbon and adding to the resultant slurry from 0,05% to 0,5% by weight relative to the weight of the slurry, of a polyelectrolyte selected from the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800 to 3.000, preferably about 2.000.
2. Process for preparing an aqueous coal slurry containing from 60% to 80% by weight of coal and a

monovalent cation salt of a polymerized naphthalenesulphonic acid as the dispersant polyelectrolyte, characterized in that it comprises the steps of beneficiating, by agglomeration in water, a coal having a grain size not greater than 300  $\mu\text{m}$  with an amount of from 0,1% to 2% by weight relative to coal of a liquid obtained from the distillation of pit-coal tar and an amount of from 5% to 30% by weigh relative to coal of a light liquid hydrocarbon having from 4 to 8 carbon atoms , flashing the light liquid hydrocarbon after that the prevailingly organic portion has agglomerated and separated from the aqueous phase in which the inorganic components remained suspended or dissolved, and dispersing the beneficiated coal in an aqueous solution of a dispersant polyelectrolyte selected from the monovalent cation salts of polymerized naphthalenesulphonic acids having a molecular weight of from 800 to 3.000, preferably about 2.000, the amount of said dispersant polyelectrolyte being from 0,05% to 0,5% by weight relative to the weight of the slurry.

3. Process according to claim 1 or 2, characterized in that a liquid obtained from the distillation of pit-coal tar, or a fuel oil derived from a mineral oil is present on the surface of the coal.
4. Process according to claim 1 or 2, characterized in that the liquid obtained from pit-coal distillation, or the fuel oil derived from a mineral oil, is present in an amount of from 0,2% to 1,2% relative to the coal.
5. Process according to claim 1 or 2, characterized in that the liquid obtained from pit-coal distillation has a distillation range of from 200° to 400° C.
6. Process according to claim 5, characterized in that the liquid obtained from pit-coal distillation has a distillation range of from 250° C to 350° C.
7. Process according to claim 6, characterized in that the liquid obtained from pit-coal tar distillation is creosote oil.
8. Process according to claim 1 or 3, characterized in that the fuel oil derived from mineral oil has a kinematic viscosity at 50° C not lower than  $21,2 \cdot 10^{-6} \text{ m}^2/\text{s}$  (3° Engler).
9. Process according to claim 1 or 2, characterized in that said coal consists of two group of particles, the particles of the first group have an average grain size of from 210  $\mu\text{m}$  to 60  $\mu\text{m}$ , their largest dimension not exceeding 300  $\mu\text{m}$ , and in that the particles of the second group have an average grain size of from one sixth to one twentieth of the grain size of said first group of particles
10. Process according to claim 1 or 2, characterized in that said light liquid hydrocarbon has 5 or 6 carbon atoms.
11. Process according to claim 10, characterized in that the light liquid hydrocarbon is n-pentane.
12. Process according to claim 10, characterized in that the light liquid hydrocarbon is n-hexane.
13. Process according to claim 2, characterized in that the light liquid hydrocarbpn used for carrying out the coal beneficiation by agglomeration is present in an amount of from 5% to 30% by weight relative to coal.

#### Revendications

1. Bouillie aqueuse de charbon, ayant une concentration en charbon comprise dans l'intervalle allant de 60 % à 80 % en poids, contenant un polyélectrolyte choisi parmi les sels de cation monovalent des acides naphthalène-sulfoniques polymérisés ayant une masse moléculaire comprise dans l'intervalle allant de 800 à 3000, de préférence d'environ 2000, **caractérisée** en ce que, sur la surface du charbon qui est constitué de particules ayant une taille de grain non supérieure à 300  $\mu\text{m}$ , est présent, en une proportion comprise entre 0,1 % et 2 % en poids par rapport audit charbon, un liquide qui est obtenu par la distillation du goudron de houille, ou une huile combustible issue du pétrole.
2. Bouillie aqueuse de charbon selon la revendication 1, dans laquelle le liquide obtenu par distillation du goudron de houille ou l'huile combustible issue du pétrole est présent en une proportion comprise

entre 0,2 % et 1,2 % en poids par rapport au charbon.

3. Bouillie aqueuse de charbon selon la revendication 1, dans laquelle le liquide obtenu par distillation du goudron de houille présente un intervalle de distillation compris entre 200 et 400 ° C.
- 5 4. Bouillie aqueuse de charbon selon la revendication 3, dans laquelle le liquide obtenu par distillation du goudron de houille présente un intervalle de distillation compris entre 250 ° C et 350 ° C.
5. Bouillie aqueuse de charbon selon la revendication 4, dans laquelle le liquide obtenu par distillation du goudron de houille est une huile de crésote.
- 10 6. Bouillie aqueuse de charbon selon la revendication 1, dans laquelle l'huile combustible issue du pétrole présente une viscosité cinématique à 50 ° C non-inférieure à  $21,2 \cdot 10^{-6} \text{ m}^2/\text{s}$  (3 ° Engler).
- 15 7. Bouillie aqueuse de charbon selon la revendication 1, dans laquelle le charbon est constitué de deux groupes de particules, les particules du premier groupe ayant une taille de grain moyenne comprise dans l'intervalle allant de 210 à 60  $\mu\text{m}$ , leur taille maximum ne dépassant pas 300  $\mu\text{m}$ , et les particules du second groupe ayant une taille de grain moyenne comprise entre 1/6<sup>ème</sup> et 1/20<sup>ème</sup> de la taille de grain moyenne des particules du premier groupe.
- 20 8. Bouillie aqueuse de charbon selon la revendication 1, pour laquelle le liquide obtenu par distillation du goudron de houille est ajouté durant l'enrichissement du charbon par agglomération, effectuée en présence d'un hydrocarbure léger ayant un nombre d'atomes de carbone de 4 à 8, ledit hydrocarbure étant éliminé par évaporation éclair après l'agglomération.
- 25 9. Bouillie aqueuse de charbon selon la revendication 8, pour laquelle l'hydrocarbure léger contient un nombre d'atomes de carbone de 5 à 6.
10. Bouillie aqueuse de charbon selon la revendication 9, pour laquelle l'hydrocarbure léger est le n-pentane.
- 30 11. Bouillie aqueuse de charbon selon la revendication 9, pour laquelle l'hydrocarbure léger est le n-hexane.
- 35 12. Bouillie aqueuse de charbon selon la revendication 8, pour laquelle l'hydrocarbure léger pour la réalisation de l'enrichissement par agglomération est présent en un pourcentage compris dans l'intervalle allant de 5 à 30 % en poids par rapport au charbon.
- 40 13. Procédé pour préparer une bouillie aqueuse de charbon selon l'une ou plusieurs des revendications précédentes, comprenant un enrichissement par agglomération dans l'eau d'un charbon ayant une taille de grain non-supérieure à 300  $\mu\text{m}$  avec un liquide obtenu par distillation du goudron de houille, présent en une proportion comprise entre 0,1 et 2 % en poids par rapport au charbon, et un hydrocarbure léger contenant un nombre d'atomes de carbone de 4 à 8, présent en une proportion de 5 à 30 % en poids par rapport au charbon, et l'élimination de l'hydrocarbure léger par évaporation éclair après que la partie à dominante organique s'est agglomérée et séparée de la solution aqueuse dans laquelle les constituants minéraux sont restés en suspension ou dissous, **caractérisé** en ce que le charbon enrichi est dispersé dans une solution aqueuse contenant, en tant qu'agent dispersant, un polyélectrolyte choisi parmi les sels de cation monovalent des acides naphthalène-sulfoniques polymérisés ayant une masse moléculaire de 800 à 3000, de préférence d'environ 2000, le pourcentage du dispersant étant compris dans l'intervalle allant de 0,05 à 0,5 % en poids par rapport au poids de la bouillie.
- 45 50 14. Procédé de préparation d'une bouillie aqueuse de charbon selon l'une ou plusieurs des revendications 1 à 12, **caractérisé** en ce qu'il comprend le délayage d'un charbon ayant une taille de grain non-supérieure à 300  $\mu\text{m}$ , dans une solution contenant un liquide obtenu par distillation de goudron de houille, présent en une proportion comprise entre 0,1 et 2 % en poids par rapport au charbon, et un hydrocarbure léger liquide ayant un nombre d'atomes de carbone de 4 à 8, présent en une proportion située dans l'intervalle allant de 50 à 200 % en poids par rapport au charbon, puis l'élimination de l'hydrocarbure léger par évaporation éclair et la formation d'une bouillie aqueuse au moyen de
- 55

l'addition d'un dispersant constitué par un polyélectrolyte choisi parmi les sels de cation monovalent des acides naphthalène-sulfoniques polymérisés ayant une masse moléculaire de 800 à 3000, de préférence d'environ 2000, le pourcentage du dispersant étant situé dans l'intervalle allant de 0,05 % à 0,5 % en poids par rapport au poids de la bouillie.

5

Revendications pour les Etats contractants suivants: AT, ES

1. Procédé de préparation d'une bouillie aqueuse de charbon, contenant de 60 % à 80 % en poids de charbon et un sel de cation monovalent d'un acide naphthalène-sulfonique polymérisé, en tant que polyélectrolyte dispersant, **caractérisé** en ce qu'il comprend les étapes de délayage d'un charbon ayant une taille de grain non-supérieure à 300  $\mu\text{m}$  dans une phase aqueuse contenant de 0,1% à 2 % en poids par rapport au charbon d'un liquide obtenu par la distillation de goudron de houille, et une proportion de 50 % à 200 % en poids par rapport au charbon d'un hydrocarbure léger liquide ayant de 4 à 8 atomes de carbone, d'élimination de l'hydrocarbure léger par évaporation éclair et d'addition à la bouillie résultante de 0,05 % à 0,5 % en poids, par rapport au poids de la bouillie, d'un polyélectrolyte choisi parmi les sels de cation monovalent d'acides naphthalène-sulfoniques polymérisés ayant une masse moléculaire de 800 à 3000, de préférence d'environ 2000.
2. Procédé de préparation d'une bouillie aqueuse de charbon contenant de 60 % à 80 % en poids de charbon et un sel de cation monovalent, d'un acide naphthalène-sulfonique polymérisé, en tant que polyélectrolyte dispersant, **caractérisé** en ce qu'il comprend les étapes d'enrichissement, par agglomération dans l'eau, d'un charbon ayant une taille de grain non-supérieure à 300  $\mu\text{m}$ , avec une proportion de 0,1 % à 2 % en poids par rapport au charbon d'un liquide obtenu par distillation de goudron de houille et une proportion de 5 % à 30 % en poids par rapport au charbon d'un hydrocarbure léger liquide ayant de 4 à 8 atomes de carbone, d'élimination de l'hydrocarbure léger liquide par évaporation éclair après que la partie à dominante organique s'est agglomérée et séparée de la phase aqueuse dans laquelle les constituants minéraux sont restés en suspension ou dissous, et de dispersion du charbon enrichi dans une solution aqueuse d'un polyélectrolyte dispersant choisi parmi les sels de cation monovalent des acides naphthalène-sulfoniques polymérisés ayant une masse moléculaire de 800 à 3000, de préférence d'environ 2000, la proportion dudit polyélectrolyte dispersant étant de 0,05 % à 0,5 % en poids par rapport au poids de la bouillie.
3. Procédé selon la revendication 1 ou 2, **caractérisé** en ce qu'un liquide obtenu par distillation du goudron de houille ou une huile combustible issue du pétrole est présent sur la surface du charbon.
4. Procédé selon la revendication 1 ou 2, **caractérisé** en ce que le liquide obtenu par distillation du goudron de houille ou l'huile combustible issue du pétrole est présent en une proportion de 0,2 % à 1,2 % par rapport au charbon.
5. Procédé selon la revendication 1 ou 2, **caractérisé** en ce que le liquide obtenu par distillation du goudron de houille a un intervalle de distillation allant de 200 à 400 °C.
6. Procédé selon la revendication 5, **caractérisé** en ce que le liquide obtenu par distillation du goudron de houille a un intervalle de distillation allant de 250 °C à 350 °C.
7. Procédé selon la revendication 6, **caractérisé** en ce que le liquide obtenu par distillation du goudron de houille est une huile de créosote.
8. Procédé selon la revendication 1 ou 3, **caractérisé** en ce que l'huile combustible issue du pétrole présente une viscosité cinématique à 50 °C non-inférieure à  $21,2 \cdot 10^{-6} \text{ m}^2/\text{s}$  (3° Engler).
9. Procédé selon la revendication 1 ou 2, **caractérisé** en ce que ledit charbon est constitué par deux groupes de particules, les particules du premier groupe ayant une taille de grain moyenne de 210  $\mu\text{m}$  à 60  $\mu\text{m}$ , leur taille maximum ne dépassant pas 300  $\mu\text{m}$ , et les particules du second groupe ayant une taille de grain moyenne comprise entre  $1/6^{\text{ème}}$  et  $1/20^{\text{ème}}$  de la taille de grain des particules dudit premier groupe.
10. Procédé selon la revendication 1 ou 2, **caractérisé** en ce que ledit hydrocarbure léger liquide a 5 ou 6

atomes de carbone.

11. Procédé selon la revendication 10, **caractérisé** en ce que l'hydrocarbure léger liquide est le n-pentane.
- 5 12. Procédé selon la revendication 10, **caractérisé** en ce que l'hydrocarbure léger liquide est le n-hexane.
13. Procédé selon la revendication 2, **caractérisé** en ce que l'hydrocarbure léger liquide utilisé pour la réalisation de l'enrichissement du charbon par agglomération est présent en une proportion de 5 % à 30 % en poids par rapport au charbon.

10

### Ansprüche

1. Wäßrige Kohlesuspension mit einer Konzentration im Bereich von 60 bis 80 Gew.-%, umfassend einen Polyelektrolyten, ausgewählt unter den einwertigen Kationensalzen von polymerisierten Naphthalinsulfonsäuren mit einem Molekulargewicht im Bereich von 800 bis 3000, vorzugsweise etwa 2000, dadurch gekennzeichnet, daß auf der Oberfläche der Kohle, die aus Teilchen mit einer Korngröße von nicht über 300 µm besteht, eine Flüssigkeit, die durch Destillation von Steinkohlenteer erhalten worden ist, oder ein von Mineralöl abstammendes Heizöl in einer Menge im Bereich von 0,1 bis 2 Gew.-% bezogen auf die Kohle, vorliegt.
- 15 2. Wäßrige Kohlesuspension nach Anspruch 1, worin die mittels Destillation von Steinkohlenteer erhaltene Flüssigkeit oder das von Mineralöl abstammende Heizöl in einer Menge im Bereich von 0,2 bis 1,2 Gew.-%, bezogen auf Kohle, vorliegt.
- 20 3. Wäßrige Kohlesuspension nach Anspruch 1, worin die mittels Steinkohlenteerdestillation erhaltene Flüssigkeit einen Siedebereich von 200 bis 400 °C aufweist.
- 25 4. Wäßrige Kohlesuspension nach Anspruch 3, worin die mittels Steinkohlenteerdestillation erhaltene Flüssigkeit einen Siedebereich von 250 bis 350 °C aufweist.
- 30 5. Wäßrige Kohlesuspension nach Anspruch 4, worin die mittels Steinkohlenteerdestillation erhaltene Flüssigkeit Kreosotöl ist.
- 35 6. Wäßrige Kohlesuspension nach Anspruch 1, worin das von Mineralöl abgeleitete Heizöl eine kinematische Viskosität bei 50 °C von nicht unter  $21,2 \cdot 10^{-6} \text{ m}^2/\text{s}$  (3° Engler) aufweist.
- 40 7. Wäßrige Kohlesuspension nach Anspruch 1, worin die Kohle aus zwei Teilchengruppen besteht, wobei die Teilchen der ersten Gruppe durchschnittliche Korngrößen im Bereich von 210 bis 60 µm aufweisen, wobei ihre größten Abmessungen 300 µm nicht überschreiten, und worin die Teilchen der zweiten Gruppe durchschnittliche Korngrößen im Bereich von einem Sechstel bis zu einem Zwanzigstel jener der ersten Gruppe aufweisen.
- 45 8. Wäßrige Kohlesuspension nach Anspruch 1, worin die mittels Destillation des Steinkohlenteers erhaltene Flüssigkeit während der Aufbereitung von Kohle durch Agglomeration zugesetzt wird, wobei die Agglomeration in Anwesenheit eines leichten Kohlenwasserstoffes mit 4 bis 8 Kohlenstoffatomen ausgeführt wird und dieser Kohlenwasserstoff nach der Agglomeration abgetrieben wird.
- 50 9. Wäßrige Kohlesuspension nach Anspruch 8, worin der leichte Kohlenwasserstoff eine Kohlenstoffatomanzahl im Bereich von 5 bis 6 aufweist.
10. Wäßrige Kohlesuspension nach Anspruch 9, worin der leichte Kohlenwasserstoff n-Pentan ist.
11. Wäßrige Kohlesuspension nach Anspruch 9, worin der leichte Kohlenwasserstoff n-Hexan ist.
- 55 12. Wäßrige Kohlesuspension nach Anspruch 8, worin der leichte Kohlenwasserstoff zur Ausführung der Aufbesserung durch Agglomeration in einem Prozentsatz im Bereich von 5 bis 30 Gew.-%, bezogen auf Kohle, vorliegt.

13. Verfahren zur Herstellung einer wäßrigen Kohlesuspension nach einem oder mehreren der vorstehenden Ansprüche, umfassend eine Aufbesserung durch Agglomeration einer Kohle mit einer Korngröße von nicht über 300  $\mu\text{m}$  mit einer durch die Destillation von Steinkohlenteer erhaltenen Flüssigkeit in einer Menge im Bereich von 0,1 bis 2 Gew.-%, bezogen auf Kohle, und einem leichten Kohlenwasserstoff mit 4 bis 8 Kohlenstoffatomen in einer Menge im Bereich von 5 bis 30 Gew.-%, bezogen auf Kohle, in Wasser, und das Abtreiben des leichten Kohlenwasserstoffes, nachdem sich der überwiegend organische Anteil agglomert und von der wäßrigen Lösung abgetrennt hat, worin die anorganischen Komponenten suspendiert oder gelöst geblieben sind, dadurch gekennzeichnet, daß die aufgebesserte Kohle in einer wäßrigen, einen Polyelektrolyten als das Dispergiermittel enthaltenden Lösung dispergiert wird, wobei der Polyelektrolyt unter den einwertigen Kationensalzen von polymerisierten Naphthalinsulfonsäuren mit einem Molekulargewicht von 800 bis 3000, vorzugsweise um 2000, ausgewählt wird und die Prozentmenge des Dispergiermittels im Bereich von 0,05 bis 0,5 Gew.-%, bezogen auf das Gewicht der Suspension, liegt.
14. Verfahren zur Herstellung einer wäßrigen Kohlesuspension nach einem oder mehreren der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß es das Aufschlännen einer Kohle mit einer Korngröße von nicht über 300  $\mu\text{m}$  in einer Lösung, die eine durch die Destillation von Steinkohlenteer erhaltene Flüssigkeit in einer Menge im Bereich von 0,1 bis 2 Gew.-%, bezogen auf Kohle, und eine leichte Kohlenwasserstoffflüssigkeit, umfassend eine Kohlenstoffatomanzahl im Bereich von 4 bis 8, in einer Menge im Bereich von 50 bis 200 Gew.-%, bezogen auf Kohle, enthält, anschließendes Abtreiben des leichten Kohlenwasserstoffes und Ausbildung einer wäßrigen Aufschlammung durch Zugabe eines Dispergiermittels, bestehend aus einem Polyelektrolyten, ausgewählt unter den einwertigen Kationensalzen von polymerisierten Naphthalinsulfonsäuren mit einem Molekulargewicht von 800 bis 3000, vorzugsweise etwa 2000, umfaßt, wobei der Prozentsatz des Dispergiermittels im Bereich von 0,05 bis 0,5 Gew.-%, bezogen auf das Gewicht der Suspension, liegt.

Patentansprüche für folgende Vertragsstaaten: AT, ES

1. Verfahren zur Herstellung einer wäßrigen Kohlesuspension mit einem Gehalt an 60 bis 80 Gew.-% Kohle und an einem einwertigen Kationensalz einer polymerisierten Naphthalinsulfonsäure als dispergierendem Polyelektrolyten, dadurch gekennzeichnet, daß es die Schritte des Aufschlänns einer Kohle mit einer Korngröße nicht über 300  $\mu\text{m}$  in einer wäßrigen Phase, die von 0,1 bis 2 Gew.-%, bezogen auf Kohle einer Flüssigkeit, die aus der Destillation von Steinkohlenteer erhalten worden ist, und eine Menge von 50 bis 200 Gew.-%, bezogen auf Kohle, eines leichten, flüssigen Kohlenwasserstoffes mit 4 bis 8 Kohlenstoffatomen enthält, des Abtreibens des leichten Kohlenwasserstoffes und des Zusetzens zu der gebildeten Aufschlammung von 0,05 bis 0,5 Gew.-%, bezogen auf das Gewicht der Aufschlammung, eines Polyelektrolyten, ausgewählt unter den einwertigen Kationensalzen von polymerisierten Naphthalinsulfonsäuren mit einem Molekulargewicht von 800 bis 3000, vorzugsweise etwa 2000, umfaßt.
2. Verfahren zur Herstellung einer wäßrigen Kohlesuspension mit einem Gehalt an 60 bis 80 Gew.-% Kohle und an einem einwertigen Kationensalz einer polymerisierten Naphthalinsulfonsäure als dem dispergierenden Polyelektrolyten, dadurch gekennzeichnet, daß die Stufen einer Aufbesserung einer Kohle mit einer Korngröße von nicht über 300  $\mu\text{m}$  durch Agglomeration in Wasser mit einer Menge von 0,1 bis 2 Gew.-%, bezogen auf Kohle, einer aus der Destillation von Steinkohlenteer erhaltenen Flüssigkeit und mit einer Menge von 5 bis 30 Gew.-%, bezogen auf Kohle, eines leichten, flüssigen Kohlenwasserstoffes mit 4 bis 8 Kohlenstoffatomen, eines Abtreibens des leichten, flüssigen Kohlenwasserstoffes, nachdem sich der überwiegend organische Anteil agglomert und von der wäßrigen Phase abgetrennt hat, worin die anorganischen Komponenten suspendiert oder gelöst geblieben sind, und des Dispergierens der aufgebesserten Kohle in einer wäßrigen Lösung eines dispergierenden Polyelektrolyten, ausgewählt unter den einwertigen Kationensalzen von polymerisierten Naphthalinsulfonsäuren mit einem Molekulargewicht von 800 bis 3000, vorzugsweise etwa 2000, umfaßt, wobei die Menge des dispergierenden Polyelektrolyten von 0,05 bis 0,5 Gew.-%, bezogen auf das Gewicht der Suspension, beträgt.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß eine aus der Destillation von Steinkohlenteer erhaltene Flüssigkeit oder ein von einem Mineralöl abgeleitetes Heizöl auf der Oberfläche der Kohle vorliegt.

4. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die aus der Steinkohlenteerdestillation erhaltene Flüssigkeit oder das von einem Mineralöl abgeleitete Heizöl in einer Menge von 0,2 bis 1,2 %, bezogen auf die Kohle, vorliegt.
- 5 5. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die aus der Steinkohlenteerdestillation erhaltene Flüssigkeit einen Siedebereich von 200 bis 400 ° C aufweist.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die aus der Steinkohlenteerdestillation erhaltene Flüssigkeit einen Siedebereich von 250 bis 350 ° C aufweist.
- 10 7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die aus der Steinkohlenteerdestillation erhaltene Flüssigkeit Kreosotöl ist.
8. Verfahren nach Anspruch 1 oder 3, dadurch gekennzeichnet, daß das von Mineralöl abgeleitete Heizöl eine kinematische Viskosität bei 50 ° C von nicht unter  $21,2 \cdot 10^{-6} \text{ m}^2/\text{s}$  (3 ° Engler) aufweist.
- 15 9. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Kohle aus zwei Teilchengruppen besteht, wobei die Teilchen der ersten Gruppe eine durchschnittliche Korngröße von 210  $\mu\text{m}$  bis 60  $\mu\text{m}$  aufweisen, wobei ihre größten Abmessungen 300  $\mu\text{m}$  nicht überschreiten, und wobei die Teilchen der zweiten Gruppe eine durchschnittliche Korngröße im Bereich von einem Sechstel bis zu einem Zwanzigstel der Korngröße der ersten Teilchengruppe aufweisen.
- 20 10. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der leichte, flüssige Kohlenwasserstoff 5 oder 6 Kohlenstoffatome hat.
- 25 11. Verfahren nach Anspruch 10, dadurch gekennzeichnet daß der leichte, flüssige Kohlenwasserstoff n-Pentan ist.
12. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß der leichte, flüssige Kohlenwasserstoff n-Hexan ist.
- 30 13. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß der leichte, flüssige Kohlenwasserstoff, der zur Ausführung der Kohleaufbesserung durch Agglomeration verwendet wird, in einer Menge von 5 bis 30 Gew.-%, bezogen auf Kohle, vorliegt.

35

40

45

50

55